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염화벤질류의 가용매분해반응에 대한 압력의 영향(제 2 보). 에탄올-물 혼합용매내에서 *p*-클로로 염화벤질의 분해반응

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The Effect of Pressure on the Solvolysis of Benzylchlorides (II). *p*-Chlorobenzyl Chloride in Ethanol-Water Mixtures

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요 약. 에탄올-물 혼합용매내에서 *p*-클로로 염화벤질의 가용매분해반응에 대한 속도상수를 압력 1~1,600bar, 온도를 30°, 40°C에서 측정하였다. 반응속도들은 온도와 압력이 증가함에 따라 증가하고, 에탄올 몰 분율이 증가함에 따라 감소하였다. ln k대 압력의 플로트는 압력에 따라 이차함수꼴로 변함을 알았고 이 플로트로부터 $\Delta V^{\neq}$와 $\Delta\beta^{\neq}$의 값을 얻었다. 그 결과 $\Delta V^{\neq}$와 $\Delta\beta^{\neq}$의 값은 약 0.20몰 분율에서 Extremum Behavior가 나타남을 알았다. 이 현상을 용매구조 변화로 논의하였다. ln k대 용매파라미터, q, 및 ln C_w의 플로트사이의 관계로부터 본 연구의 반응은 $S_N1(2)$ 메카니즘으로 진행됨을 추정할 수 있었다.

ABSTRACT. The rate constants for the solvolysis reactions of *p*-chlorobenzyl chloride in ethanol-water mixtures were determinded at 30° and 40°C up to 1,600bar. Rates of reaction were increased with increasing temperature and pressure, and decreased with increasing solvent composition of ethanol mole fraction. The plots of ln k against pressure are fitted to a secondorder function in P, and values of $\Delta V^{\neq}$ and $\Delta\beta^{\neq}$ are obtained. The values of $\Delta V^{\neq}$ and $\Delta\beta^{\neq}$ exhibit the extremum behavior at about 0.20mole fraction of ethanol. This behavior is discussed in terms of solvent structure variation. From the relation between the plots of ln k versus the solvent parameter, $q\equiv(D-1)/(2D+1)$, or the logarithmic molar water concentration, ln C_w, it could be estimated that the reaction proceeds through $S_N1(2)$ mechanism.

INTRODUCTION

In a previous paper we reported a study of the effect of pressure on the solvolysis of *p*-methylbenzyl chloride in aqueous ethanol[1].

The activation volume, $\Delta V^{\neq}$, defined as difference in the partial molal volumes between the initial and the transition states, can be determined experimentally from the rate data under pressure by means of the following equation;

$$\Delta V^{\neq}=-RT(\partial \ln k/\partial P)_T \qquad (1)$$

In general, an examination of the pressure effect on the kinetic rates can give a great deal of information about the transition states of the reactions. Moreover the utility of the activation volume as a diagnostic tool for studing solvolytic reaction mechanisms is well recognized[2,3].

Whalley[4] has reviewed the significance of activation volumes in the determination of reaction mechanism, and has suggested that the volume of activation is probably easier to rationalize in terms of reaction mechanism than the other important parameters of activation, $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

Hyne and his co-workers have also investigated the study of the behavior of the activation volume, $\Delta V^{\neq}$, and the temperature dependence of the activation volume, $(\partial \Delta V^{\neq}/\partial T)_P$. However, they have been concentrated on the effect of the change in solvent composition on the activation volume for solvolysis in aqueous binary solvent mixtures.

In this papar, we calculated various pseudo thermodynamic quantities from the pseudo rate constants and discussed in terms of solvent structure variation of initial and transition state (electrostriction), because these parameters are essential for getting detailed information about the transition states of the solvolysis reactions. In order to determine the reaction mechanism of *p*-chlorobenzyl chloride in various mole fractions of ethanol-water mixtures under high pressure, we compared the rate constants of solvolysis with the dielectric constants of ethanol-water mixture and the number of water molecule participated in the transition state.

EXPERIMENTAL

p-chlorobenzyl chloride was purified by triple recrystallization from ethyl ether (GR grade, Tokyo Kasei, Japan). Ethyl alcohol (GR grade, Merck, Germany) was used without purification.

