

Benzyl Benzenesulfonate 와 피리딘과의 고압반응에 대한 반응속도론적 연구

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Kinetics for the Reaction of Benzyl Benzenesulfonate with Pyridine in Acetone Under High Pressure

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요 약. Benzyl benzenesulfonate 와 피리딘의 반응속도를 아세톤 용매중에서 20~40 °C 및 1~2000 bars 에서 전기전도도법으로 측정하였다. 반응속도는 온도 및 압력이 증가함에 따라 증가하였다. 이 반응의 활성화엔탈피 (ΔH^\ddagger), 엔트로피 (ΔS^\ddagger) 그리고 활성화부피 (ΔV^\ddagger)를 구하였다.

이 반응에서 압력변화에 대한 ΔH^\ddagger 와 ΔS^\ddagger 사이에 등속관계가 성립하였으며 등속온도는 342 °K였다. 이상의 결과로 본 반응은 전이상태에서 C...N 결합형성이 주로 반응속도를 결정하는 S_N2 반응 메카니즘으로 진행된다는 것을 알았다.

ABSTRACT. Kinetic studies of the reaction of benzyl benzenesulfonate with pyridine in acetone were carried out by the electric conductivity method under 1 to 2000 bars and at 20 to 40 °C. The rate increases with increasing pressure and temperature. The activation enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger) and activation volume (ΔV^\ddagger) of the reaction are obtained by the above experiment. The isokinetic relationship between ΔH^\ddagger and ΔS^\ddagger for pressure change in the reaction was shown, and its isokinetic temperature was 342 °K.

From all of the above results it was found that this reaction precedes on the S_N2 reaction mechanism in which the rate of the reaction was determined by C...N bond formation at transition state.

1. INTRODUCTION

Menshutkin reactions-typical S_N2 -type reactions of alkyl halides with amines to form

quaternary ammonium salts-have been widely investigated for the effects of pressure¹⁻⁵

Recently, the rate constants of the reaction of 3- or 4-substituted pyridines with benzyl

benzenesulfonate in acetone at 35 °C were determined by an electric conductivity method under atmospheric pressure.^{6,7} According to the Hammett plot, the mechanism of the reaction was evaluated to be S_N2 type.⁶

The objective of this work was to investigate the pressure dependence of the rate constant of the reaction of pyridine with benzyl benzenesulfonate in acetone because of the following reasons: 1) of the various activation parameters that characterize the kinetics of a chemical reaction in terms of transition state theory, the volume of activation ΔV^\ddagger is potentially the most useful criterion of reaction mechanism, because the spatial requirements of the various alternative models can be visualized relatively easily. 2) the reaction mentioned above has not been studied for the pressure effect and we attempted for the first time to examine whether the isokinetic relationship between ΔH^\ddagger and ΔS^\ddagger for pressure change in the reaction can be realized or not.

EXPERIMENTAL

Materials. All chemicals used in this experiment are first grade products from Wako, Japan. But pyridine was purified by several distillations with potassium hydroxide before use.⁷ Benzyl benzenesulfonate was prepared by normal method^{6,8}. Benzyl benzenesulfonate was recrystallized and stored in a cold petroleum ether before use. Acetone solvent¹ was refluxed with potassium permanganate for a day and distilled in the Widmer distillatory apparatus.

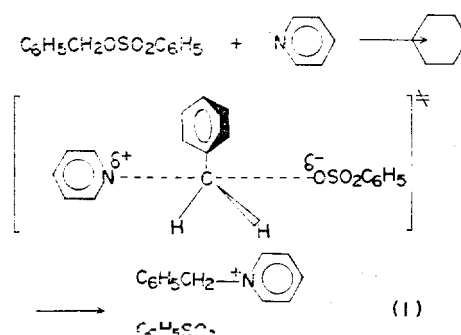
Conductivity bridge and conductivity cell; The conductivity bridge is composed of B. N. 532 capacitor, B. N. 332 resistor and B. N. 12 12/2 detector made by Rohde Schwarz Co., Germany.

