KINETIC STUDIES FOR THE REACTIONS OF PHENACYL p-BROMOBENZENESULFONATE WITH SUBSTITUTED PYRIDINES UNDER HIGH PRESSURES

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ABSTRACT- Kinetic studies of the reactions of phenacyl p-bromobenzenesulfonate(brosylate) with substituted pyridines at 1-1500 atm and 35, 45, and 55°C in acetonitrile were carried out by electric conductivity method. From the activation volumes and activation entropies, it can be deduced that phenacyl brosylate has S_N^2 character in the transition state like other Menschutkin reactions of benzyl benzenesulfonate, 2-phenylethyl arenesulfonates, ethyl iodide, and hexadecyl bromide with pyridine. Upon raising the pressure, the Hammett $|\rho|$ and Brønsted β values increase indicating that the reaction has increasing S_N^2 character with increasing pressure.

In a previous paper¹ we reported that kinetic studies of the reactions of 2-phenyl ethyl arenesulfonates with pyridine in acetonitrile were carried out by conductivity method under 1 to 2000 atm at 40, 50, and 60° C. From the enthalpy, entropy, and volume of activation, it can be deduce that 2-phenylethyl system has more S_N2 character in the transition state, comparing with the reaction of benzyl system. With raising pressure the Hammett reaction parameters, ρ , decreased, indicating that the reaction is probably closer to tight S_N2 character at higher pressures.

In this connection, we have studied a similar, Menschutkin-type reaction, the reaction of phenacyl brosylate with substituted pyridines under high pressure at 35, 45, and 55°C in acetonitrile, in order to investigate the pressure dependence of the rate and the substituent effect in nucleophile. This yielded detailed information on the transition state.

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Experimental

<u>Instrumental.</u> The conductivity bridge was composed of a B.N. 532 capacitor, B.N.332 resistor, and B.N. 1212/2 detector (Rhode Schwartz Co.). The cell was in two part, a glass cylinder (5cm³) in which two Pt circular plate electrodes are sealed and a two branched teflon tube (6cm x 0.4cm). The former acts as a conducting cell and the latter as a pressure conductor. The cell is set in pressure vessel. Pressure was generated with the hand operating pressure pump. Conductance was measured with BARNSTED model PM 70 CB conductivity meter (U.S.A.).

<u>Materials</u>. All materials were commercially available (Wako). Acetonitrile and pyridines were purified with the method of previously reported¹. All purified pyridines were stored in brown ampoules or bottles filled with nitrogen gas.

Over-all scheme of the synthesis of reagents is shown in Fig.1.



Figure 1. Over-all Scheme of the synthesis of reagents.

Phenacyl brosylate. Silver p-bromobenzenesulfonate (18.9g, 0.055 mole) was dissolved in acetonitrile (ca. 500 ml) and phenacyl bromide (10.0g, 0.05mole) was introduced and the solution was heated at 50° C for 15 hrs. After filtering silver bromide precipitated and evaporating the filtrate under reduced pressure, solid was obtained. By extracting the solid using dry ethyl ether and then evaporating the solvent, white crystals were obtained and recrystallized from benzene-isopropyl alcohol; mp 104° C, yield 9.2g (52%). Anal. Calcd. for $C_{14}H_{11}O_{4}SBr$: C, 47.34; H,3.12, Found: C, 47.71; H,3.12. ¹H nmr (CDCl₃ + DMSO-d₆), 5.4 (s, 2H, CH₂), 7.4-7.9 (m, 9H, aromatic). Phenacylpyridinium benzenesulfonate. Phenacyl benzenesulfonate (4.2g, 0.015 mole) was dissolved in acetonitrile (ca. 50 ml) and pyridine (1.4g, 0.015 mole) was introduced in the solution. The mixture was refluxed for five days. After evaporating the solvent under reduced pressure, white crystals were obtained, washed with dry ethyl ether, and recrystallized from isopropyl alcohol; mp 127° C. Anal. Calcd for $C_{19}H_{17}O_4NS$: C, 64.19; H, 4.82; N, 3.94. Found: C, 64.11; H, 5.02; N, 3.88. <u>Kinetics.</u> All kinetic runs were carried out under pseudo-first order condition, which a concentration of pyridine 50 times that of phenacyl brosylate. Guggenheim plot² were used for determining the pseudo-first order rate constant, from which the second-order rate constants were calculated. A typical kinetic run is described at previous paper^{1,3}.

Results and Discussion

Second-order rate constants for the reactions of phenacyl brosylate with substituted pyridines in acetonitrile at various pressures are listed in Table 1.



The rate constants increase with both pressure and electron-donating power of substituent. This is expected for nucleophilic attack of pyridine on a carbon atom. The rate constants for the reaction of phenacyl brosylate with pyridine are about 10 times larger than that of 2-phenylethyl brosylate with pyridine for which the rate constant¹ at 50° C and 1500 atm is 1.851×10^{-4} mol 1^{-1} s⁻¹. This striking rate increase is almost certainly caused by overlap of the orbital on the carbon atom, at which displacement take place, with the π -orbital of the carbonyl group⁴.