Distilled water was first passed through an ionexchange resin and then redistilled in a pyrex apparatus from which carbon dioxide was excluded. The specific conductance of distilled water was about 9×10^{-7}mho·cm^{-1} at 25°C.

The high pressure apparatus and technique have already been described. Temperature was controlled within ±0.02°C for all the kinetic runs. The reactions were followed by a conductometric method described previously[1].

The rates of solvolysis of *p*-chlorobenzyl chloride were studied in ethanol-water mixtures at 30 and 40°C over a pressure range from 1 to 1600bar. The solvent compositions used were 0, 0.10, 0.20, 0.30 and 0.40 mole fraction of ethanol. The concentration of the kinetic solution was 4.0×10^{-3}mole·l^{-1}. All rate constants were determined by following the change of conductance of the reaction mixture due to HCl formation as a function of time. The pseudo first-order rate constants were determined by the Guggenheim plots[8] using the method of least squares.

RESULTS

Rates and Activation parameters; The solvolysis of *p*-chlorobenzyl chloride under various conditions of temperature, pressure and solvent composition followed first-order kinetics. The rate constants are listed in *Table* 1. Each rate constant represents the average of two or more experiments. In all cases, the rates of reaction increase with increasing temperature and pressure, and decrease with increasing solvent composition.

The volume of activation at a given temperature, pressure and solvent composition, $\Delta V^{\neq}$, is related to the pressure dependence of rate constant by *eq.* (1)[9]. *Fig.* 1. is typical plots of ln *k* *vs.* pressure in various mole fractions of ethanol-water mixture. The plots are clearly non-linear demanding at least a second-order function to describe the dependence of ln *k* upon pressure. The method used in this work is therefore described by means of the following equation[10];

Table 1. Rate constants for the solvolysis of *p*-chlorobenzyl chloride at 30° and 40°C in aqueous ethanol at various pressures

Temp. (°C)	Pressure (bar)	$k\times10^5$(sec^{-1}) for mole fraction of ethanol				
		0	0.10	0.20	0.30	0.40
30	1	1.67	0.523	0.138	0.0582	0.0354
	200	1.77	0.584	0.167	0.0643	0.0392
	400	1.89	0.679	0.194	0.0715	0.0452
	800	2.39	0.878	0.252	0.0895	0.0543
	1200	2.77	1.07	0.339	0.114	0.0664
	1600	3.20	1.39	0.426	0.133	0.0778
40	1	5.02	1.48	0.410	0.180	0.111
	200	5.33	1.67	0.498	0.200	0.123
	400	5.71	1.98	0.571	0.223	0.140
	800	7.05	2.47	0.745	0.277	0.169
	1200	8.44	3.01	0.990	0.351	0.206
	1600	9.81	3.87	1.24	0.408	0.242

$$\ln k = A + BP + CP^2 \qquad (2)$$

The parameters A, B and C in *eq.* (2) were calculated by the method of least squares in the range from 1 to 1600 bar.

Substitution of *eq.* (2) into *eq.* (1) gives

$$\Delta V^{\neq} = -RT(B+2CP) \qquad (3)$$

The volume of activation at atmospheric pressure (zero applied pressure), $\Delta V_0^{\neq}$ is therefore determined according to *eq.* (4).

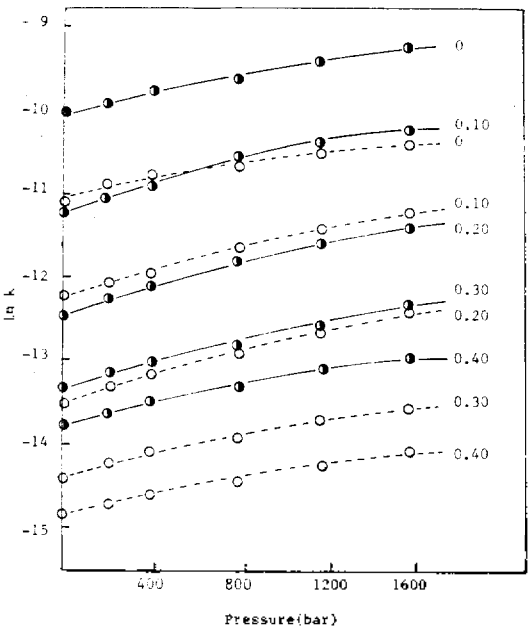

Fig. 1. Pressure dependence of ln *k* for the solvolysis of *p*-chlorobenzyl chloride in various mole fractions of ethanol-water mixture (··· : 30°C, — : 40°C).