The conductivity cell shown in Fig. 1 It is composed of two parts, a glass cylinder of 5 cm³

in volume 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 conducting cell and the latter acts as pressure conductor by pressing. The cell is set in the pressure vessel and the pressure measurement system was described else where.⁹

Kinetics, The conductivity cell (Fig. 1) is also used as the reaction vessel of the following reaction;



The rates of the reaction of Eq. (1) were determined by measuring the conductance of the solution, which increases as reaction proceeds because of the production of the ionic quaternary ammonium salts as shown in Eq. (1).

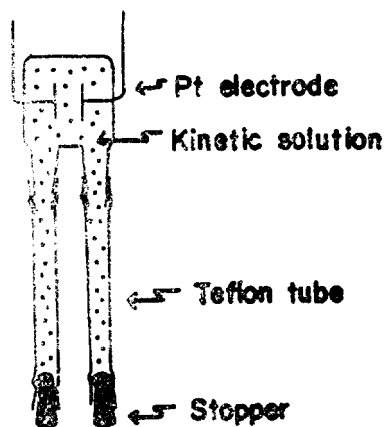


Fig. 1. Schematic drawing of the electroconductivity cell.

The conductivity cell is suspended in a high pressure vessel⁹ with electrode leads, and the vessel was set in a thermostat keeping in experimental temperature. All kinetic runs were carried out under pseudo first order conditions,¹⁰ maintaining the mole concentration of

Table 1. Second order rate constants $k_2 \times 10^4$ ($l \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$) of the reaction of pyridine with benzylbenzenesulfonate in acetone at various temperatures and pressures.

T(°C)	P(bars)			
	1	500	1000	2000
20	0.917	1.313	2.167	5.208
25	1.917	2.875	4.333	8.125
30	3.063	4.646	7.144	11.04
40	6.063	7.417	11.46	22.71

Table 2. Activation volume (ΔV^\ddagger) for the reaction of pyridine with benzyl benzenesulfonate in acetone at various temperatures.

T(°C)	20	25	30	40
ΔV^\ddagger (cm ³ /mole)	-20.92	-16.87	-14.42	-12.97

pyridine twenty times more than that of benzyl benzenesulfonate. The Guggenheim plots¹¹ were used for determining the pseudofirst-order rate constant.

Second-order rate constants (k_2) were calculated from the slopes of plots of the observed first-order rate constants against pyridine concentration. Rate constants are accurately estimated within the range of $\pm 5\%$ from 1 to 2000 bars and 20 to 40 °C.

RESULTS AND DISCUSSION

Second-order rate constants (k_2) determined for the reaction of pyridine with benzyl benzenesulfonate in acetone at various pressures and temperatures are shown in Table 1. The value of k_2 increases with temperature and pressure.

The activation volume change (ΔV^\ddagger) calculated from the equation (2) which are related to the slope of Fig. 2 is given in Table 2.

