Influence of Pressure on the Menschutkin-Type Reaction of Phenethyl Arenesulfonates with Pyridine

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Kinetic investigation of β-phenylethyl arenesulfonates with pyridine in acetonitrile revealed that the rates of these reactions which were lower than those of the reaction of benzyl benzenesulfonate with pyridine in acetone were increased with raising temperatures and pressures. The activation volumes were comparable to those of benzyl system, but activation entropies were negatively larger than those of benzyl system. From these phenomena it can be deduced that phenethyl system has more S_N2 character in the transition state, comparing with the reaction of benzyl system. With raising pressures the Hammett reaction parameters (ρ) were decreased, indicating that the reaction is probably closer to tight S_N2 character at higher pressures.

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.[1—5] Recently kinetic studies of Menschutkin type reactions of benzyl benzenesulfonate with pyridine in acetone were carried out by the electric conductivity method under 1 to 2000 bars at 20 to 40 °C.[6] From the enthalpy, entropy, and volume of activation, it was found that this reaction precedes 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 rate of the reaction of phenethyl arenesulfonates with pyridine which is expected to be more typical S_N2 under high pressure at 40 to 60 °C in acetonitrile to get some detailed information about the transition state.

Experimental

Instruments. Conductivity bridge and conductivity cell. The conductivity bridge is composed of B.N. 532 capacitor, B.N. 332 resistor and B.N. 1212/2 detector made by Rhode Schwarz Co., Germany. The conductivity cell shown in Fig. 1. It is composed of two parts, a glass cylinder of 5 cm³ in which two Pt circular plate electrodes are sealed, and two-branched teflon tube of 6 cm long and 0.4 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.

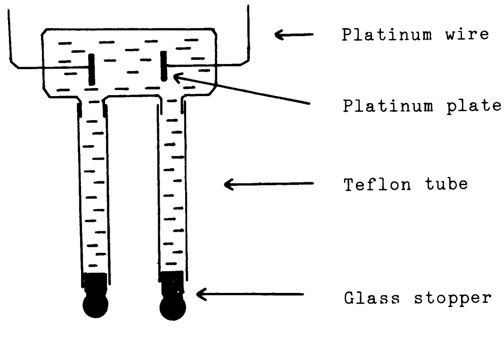


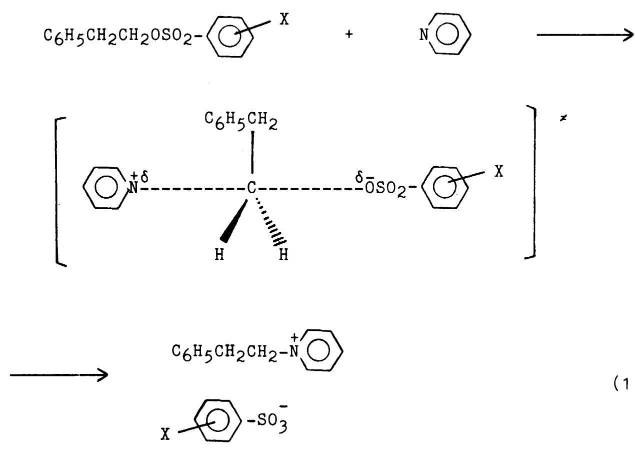
Fig. 1. Schematic drawing of the conductivity cell.

Materials. All materials used throughout were commercially available (Wako, Japan). Acetonitrile was purified by distillation after standing with anhydrous potassium carbonates for three days at room temperature. Pyridine dried over NaOH pellet was fractionated twice, bp 115—115.5 °C and stored in brown ampoule filled with nitrogen gas. IR spectra were recorded on a Hitachi EPI-2G Infrared Grating Spectrophotometer and ^{1}H NMR spectra were Varian 60 MHz Spectrometer.

The following arenesulfonyl chlorides were synthesized by chlorosulfonation of the corresponding substituted benzenes; *p*-Br derivative,[7] recrystd. from ligroine, (70%), mp 73 °C. Found: C, 38.05; H, 2.14%. Calcd for $C_6H_4BrClO_2S$: C, 38.33; H, 2.14%. *p*-Cl,[8] from ligroine, (58%), mp 52 °C (lit, 53 °C). *p*-MeO,[9] from pet. ether, (60%), mp 41 °C (lit, 41—42 °C). Unsubstituted benzenesulfonyl chloride[7] was obtained by purification of commercial chemicals, bp 137 °C/24 mmHg (1 mmHg=133.322 Pa) (lit, 119—121 °C/15 mmHg, mp 14.5 °C). *m*-Nitrobenzenesulfonyl chloride was prepared by chlorosulfonylation of sodium *m*-nitrobenzenesulfonate with chlorosulfuric acid. Recrystd. from ligroine, (57%), mp 61 °C (lit,[10] 61—62 °C). Found: C, 32.48; H, 1.67; N, 6.40%. Calcd for $C_6H_4ClNO_4S$: C, 32.51; H, 1.81; N, 6.32%. Phenethyl arenesulfonates were prepared from phenethyl alcohol with arenesulfonyl chloride by the Tipson's procedure[11] and purified by recrystallization from appropriate solvents.