$$\Delta V_0^{\neq} = -RTB \qquad (4)$$

The pressure dependence of $\Delta V^{\neq}$ is given by differentiation of *eq.* (3) with respect to

Table 2. Activation volume parameters for the solvolysis of *p*-chlorobenzyl chloride in aqueous ethanol at 30° and 40°C

Temp. (°C)	Mole fraction of ethanol	$-\Delta V^{\neq}$(ml. mole^{-1})						$-\Delta\beta^{\neq}\times10^3$ (ml. bar mole^{-1})
		1 bar ($-\Delta V_0^{\neq}$)	200	400	800	1200	1600	
30	0	11.6	11.4	11.2	10.7	10.3	9.83	1.11
	0.10	17.6	17.3	17.0	16.4	15.9	15.3	1.46
	0.20	21.2	20.4	19.6	17.9	16.2	14.5	4.18
	0.20	15.0	14.6	14.2	13.4	12.6	11.8	2.02
	0.40	15.3	14.6	13.9	12.5	11.1	9.62	3.58
40	0	11.2	11.1	11.1	11.0	10.9	10.8	2.08
	0.10	17.4	16.9	16.4	15.4	14.4	13.4	2.50
	0.20	21.4	20.5	19.6	17.8	16.0	14.2	4.48
	0.30	15.7	15.2	14.7	13.7	12.7	11.7	2.50
	0.40	15.3	14.6	14.0	12.7	11.5	10.2	3.15

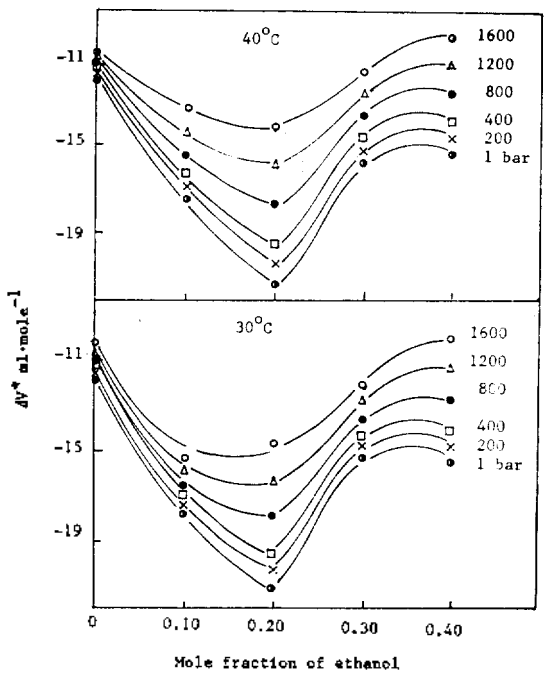

Fig. 2. Solvent dependence of activation volume under various pressures.

pressure[3].

$$\Delta\beta^{\neq} = -(\partial\Delta V^{\neq}/\partial P)_T$$
$$= -\{(\partial\bar{V}_i/\partial P)_T - (\partial\bar{V}_i/\partial P)_T\}$$
$$= +2RTC \qquad (5)$$

Where $\Delta\beta^{\neq}$ represents the pressure dependence of the volume of activation. The values of $\Delta V^{\neq}$ and $\Delta\beta^{\neq}$ were calculated by B and C. The results are shown in *Table* 2 and *Fig.* 2.

The activation enthalpies($\Delta H^{\neq}$) and entropies ($\Delta S^{\neq}$) used in this work were all calculated using *eqs.* (6) and (7).

$$\Delta H^{\neq} = R(T_1T_2/T_2 - T_1)\ln(k_2T_1/k_1T_2) \qquad (6)$$
$$\Delta S^{\neq} = \Delta H^{\neq}/T + R\ \ln(hk/\kappa T) \qquad (7)$$

The calculated values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the solvolysis of *p*-chlorobenzyl chloride in ethanol-water mixtures as various pressures at 30° and 40°C are presented in *Table* 3.

