Kinetics and Mechanism for the Reaction of Phenethyl *p*-Bromobenzenesulphonate with Substituted Pyridines under High Pressures

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Kinetic studies of the reaction of phenylethyl *p*-bromobenzenesulphonate with substituted pyridines at 1—2 000 atm. and 35—50 °C in acetonitrile were carried out by the electrical conductivity method. From the activation volume and activation entropies, it can be deduced that the phenethyl system has more S_N2 character in the transition state, comparing with the benzyl function upon raising the pressure, the Hammett ρ and Brönsted β values increase, indicating that the reaction has increasing S_N2 character with increasing pressure.

The effect of pressure on the Menschutkin reaction, a typical S_N2 reaction of alkyl and aromatic halides with tertiary amines to form quaternary ammonium salts, has been widely investigated.[1–5] Recently, kinetic studies of Menschutkin-type reactions of phenethyl arenesulphonates with pyridine at 1—2 000 atm. and 40—60 °C in acetonitrile were carried out by the electrical conductivity methods.[6] From the ρ values of the Hammett plots, it can be deduced that the phenylethyl system has more S_N2 character in the transition state, compared with the reaction of the benzyl system.[7]

When raising the pressure the Hammett reaction parameter ρ decreased, indicating that the reaction probably moves closer to tight S_N2 character. In this connection, we have studied a similar system of more definite S_N2-type mechanism, the reaction of phenethyl *p*-bromobenzenesulphonate (brosylate) with substituted pyridines under high pressure at 35—50 °C in acetonitrile in order to investigate the pressure dependence of the rate and the substituent effect in the nucleophile. This yielded detailed information on the transition state.

Results and Discussion

The reaction of 2-phenylethyl brosylate with substituted pyridines in acetonitrile yields phenethylpyridinium brosylate quantitatively. Second-order rate constants for the reaction in acetonitrile at various pressures are summarized in Table 1. As shown in Table 1, the rate constants increase with both pressure and the electron-donating power of the substituent. This is expected for nucleophilic attack of amine on a carbon atom.

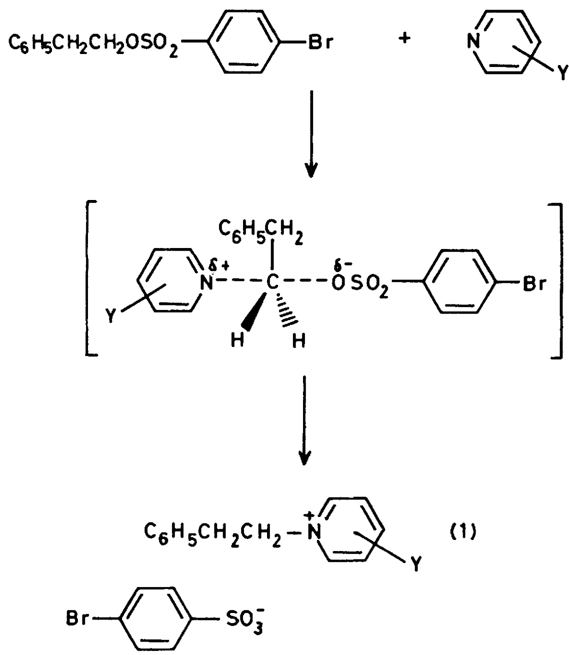
The rate constant for the reaction of phenethyl brosylate with pyridine is less than that of phenacyl bromide with pyridine for which the rate constant at 40 °C and 1 000 bar is 5.78 × 10^{-1} l mol^{-1} s^{-1}.[8] This striking rate increase is almost certainly caused by overlap of the orbital on the carbon atom, at which displacement takes place, with the π-orbital of the carbonyl group.[9]

Second-order rate constants (k_2) for the reaction of phenethyl brosylate with 3,5-dimethylpyridine in acetonitrile at various temperatures and pressures are listed in Table 2. The k_2 values increase upon increasing both the pressure and temperature. The activation volumes obtained from the slope of Figure 1 and from the data calculated from equation (2) are in Table 2. If $\Delta V^‡$

$$(\partial \ln k_2/\partial P)_T = -\Delta V^‡/RT \qquad (2)$$

is independent of pressure, equation (2) can be integrated to yield (3) where k_0 is the rate constant at 1 atm.