N-Phenethylpyridinium *m*-nitrobenzenesulfonate. Pyridine (0.554 g, 0.007 mol) was added in a solution of phenethyl *m*-nitrobenzenesulfonate (2.15 g, 0.007 mol) in anhydrous acetonitrile (80 ml). The reaction mixture was heated under reflux for 4 h and then allowed to stand over night at room temperature. The product obtained was separated from solvent and washed with anhydrous ether. Recrystallization from 2-propanol gave colorless crystals, (40%), mp 122—123 °C, ^{1}H NMR ($CDCl_3$) δ=3.25 (2H, t, β-H), 5.15 (2H, t, α-H), 9.00 (2H, d, α-H of pyridine), 8.7 (1H, s, γ-H of pyridine); IR (Nujol) 3300, 1600, 1355, 1200, 1050, 835 cm^{-1}. Found: C, 59.52; H, 4.94; N, 7.33%. Calcd for $C_{19}H_{18}N_2O_5S$: C, 59.06; H, 4.70; N, 7.25%.

Kinetics. The reaction of phenethyl arenesulfonates with pyridine at various temperatures and pressures were followed by the conductometric method. As the reaction proceeds, the electric conductance was increased because formation of the salt increases as shown Eq. 1.[12] The conductivity cell was suspended in the high pressure vessel



(1)

with electrode leads, and the vessel was set in a thermostat kept at given temperature within ±0.1 °C. All kinetic runs were carried out under pseudo-first-order conditions, being the molar concentration of pyridine more than fifty times of that of phenethyl arenesulfonate. The Guggenheim plots[13] were used for determining the pseudo-first-order rate constant, from which the second-order rate constants were calculated. Rate constants were accurately estimated with the range of ±5% under 1 to 2000 bars and at 40, 50, and 60 °C.

Results and Discussion

Rate constants and thermodynamic parameters. The second-order rate constants for the reaction of phenethyl *p*-bromobenzenesulfonate with pyridine in acetonitrile under various pressures and at various temperatures are summarized in Table 1. As shown in Table 1, the rate constants increase with temperature and pressure and the rate constants are lower than those of the reaction of benzyl benzenesulfonate with pyridine[6] (11.46×10^{-4} dm^3 mol^{-1} s^{-1} at 40 °C, 100 bars). This is probably due to larger stability of benzyl cation.

Table 1. Second-Order Rate Constants, $k_2\times10^4$ (dm^3 mol^{-1} s^{-1}), of the Reaction of Phenethyl *p*-Bromobenzenesulfonate with Pyridine in Acetonitrile at Various Temperatures and Under Various Pressures

T/°C	P/bar			
	1	500	1000	1500
40	0.517	0.671	0.823	
50	1.091	1.259	1.607	1.851
60	1.813	2.805	2.671	3.170

Table 2. Activation Volume ($\Delta V^{\neq}$) for the Reaction of Phenethyl *p*-Bromobenzenesulfonate with Pyridine in Acetonitrile at Various Temperatures

T/°C	40	50	60
$\Delta V^{\neq}$/cm^3 mol^{-1}	−12.33	−10.33	−9.56

The activation volumes obtained from the slope in Fig. 1, on the basis of Eq. 2, are shown in Table 2.

$$\left(\frac{\partial \ln k_2}{\partial P}\right)_T = \frac{-\Delta V^*}{RT} \tag{2}$$

If $\Delta V^{\neq}$ is independent of pressure, Eq. 2 can be integrated as follows

$$k_2 = k_0 \exp\left(\frac{-P\Delta V^*}{RT}\right), \tag{3}$$

where k_0 is the rate constant under 1 atm. From Table 2, we can see that the activation volumes, $\Delta V^{\neq}$, are all negative at various temperatures and the value of $|\Delta V^{\neq}|$ decrease with increasing temperature. These results are valuable to consider the physical meaning involved in each item for the reaction mechanism.

