DAEHAN HWAHAK HWOEJEE
(*Journal of the Korean Chemical Society*)
Vol. 28, No. 2, 1984
Printed in the Republic of Korea

단 신

β-phenylethyl P-Bromobenzenesulfonate와 피리딘과의 고압반응에 관한 반응속도론적 연구

呂壽東† · 朴鍾煥
경북대학교 사범대학 화학교육과
(1983. 8. 8 접수)

Kinetics and Mechanism for the Reaction of β-Phenylethyl *p*-Bromobenzensulfonate with Pyridine under High Pressure

Soo-Dong Yoh† and **Jong-Hwan Park**
Deparment of Chemistry, Teacher's College, Kyungpook National University, Daegu 635, Korea
(Received August 8, 1983)

Recently[1], Kinetic studies of the reaction of benzylbenzenesulfonate with pyridine in acetone were carried out by the electric conductivity method under 1 to 2,000 bars at 20 to 40°C. From the activation enthalpy, activation entropy and activation volume, 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 at the transition state. In this connection, we studied a similar system of more firmly central S_N2-type mechanism such as the reaction of β-phenylethyl arene sulfonates with pyridine under high pressure at 40 to 60°C in acetonitrile and the purpose of this study was to investigate the pressure dependence of the rate constant of the reaction to give us some detailed information for the reaction mechanism. The reaction of β-phenylethyl brosylate with pyridine in acetonitrile yields β-phenylethylpyridinium brosylate quantitatively. Second-order rate constants for the reaction of β-phenyl ethyl brosylate with pyridine in acetonitrile at various pressure and temperature are summarized in *Table* 1.

As shown in *Table* 1, the rate constants are increased by temperature and pressure and the rate constants are less than that of the reaction of benzyl benzenesulfonate with pyridine in which the rate constant[1] at 40°C, 1,000 bars is $11.46\times10^{-4}l$/mole, sec. The reason is large stability of benzyl cation by conjugation of electron of the ring after the departure of benzenesulfonate anion.

The activation volumes obtained from the slo-

Table 1. Second order rate constants, $k_2\times10^4(l\cdot mol^{-1}\cdot sec^{-1})$, of the reaction of β-phenylethyl brosylate with pyridine in acetonitrile at various temperature and pressures

T(°C)	P(bars)			
	1	500	1000	1500
40	0.517	0.671	0.823	
50	1.091	1.259	1.607	1.851
60	1.813	2.085	2.671	3.170

Table 2. Activation volume (ΔV^*) for the reaction of β-phenylethyl brosylato with pyridine in acetonitrile at various temperature.

T(°C)	40	50	60
ΔV^*(cm³/mole)	−12.33	−10.33	−9.56

pe of *Fig.* 1 which are related to the data calculated from eq. (1) are in *Table* 2.

$$\left(\frac{\partial \ln k_2}{\partial p}\right)_T = -\frac{\Delta V^{\neq}}{RT} \quad (1)$$

From *Table* 2, we found following results that the activation volumes, $\Delta V^{\neq}$, are all negative at various temperature and the value of $|\Delta V^{\neq}|$ decreased with increasing temperature.

These results are valuable for us to consider the physical meaning involved ineach item for reaction mechanism.

The $\Delta V^{\neq}$ is equal to $V^{\neq} - V_0$, where $V^{\neq}$ is the volume of the activated cpmplex, and V_0 is the volume of reactants. V_0 is composed of substrate V_1 (β-phenylethylbrosylate), nucleophile V_2 (pyridine) and solvent V_3 (acetonitrile). But the apparent volume of complex is the sum of the volume of activated complex ($V^{\neq}$) and solvent $V_3^{\neq}$ (acetonitrile). In particular, $V_3^{\neq}$ (acetonitrile) is somewhat different from solvent V_3 (acetonitrile). We can assume that the sum of the volume of V_1 and V_2 of reactants are not so different from that of activated complex $V^{\neq}$ even though the complex is electrically somewhat distorted but the volume of solvents $V_3^{\neq}$ (acetonitrile) are much different from that of initial state because the charged complex causes more electrostriction than the reactants.

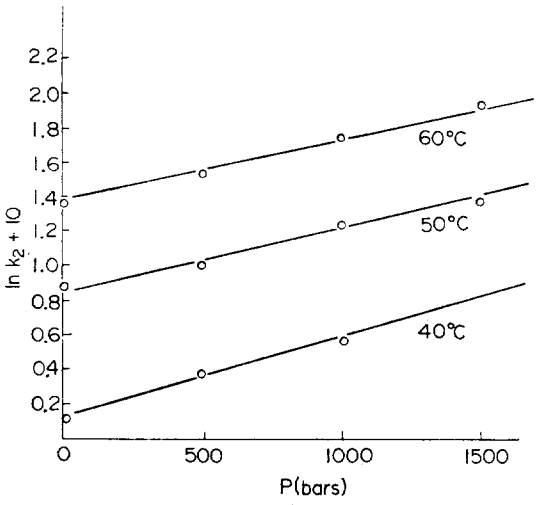

Fig. 1. The Plots of $\ln k_2$ *vs* pressure.

As we mentioned above, if the complex is more charged than reactants, it is reasonable that activation volume ($\Delta V^{\neq}$) is negative.