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

Since ΔV^\ddagger is independent of P , Eq. (2) can be

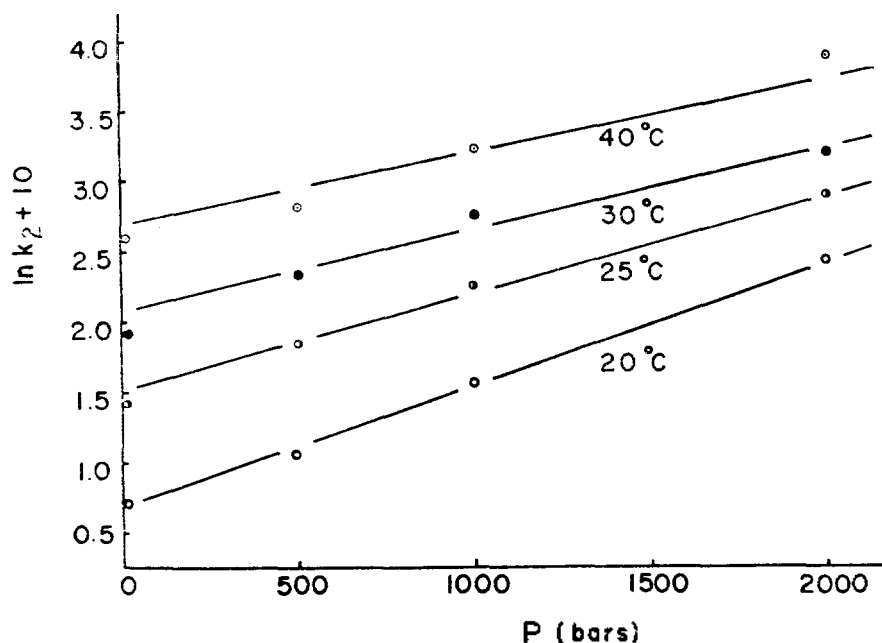


Fig. 2. The plots of $\ln k_2$ vs. P .

integrated as follows:

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

Where k_2 and k_0 are the rate constants of the reaction of Eq. (1) at pressure P and $P=0$, where $P=0$ means $P=1$ bar because P takes 1 bar as standard state, respectively. We found from Table 2. that 1) the ΔV^\ddagger values are negative, 2) the value of $|\Delta V^\ddagger|$ decreases with increasing temperature. It will be valuable for us to consider the physical meaning embodied in each item for reaction mechanisms. The ΔV^\ddagger is equal to $V^\ddagger - V_0$, where V^\ddagger is the volume of the activated complex shown in the reaction mechanism of Eq. (1), and V_0 is the volume of reactants. The volume of reactants (V_0) is composed of $V(\text{BBS})$, $V(\text{PY})$ and solvent volume $V(\text{acetone})$. But the apparent volume of complex is the sum of the volume of complex (V^\ddagger) and solvent $V^\ddagger(\text{acetone})$ which are somewhat different from $V(\text{acetone})$. It is supposed that the volume of reactants $V(\text{BBS}) + V(\text{PY})$ is not so different from that of activated complex even though the complex is electrically somewhat distort but the volume of solvents are much different *i. e.* because the charged complex causes more electrostriction than reactants.

As described, if the complex is more charged than reactants of Eq. (1) it is reasonable that the activation volume (ΔV^\ddagger) is negative. Next the temperature dependence on ΔV^\ddagger can be also deduced from the charge separation of the activated complex. When temperature is increased, the electrostriction is less effective than that of low temperature.

The Activation enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger) and free energy (ΔG^\ddagger) of the reaction of Eq. (1) calculated from the following equations are shownn Table 3.

Table 3. Activation enthalpy (ΔH^\ddagger), activation entropy (ΔS^\ddagger) and activation free energy (ΔG^\ddagger) for the reaction of pyridine with benzyl benzenesulfonate in acetone at various pressure.

P (bars)	1	500	1000	2000
ΔH^\ddagger (kcal/mole)	18.98	16.89	14.80	13.02
ΔS^\ddagger (e. u. /mole)	-12.01	-18.08	-24.12	-29.13
ΔG^\ddagger (kcal/mole)	22.62	22.37	22.11	21.85

$$\ln(k_2/T) = -\frac{\Delta H^\ddagger}{R} \cdot \frac{1}{T} + \text{const.} \quad (4)$$

$$\Delta G^\ddagger = -RT \ln \frac{hk_2}{kt} \quad (5)$$

$$\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger) / T \quad (6)$$

As shown in Fig. 3, we can obtain a good linear relationship of the plot of $\ln(k_2/T)$ vs. $\frac{1}{T}$ at 2000 bars, and the convex curve at other low pressures. This fact means that the other effects such as steric hinderance as well as temperature are predominant in the reaction of Eq. (1) because of the bulky molecular structure of