Correlations involving solvent effects; Laidler and Eyring[11] applied the continuum concept for

Table 3. Dependence of $\Delta H^{\neq}$ ($\Delta S^{\neq}$) on pressure and solvent composition

Press. (bar)	$\Delta H^{\neq}$ kcal. mole^{-1} ($\Delta S^{\neq}$ e. u) mole fraction of ethanol				
	0	0.10	0.20	0.30	0.40
1	20.1 (14.1)	19.0 (20.1)	19.9 (19.6)	20.7 (18.4)	20.9 (19.0)
200	20.2 (13.7)	19.2 (19.4)	20.0 (19.0)	20.8 (18.3)	20.8 (18.7)
400	20.4 (13.5)	19.6 (20.1)	19.8 (19.5)	20.8 (17.9)	20.7 (19.3)
800	20.3 (12.4)	18.9 (19.4)	19.8 (18.8)	20.7 (18.0)	20.8 (18.6)
1200	20.3 (12.5)	19.0 (19.0)	19.6 (18.9)	20.6 (17.8)	20.7 (18.4)
1600	20.1 (11.5)	18.7 (19.1)	19.5 (18.7)	20.5 (17.7)	20.8 (17.9)

*All entropies negative.

the solvent to interpret the free energy of activation of reactions between dipole molecules:

$$\Delta G^{\neq} = -RT\ \ln(kh/\kappa T)$$
$$= \Delta G_0^{\neq} - N\frac{D-1}{2D+1}\Sigma\frac{\mu_i^2}{a_i^3} + N\Sigma\phi_i \qquad (8)$$

Using the reaction $A+B \longrightarrow M^{\neq} \longrightarrow$products and applying *eq.* (8), the equation for the rate constant,

$$\ln\ k = \ln\ k_0 - \frac{1}{\kappa T}\left(\frac{\mu_A^2}{a_A^3} + \frac{\mu_B^2}{a_B^3} - \frac{\mu_{M^{\neq}}^2}{a_{M^{\neq}}^3}\right)$$
$$\frac{D-1}{2D+1} + \frac{\Sigma\phi}{\kappa T} \qquad (9)$$

can be obtained. The first term on the right of the *eq.* (9) gives the rate in a solvent $D=1$, and the last term on the right of the *eq.* (9) is the nonelectrostatic term. Provieded the nonelectrostatic terms are negligibly small, the plot of ln k versus the solvent parameter $q \equiv (D-1)/(2D+1)$ should give a straight line. The results are shown in *Fig.* 3.

If the water molecules in the transition state would have related to the solvolysis reactions, the rates would be taken the following equation, *i.e.* Rate$=k_2$[Cl—⬡—CH_2Cl] [H_2O]*. Putting $k=k_2[H_2O]^*$, we can write it as follows; ln $k=n$ ln[H_2O]+constants. n is frequently iden-

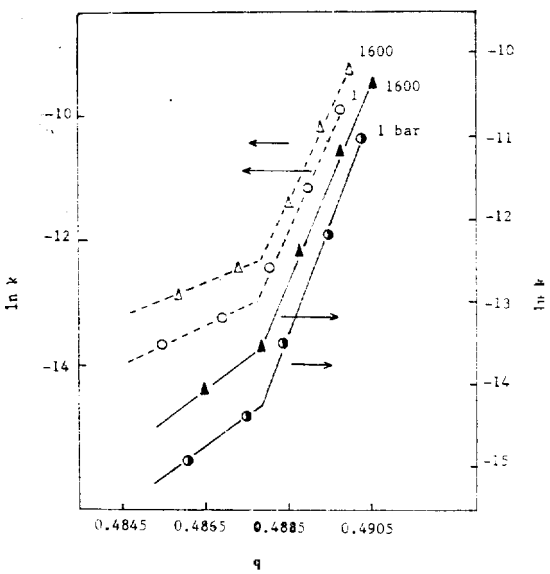

Fig. 3. Plots of the first-order rate constants as a function of the solvent parameter q under various pressures (—— : 30°C, ····· : 40°C).