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, being composed of the substrate V_m (phenethyl *p*-bromobenzenesulfonate), the nucleophile V_n (pyridine) and the solvent V_s (acetonitrile). 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 $V_s^{\neq}$ (acetonitrile). In particular, $V_s^{\neq}$ is somewhat different from solvent V_s. We can assume that the sum of the volume of V_m and V_n of reactants are not so different from that of activated complex $V_a^{\neq}$ even though the complex is somewhat electronically distorted, but the volume of solvents $V_s^{\neq}$ (acetonitrile) are much different from that of initial state because the charged complex causes more electrostriction than the reactants. As we mentioned above, if the complex is more charged than reactants, it is reasonable that activation volume ($\Delta V^{\neq}$) is negative. From the Eq. 3, we could know that k_2 increase with increasing pressure because of this negative $\Delta V^{\neq}$ value. It is shown in Fig. 2 that the pressure dependence of ln k_2 has a linear relationship. This fact shows that $\Delta V^{\neq}$ is independent of pressure. The temperature dependence of $\Delta V^{\neq}$ can be also explained from the charge separation of the activated complex with the change of temperature. In other words, if temperature is elevated, it is expected that the charge separation of the activated complex is larger and the bond enlargement of the activated complex and so the $|\Delta V^{\neq}|$ value increase with temperature because of the more electrostrict effect at higher temperature.

Generally, a negative $\Delta V^{\neq}$ would be expected for S_N2 reaction where two molecules are brought together in the transition state. $\Delta V^{\neq}$ of S_N2 reaction of benzyl benzenesulfonate with pyridine in acetone at 40 °C at various high pressure was −12.97 cm^3 mol^{-1},[6] and its negative value was about the same to that of phenethyl

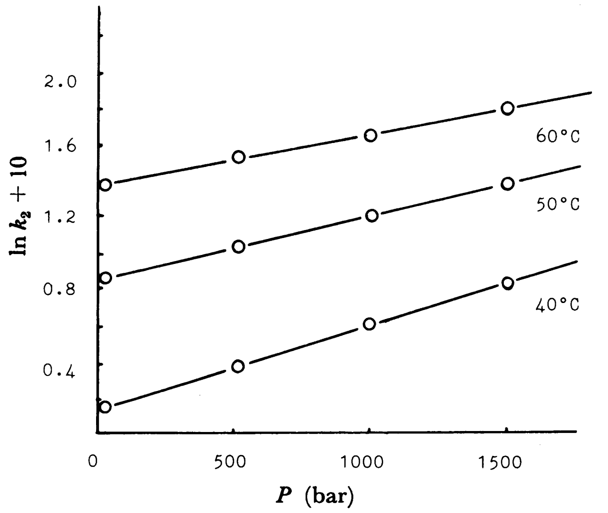


Fig. 2. The plots of ln k_2 vs. pressure at various temperatures.

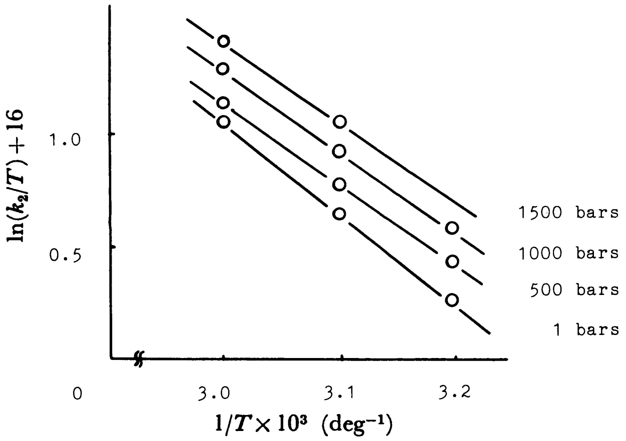


Fig. 3. The plots of ln (k_2/T) vs. 1/T at various temperatures.

p-bromobenzenesulfonate, but smaller than that of phenethyl *m*-nitrobenzenesulfonate.[14] This means that the S_N2 character of phenethyl *m*-nitrobenzenesulfonate is more predominant in the reaction of phenethyl *m*-nitrobenzenesulfonate than in that of benzyl benzenesulfonate.

There are other resemblance with the S_N2 Menschutkin reaction for example, of the reaction of EtI with pyridine[15] and that of hexadecyl bromide with pyridine in acetone at 40 °C, in which $\Delta V^{\ddagger}$ is −15—−20 ml per mole in both case. The activation parameters of the reaction of phenethyl *p*-bromobenzenesulfonate with pyridine are given in Table 4, in which the values of activation enthalpy are calculated from the slopes in Fig. 3. The plots of ln (k_2/T) against 1/T at various pressure for the reaction of phenethyl *p*-bromobenzenesulfonate with pyridine exhibit good linearity as shown in Fig. 3.