When temperature is increased, the electrcstriction is less effective than that of low 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 benzylbenesulfonate with pyridine in acetone at 40°C at various high pressure was $-12.97 cm^3$/mole, and its value was about the same with that of this work. There are ample resemblance with the S_N2 Menschutkin reaction, for example, of the reaction of EtI with pyridine[3] and that of cetylbromide with pyridine in acetone at 40°C, in which $\Delta V^{\neq}$ is $-15 \sim -20$cc per mole in both case.

The activation enthalpy, activation entropy and activation free energy for the reaction of β-phenylethyl brosylate with pyridine are calculated from the equations reported[1] and are

Table 3. Activation enthalpy, activation entropy and activation free energy for the reaction of β-phenylethyl brosylate with pyridine in actonitrile at 50°C

P(bars)	1	500	1000	1500
$\Delta H^{\neq}$ (Kcal/mole)	12.36	11.10	10.91	10.73
$\Delta S^{\neq}$ (e. u/mole)	−38.59	−42.18	−42.30	−42.58
$\Delta G^{\neq}$ (Kcal/mole)	24.83	24.73	24.58	24.49

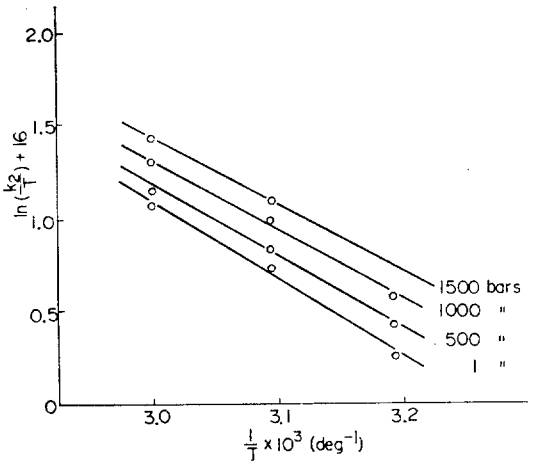

Fig. 2. The plots of ln (k_2/T) *vs.* $1/T$.

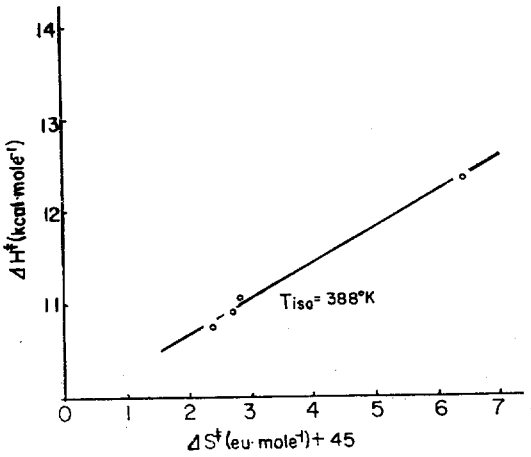

Fig. 3. The isokinetic relationship for the reaction of β-phenylethyl brosylate with pyridine in acetonitrile for pressure change.

given in *Table* 3.

The plots of $\ln\left(\frac{k_2}{T}\right)$ against $\frac{1}{T}$ at 1,500 bars for the reaction of β-phenylethyl brosylate with pyridine at various pressure exhibit good linearity as shown in *Fig.* 2.

The values of the activation enthalpy in *Table* 3 are calculated from the slopes in *Fig.* 2. As shown in *Table* 4, $\Delta H^{\neq}$ values decrease with the pressure increase and $\Delta S^{\neq}$ values increase negatively. These phenomena can be deduced that the S_N2 character are predominant as the pressure increases because the S_N2 mechanism is predominant when $\Delta H^{\neq}$ value is comparatively small and $\Delta S^{\neq}$ values negatively large.[4,5] Comparison of $\Delta S^{\neq}$ for the reactiion of benzyl system with that of β-phenylethyl system shows that the latter is more negative[6] than the former. This result suggests that S_N2 character in the transition state of the latter is greater than that of former system.

The isokinetic relationship between $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ was well correlated and its temperature was 388°K (*Fig.* 3).

From all the above results, this reaction was found to be an S_N2 type in which the rates of reaction are determined by C···N bond formation at the transtion state.

EXPERIMENTAL

β-phenylethyl brosylate was prepared by the Tipson's[8] procedure as follows:

While stirring the temperature was kept at 0°C in a ice-water bath, 2.73g(0.022*M*) of β-phenylethyl alcohol was dissolved in ca. 40m*l* of pure pyridine and subsequently 5.71g(0.022 *M*) of *p*-bromobenzenesulfonyl chloride was gradually added at 0°C. After stirring for 3 hours at 0°C, the mixture was poured into ice-water and then collected colorless crystals.

Recrystallization from *n*-hexane: Yields 65 %, mp 57°C (*lit.*[7] 58~59°C). Conductance measurements were used BARN STEAD Model PM 70 CB conductivity meter(U. S. A) and conductivity cell is composed of two parts, a glass cylinder of 4cc in volume in which two Pt circular plate electrodes are sealed, and two branched teflon tube of 6cm long and 4mm diameter.

The solvolysis reactions are always negligible with respect to the nucleophilic addition.

The reproducibility of the data (λ_∞ and λ_0)

was difficult to bedetermined, so the pseudo-first order rate constant was calculated from the Guggenheim equation.[9]

ACKNOWLEDGEMENT

The authors wish to thank the Ministry of Education for financial support of this work.

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