$$k_2 = k_0 \exp(-P\Delta V^‡/RT) \qquad (3)$$



(1)

Table 1. Second-order rate constants 10^4k_2/l mol^{-1} min^{-1} for the reaction of phenethyl brosylate with pyridines in acetonitrile at 50 °C and various pressures

Pyridine substituent	*p*/atm 1	500	1 000	1 500	2 000
4-NH_2	206.27	282.67	359.35	487.34	647.68
3,5-$(CH_3)_2$	36.40	47.47	63.59	82.31	106.52
3-CH_3	32.58	42.64	54.55	71.43	94.13
H	18.80	25.41	36.67	47.67	62.54
3-Cl		6.80	8.16	10.71	13.86

Table 2. Second-order rate constants 10^4k_2/l mol^{-1} min^{-1} for the reaction of phenethyl brosylate with 3,5-dimethylpyridine in acetonitrile at various temperatures and pressures

t/°C	*p*/atm 1	500	1 000	1 500	2 000
35	12.14	16.71	22.82	31.04	41.11
40	17.35	22.96	31.87	42.46	55.85
45	26.93	38.13	51.73	65.40	83.14
50	36.40	47.47	63.59	82.31	106.52

Table 3. Activation volume ($\Delta V^‡$) for the reaction of phenethyl brosylate with 3,5-dimethylpyridine in acetonitrile at various temperatures

t/°C	35	40	45	50
$\Delta V^‡$/cm^3 mol^{-1}	−15.47	−15.18	−14.59	−14.31

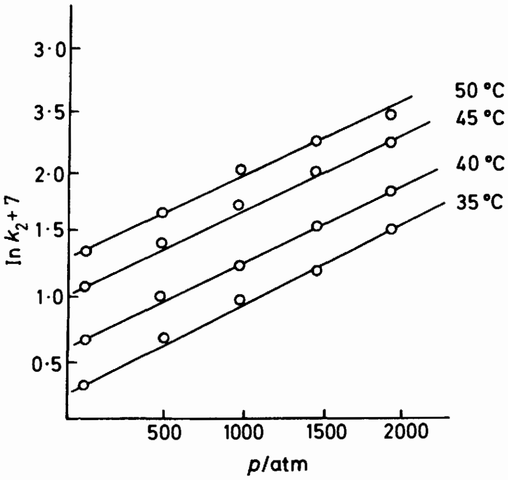


Figure 1. Plots of ln k_2 against pressure for the reaction of phenethyl brosylate with 3,5-dimethylpyridine

Table 4. Activation enthalpy, entropy, and free energy for the reaction of phenethyl brosylate with 3,5-dimethylpyridine in acetonitrile at 50 °C

p/atm	1	500	1 000	1 500	2 000
$\Delta H^‡$/kJ mol^{-1}	59.16	57.61	56.32	52.97	51.21
$-\Delta S^‡$/J mol^{-1} K^{-1}	66.60	69.19	70.71	79.04	82.26
$\Delta G^‡$/kJ mol^{-1}	80.67	79.96	79.16	78.50	77.78

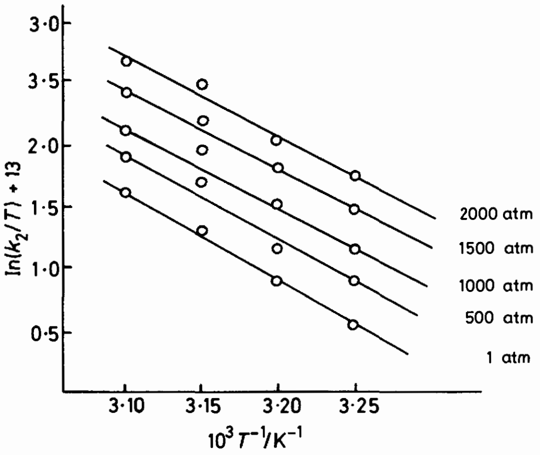


Figure 2. Plots of ln (k_2/T) against $1/T$ for the reaction of phenethyl brosylate with 3,5-dimethylpyridine at various pressures

From Table 3, we found that the activation volume $\Delta V^‡$ is negative at all temperature and decreases with increasing temperature.