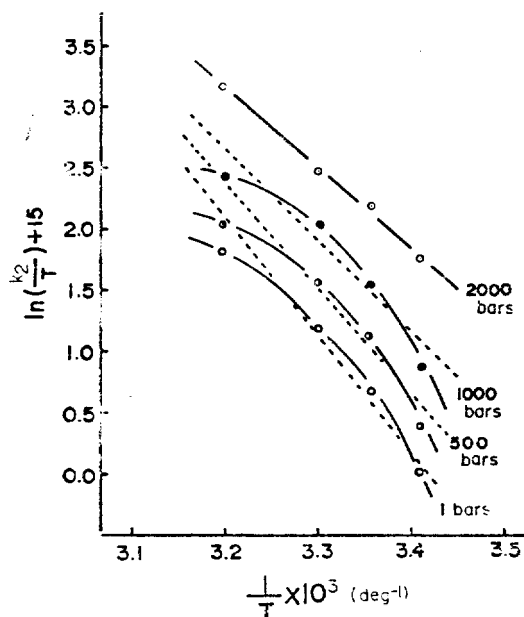


Fig. 3. The plots of $\ln(k_2/T)$ vs. $1/T$.

reactants. The ΔH^\ddagger values in Table 3 are the average value calculated from the basis of the dotted lines in Fig. 3. As shown in Table 4, ΔH^\ddagger values decrease as the pressure increases and ΔS^\ddagger values can negatively increase. These phenomena can deduce the S_N2 character are predominant as the pressure increases because the S_N2 mechanism is predominant when ΔH^\ddagger value is comparatively small and ΔS^\ddagger value negatively large.^{7,12}

The linear relationship of the plot of ΔH^\ddagger vs. ΔS^\ddagger , what is called isokinetic relationship, is correlated with pressure changes. The isokinetic temperature calculated from the slope of Fig. 4 was 342 °K. Accordingly, this reaction is expected to have S_N2 type reaction mechanism in the experimental temperature in which

the rates of reaction is determined by C...N bond formation at transition state. This result agrees with that of the isokinetic relationship with pyridine derivatives.⁷

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REFERENCE

1. M. G. Gonikberg and A. L. Kitaigorodsky, *Dokl. Akad. Nauk SSSR*, **122**, 231 (1958).
2. S. D. Hamann, "High Pressure Physics and Chemistry", Vol. 2, P.191, R. S. Bradley, Ed., Academic Press, New York, N.Y., 1963.
3. W. J. Le Noble, *J. Chem. Educ.*, **44**, 729 (1967).
4. K. Tamura, Y. Ogo and T. Imoto, *Bull. Chem. Soc. Japan*, **46**, 2988 (1973).
5. Y. Okamoto and K. I. Lee, *J. Amer. Chem. Soc.*, **97**, 4015 (1975).
6. W. B. Lee, S. D. Yoh and S. Y. Hong, *J. Korean Chem. Soc.*, **21**, 38 (1977).
7. K. A. Lee, K. T. Howang and S. D. Yoh, *J. Korean Chem. Soc.*, **23**, 243 (1979).
8. W. D. Emmons and A. F. Ferris, *J. Amer. Chem. Soc.*, **75**, 2257 (1953).
9. J. G. Jee, J. J. Jung and J. U. Hwang, *J. Korean Chem. Soc.*, **18**, 320 (1974).
10. W. K. Kim and I. C. Lee, *J. Korean Chem. Soc.*, **17**, 235 (1973).
11. E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).
12. D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 3352 (1953).

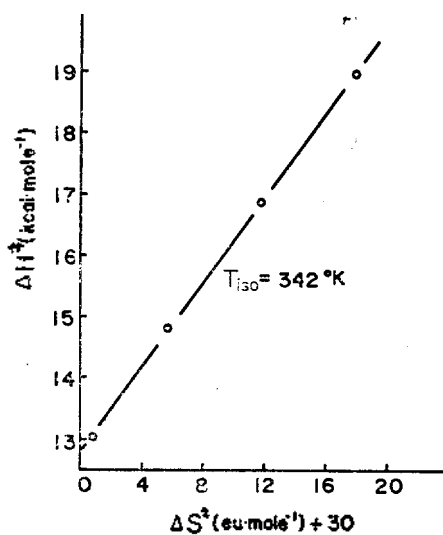


Fig. 4. The isokinetic relationship for the reaction of benzyl benzenesulfonate with pyridine in acetone for pressure change.