Table 1. Second-order rate constants for the reactions of phenacyl brosylate with substituted pyridines in acetonitrile at 45⁰C and various pressures

 $(10^{5}k_{2}(1/mol s))$

pyridines	P (atm)			
	1	500	1000	1500
4-CH3	198.2	269.7	352.3	455.1
3-СН3	143.6	202.2	278.8	376.7
н	86.58	112.6	146.3	187.3
3-C1	10.43	13.60	17.92	23.15
3-сосн3	9.88	12.84	16.45	20.44

Second-order rate constants for the reaction of phenacyl brosylate with pyridine in acetonitrile at various temperatures and pressures are shown in Table 2.

The rate constants increase upon increasing both the pressures and temperatures. The activation volumes (ΔV^{\neq}) obtained from the slopes of Fig. 2 and from the data calculated from equation (2) are listed in Table 3. If ΔV^{\neq} is independent of pressure, equation (2) can be integrated to yield (3), where k_{0} is rate constant at 1 atm.

From Table 3, we can see that the activation volumes are all negative at various temperatures and the values of $|\Delta V^{\neq}|$ decrease with increasing temperatures. These results are the same tendencies for the reaction of 2-phenylethyl brosylate¹ with pyridine and valuable to consider the physical meaning involved in each item for the reaction mechanism. The ΔV^{\neq} is equal to $V^{\neq}-V_0$, where V^{\neq} is the apparent volume of the activated complex, and V_0 is the volume of reactants. If the complex is more charged than reactants, it is reasonable that ΔV^{\neq} is negative. From the eq.(3), we could know that k_2 increase with increasing pressure because of the negative ΔV^{\neq} value. The temperature dependence of ΔV^{\neq} can be also explained from the charge separation of the activated complex with the change of the temperature. In other word, if temperature is elevated, it is expected that the charge separation of the activated complex and so the $|\Delta V^{\neq}|$ value decrease with temperature because of the less electrostrict effect at higher temperature.

Generally, a negative ΔV^{\neq} would be expected for S_N^2 reaction where two molecules are brought together in the transition state. Activation volume of S_N^2 reaction of benzyl benzenesulfonate with pyridine in acetone⁵ at 40°C was -12.97 cm³mol⁻¹ and that of 2-phenylethyl brosylate in acetonitrile¹ at 40°C -12.33 cm³mol⁻¹, -13.70 cm³mol⁻¹ for phenacyl brosylate at 45°C (this study).

Other similar $S_N 2$ Menschutkin reactions of ethyl iodide⁶ and hexadecyl bromide with pyridine in acetone at 40°C, gave ΔV^{\neq} of -15--20 ml per mole.

As shown in Table 4, in which the values of activation enthalpy are calculated from the slopes in Fig.3, ΔH^{\neq} values decrease and ΔS^{\neq} values increase negatively on going to high pressure. These phenomena can be explained by an increase in S_N^2 character as the ΔH^{\neq} values become comparatively small and ΔS^{\neq} values were negative^{7,8}.

Table 2. Second-order rate constants for the reaction of phenacyl brosylate with pyridine in acetonitrile at various temperatures and pressures($10^5 k_2(1/mol s)$)

		Р	(atm)		
т (^о с)	1	500	1000	1500	
35	44.30	61.52	79.80	103.2	
45	86.58	112.6	146.3	187.3	
55	169.1	219.7	277.4	348.3	

Table 3. Activation volume (ΔV^{\neq}) for the reaction of phenacyl brosylate with pyridine in acetonitrile at various temperatures

т (⁰ с)	35	45	55
$\Delta v^{\neq} (cm^3/mol)$	-14.64	-13.70	-13.28
$(\partial \ln k_2 / \partial P)_T = -\Delta V^{\neq} / RT$			(2)
$k_2 = k_0 exp (-P \Delta V^{\neq}/RT)$			



Figure 2. Plots of ln k_2 against pressure for the reaction of phenacyl brosylate with pyridine at various temperatures.

p (atm)	1	500	1000	1500
$\Delta H^{\neq}(Kcal/mol)$	12.82	12.15	11.89	11.59
∆s [≠] (e.u./mol)	-32.38	-33.98	-34.26	-34.73
∆G [≠] (Kcal/mol)	23.12	22.96	22.79	22.64

Table 4. Activation enthalpy, entropy, and free energy for the reaction of phenacyl brosylate with pyridine in acetonitrile at 45°c



Figure 3. Plots of ln k₂ against 1/T for the reaction of phenacyl brosylate with pyridine at various pressures.

From Table 5, (Figs.4 and 5), we found that the Hammett reaction constants, ρ , become more negative upon raising the pressure, indicating that the reaction has increased S_N^2 character in the transition state. The ρ values of these plots, though the value is very similar, increase with increasing pressures, and it can be inferred that N····C bond formation increases progressively going to high pressures.



Figure 4. Hammett plot for the reactions of phenacyl brosylate with pyridines in acetonitrile at 45^oC. The substituents included in this plot are the 4-CH₃, 3-CH₃, H, 3-Cl, and 4-COCH₃.



Figure 5. Brønsted plot for the reactions of phenacyl brosylate with pyridines in acetonitrile at 45° C. The substituents included in this plot are the 4-CH₃, 3-CH₃, H, 3-Cl, and 4-COCH₃.

Table 5. The Hammett ρ and β values for the reactions of phenacyl brosylate with substituted pyridines in acetonitrile at 45° C and various pressures

P (atm)	1	500	1000	1500
ρ	-2.446	-2.489	-2.510	-2.539
	(r=0.998)	(0.996)	(0.996)	(0.995)
β	0.403	0.410	0.412	0.414
	(r=0.999)	(0.998)	(0.997)	(0.996)

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