$\Delta V^‡$ Is equal to $V^‡ - V_0$, where $V^‡$ is the volume of the activated complex and V_0 is the volume of reactants, composed of the substrate V_m(phenethyl p-bromobenzenesulphonate), the nucleophile V_n(pyridine), and the solvent V_s(acetonitrile). The apparent volume of the activated complex ($V^‡$) is the sum of the volume of the complex ($V_a{}^‡$) and the solvent $V_s{}^‡$(acetonitrile). In particular, $V_s{}^‡$ is somewhat different from V_s. We can assume that the sum of V_m and V_n is not so different from that of activated complex $V_a{}^‡$ even though the complex is somewhat distorted electronically, but the volume of solvent V_s (acetonitrile) 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 ($\Delta V^‡$) is negative. From equation (3), k_2 increases with increasing pressure because of the negative $\Delta V^‡$ value. Figure 1 shows that the dependence of the pressure on ln k_2 yields a linear relationship. This shows that $\Delta V^‡$ is independent of pressure. The temperature dependence of $\Delta V^‡$ can also be explained by charge separation of the activated complex with change of temperature. In other words, if the temperature is elevated, it is expected that the charge separation of the activated complex increases, there is bond enlargement of the activated complex, and so the $|\Delta V^‡|$ value decreases with temperature because of less electrostriction at higher temperature. Generally, a negative $\Delta V^‡$ would be expected for the S_N2 reaction where two molecules are brought together in the transition state. $\Delta V^‡$ For the S_N2 reaction of benzyl benzenesulphonate with pyridine in acetonitrile at 40 °C and high pressure is -12.97 cm^3 mol^{-1}.[10] The negative value is the same as that for phenethyl brosylate with pyridine,[11] but smaller than that for phenethyl brosylate with 3,5-dimethylpyridine (Table 3). This means that there is more S_N2 character in the reaction of phenethyl brosylate with 3,5-dimethylpyridine than for that of benzyl benzenesulphonate and phenethyl brosylate with pyridine.

The activation enthalpy, entropy, and free energy for the reaction of phenethyl brosylate with 3,5-dimethylpyridine are calculated from the slopes of Figure 2. Plots of ln(k_2/T) against $1/T$ at various pressures for the reaction of phenethyl brosylate with 3,5-dimethylpyridine exhibit good linearity as shown in Figure 2. As shown in Table 4, $\Delta H^‡$ values decrease and $\Delta S^‡$ values become more negative at high pressure. These phenomena can be explained by an increase in S_N2 character as the $\Delta H^‡$ value becomes comparatively small and $\Delta S^‡$ was negative.[12,13]

The effect of structural variation in the nucleophile is apparent from the Hammett and Brönsted plots. The reaction constant, which is a measure of the change in charge at the reaction centre, is related to the extent of N···C bond formation in the transition state. The more negative is ρ, the more positive is the charge developed at the reaction centre, *i.e.* that an electron moves from the nitrogen atom of the substituted pyridine to the α-carbon atom of the phenethyl brosylate. Bond making has progressed, in other words.

Upon raising the pressure, the Hammett reaction constants ρ become more negative, indicating that the reaction has increased S_N2 character as shown (Table 5 and Figure 3). Since the Brönsted β value provides a measure of the degree of bond formation in the transition state, it is apparent (Table 5 and Figure 4) that bond formation increases with stronger electron-donating substituents in the nucleophile. This is in agreement with the tendency of the Hammett ρ values and the predictions of substituent effects on S_N2 transition-state structures.