Table 3. Activation Parameters of the Reaction of Phenethyl *p*-Bromobenzenesulfonate with Pyridine in Acetonitrile at 50 °C

P/bar	1	500	1000	1500
$\Delta H^{\neq}$/kcal mol^{-1}	12.36	11.10	10.91	10.73
$\Delta S^{\neq}$/e.u. mol^{-1}	−38.59	−42.18	−42.30	−42.58
$\Delta G^{\neq}$/kcal mol^{-1}	24.83	24.73	24.58	24.49

Table 4. Second-Order Rate Constants, $k_2 \times 10^4$ (dm^3 mol^{-1} s^{-1}), of the Reaction of Phenethyl Arenesulfonates with Pyridine in Acetonitrile under Various Pressures at 50 °C

Substituents	P/bar				
	1	500	1000	1500	2000
m-NO_2	4.264	4.584	4.923	5.313	5.918
p-Cl	1.272	1.458	1.874	2.158	2.459
p-Br	1.091	1.259	1.607	1.851	
H	0.636	0.792	1.053	1.251	1.441
p-CH_3	0.403	0.533	0.728	0.885	1.027

As shown in Table 4, $\Delta H^{\ddagger}$ values decrease and $\Delta S^{\ddagger}$ values increase negatively under higher pressure. These phenomena can be explained by that the S_N2 characters are predominant under higher pressure because the S_N2 mechanism is predominant when $\Delta H^{\ddagger}$ value is comparatively small and $\Delta S^{\ddagger}$ values negatively large.[12,16] Comparison of $\Delta S^{\ddagger}$ values for the reaction of benzyl system with that of phenethyl one shows that the latter is more negative[6] than the former. This result suggests that S_N2 character in the transition state of the phenethyl system is greater than that of the benzyl one, i.e., the former one should be closer to tight S_N2 than that of the latter, in the sense of concerted mechanism that the bond formation with nucleophile cooperates with the fission of leaving group in the transition state.

As shown in Table 4, the rate constants increase with increasing both the pressure and the electron-withdrawing power of the substituent, which stabilize the sulfonate anion in the transition state by dispersing the charge. Hammett plots for these reactions at various pressures exhibit good linearity as shown in Fig. 4 and all the results are listed in Table 5. Hammett equation may be written in the form as linear free energy relationship.

$$\Delta\Delta G^{*} = -2.303\,RT\,\rho\sigma \qquad (4)$$

From Eq. 4, by partial differentiation with respect to pressure P,

$$\frac{\partial \rho}{\partial p} = (\partial/\partial p)[-\Delta\Delta G^{*}/2.303\,RT\sigma)]$$

$$= (-\Delta\Delta V^{*})/2.303RT\sigma\,. \qquad (5)$$

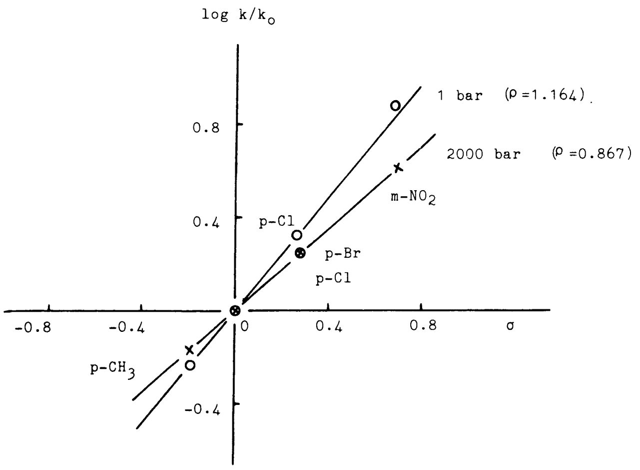


Fig. 4. Hammett plot for the reaction of phenethyl arenesulfonate with pyridine in acetonitrile at 50 °C.

Table 5. Hammett ρ Values for the Reaction of Phenethyl Arenesulfonates with Pyridine at 50 °C and Various Pressures

P/bar	1	500	1000	1500	2000
ρ	1.164	1.063	0.943	0.885	0.867
r	0.998	0.997	0.997	0.997	0.999
n	5	5	5	5	4

When neutral molecules react to produce ions like Menschutkin reaction the Hammett ρ values decrease with increase in pressure (see Table 5). This fact is probably explained by that, when P increases and the solvent becomes more compressed in the solution reaction, the contraction of the solution produced on ionization becomes smaller than the ordinary state. Due to these results, activation volume and, consequently, $|\Delta\Delta V^{\ddagger}|$ decrease and from right hand side of Eq. 5, $-\partial\rho/\partial p$ value decreases too; i.e., ρ should be decrease with increase in P. All above results and assumptions are also agreed perfectly with the idea of Fischer and his co-workers.[17]

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