Experimental

Instruments.—Conductivity bridge and cell. The conductivity bridge was composed of a B.N. 532 capacitor, B.N. 332 resistor,

Table 5. Hammett ρ values and Brönsted β values for the reaction of phenethyl brosylate with pyridines in acetonitrile at 50 °C and various pressures

p/atm	1	500	1 000	1 500	2 000
ρ	−1.49	−1.57	−1.59	−1.60	−1.61
	(r 0.992)	(0.996)	(0.996)	(0.994)	(0.997)
β	0.256	0.259	0.261	0.264	0.265
	(r 0.993)	(0.998)	(0.998)	(0.999)	(0.999)

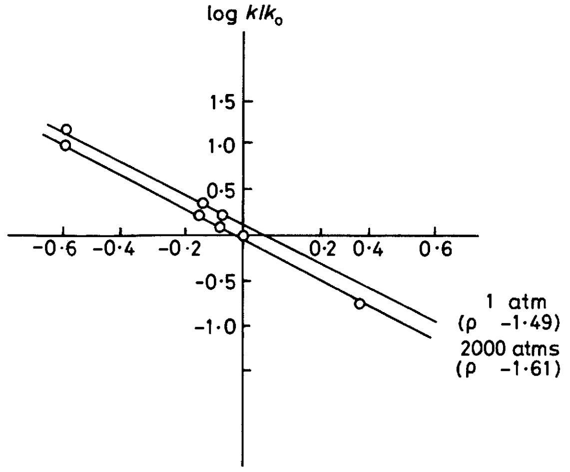


Figure 3. Hammett plots for the reaction of phenethyl brosylate with substituted pyridines in aceonitrile at 50 °C. Substituents are 4-NH_2, 3,5-$(CH_3)_2$, 3-CH_3, H, and 3-Cl

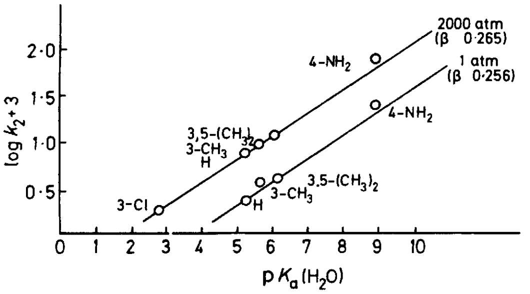


Figure 4. Brönsted plots for the reaction of phenethyl brosylate with pyridines in acetonitrile at 50 °C

and B.N. 1212/2 detector (Rhode Schwarz Co.). The cell was in two parts, a glass cylinder (5 cm^3) in which two Pt circular plate electrodes are sealed and a two-branched Teflon tube (6 cm × 0.4 cm). The former acts as a conducting cell and the latter as a pressure conductor. The cell is set in the pressure vessel.

N.m.r. spectra were recorded with a Varian 60 MHz spectrometer.

Materials.—All materials were commercially available (Wako). Acetonitrile was purified by distillation after standing over anhydrous potassium carbonate for three days at room temperature. Pyridine was commercial and was purified by several distillations over potassium hydroxide. Other liquid pyridines were used without further purification, but solids were recrystallized before use. All purified pyridines were stored in brown ampoules or over nitrogen.

Phenylethyl brosylate was prepared by Tipson's[14] procedure as follows. Phenylethyl alcohol (2.73 g, 0.022 mol) was dissolved in pure pyridine (*ca.* 40 ml) and subsequently *p*-bromobenzenesulphonyl 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 (from n-hexane) (lit.,[15] 58—59 °C).

N-*Phenylethylpyridinium* p-*bromobenzenesulphonate*. Pyridine (0.554 g, 0.007M) was added to a solution of phenethyl *p*-bromobenzenesulphonate (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, crystals (45%), m.p. 156—157 °C (from propan-2-ol) (Found: C, 54.3; H, 4.8; N, 3.45. Calc. for $C_{19}H_{18}BrNO_3$: C, 54.3; H, 4.3; N, 3.3%); δ(DMSO) 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), and 7.5 (9 H, m, phenyl).

Kinetics.—The reaction of phenethyl brosylate with pyridine at various temperatures and pressures was followed by a conductometric method. As the reaction proceeds, the electrical conductance increased because of formation of the salt.[13] 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 were always negligible relative to nucleophilic addition.

The reproducibility of the data (λ_∞ and λ_0) was difficult to confirm, so all kinetic runs were carried out under pseudo-first-order conditions, with a molar concentration of pyridine 50 times that of phenethyl brosylate. Guggenheim[16] 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—2 000 bar and 35, 40, and 50 °C.

Acknowledgements

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