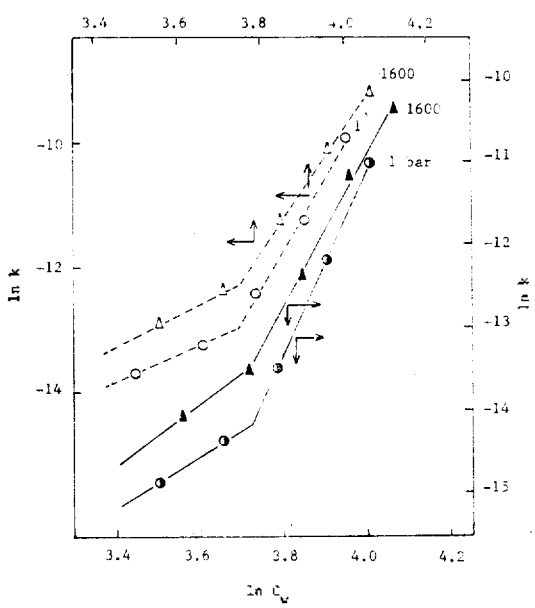

Fig. 4. Plots of ln k vs. ln C_w under various pressures (—— : 30°C, ····· : 40°C).

tified with the number of water molecules that are needed to solvate the transition state[12~14]. The plots of ln k versus ln C_w=ln[H_2O] are shown in *Fig.* 4.

DISCUSSION

As has been pointed out by Evans and Polanyi[15], $\Delta V^{\neq}$ may conveniently be regarded as being constituted of two terms; $\Delta_1 V^{\neq}$, which represents a change in the volume of a reacting molecule during an activation process, and $\Delta_2 V^{\neq}$, which is a corresponding change in the volume of the surrounding solvent molecules caused by their rearrangement. In a unimolecular ionization process, $\Delta_2 V^{\neq}$ is actually the dominating term[2].

All the activation volumes presented in *Table* 2 are negative. Negative values of $\Delta V^{\neq}$ have long been observed for solvolytic reactions and other unimolecular ionization processes. This phenomenon has been interpreted in terms of the pressure of a predominant electrostrictive volume contraction in the transition state which is undoubtedly more polar than the initial state[2]. In other words, these values represent that the contraction of the surrounding solvent due to the appearance of the partial charges is greater than the increase in volume caused by the lengthening of the C—Cl bond. And the variation of $|\Delta V^{\neq}|$ with pressure decreases with increasing pressure as shown in *Table* 2. This fact indicates that increased compression of the reaction medium lessens the difference between the partial molal volumes of the initial state and the transition state ($\Delta V^{\neq}=\bar{V}_t-\bar{V}_i$). Namely, we could know that the electrostrictive effect decreases with increasing pressure.

Fig. 2. shows the solvent dependence of activation volume under various pressures. Here, the values of $\Delta V^{\neq}$ exhibit the extremum behavior at about 0.20mole fraction of ethanol. It implies that the electrostricted solvent shell around the strongly dipolar transition state is harder than the solvent shell around the initial state at this solvent composition[10]. As a result,

volume contraction occurs largely in this region. And also, activation parameters in *Table* 2 and 3 are characterized by the large values of $\Delta H^{\neq}$ (18.7−20.9kcal·mole^{-1}), $-\Delta V_0^{\neq}$(11.2−21.4 ml·mole^{-1}) and the small negative values of $-\Delta S^{\neq}$ (11.5−20.1e.u.). These values are general characteristics of the S_N1 mechanism in ethanol-water mixtures[3,16].

As shown in *Fig.* 3, the plots of ln k *vs.* q show a good linear relationship at high dielectric constant and deviation from linearity at low dielectric constant under various pressures, because the nonelectrostatic term in ethanol-water mixtures of high dielectric constant is smaller than that of low dielectric constant[17]. Also, from *Fig.* 3, deviation from linearity in the 0.20∼0.30 mole fraction ethanol region indicates changes of mechanism and solvent structure. In fact, Hilton and Jefferson have suggested that a deviation from linearity between ln k *vs.* q indicates a change of mechanism in a solvolytic reaction in binary solvent mixture[18]. But this conclusion does not seem justified when the more extensive graph is considered. Accordingly, as has been pointed out by Kivinen[14], the use of the relation between ln k *vs.* ln C_w as a criterion of reaction mechanism is discussed. According to Kivinen, it has been proposed that $n \leq 2$ for the S_N2 type of displacement reactions and $n > 5$ for the S_N1 type. In this study, we could know that the n-values are 4.49∼5.82 for 0.20∼0.40 mole fraction of ethanol and 6 or more value for 0∼0.20 mole fraction of ethanol (see *Table* 4). In view of these facts, the solvolysis of p-chlorobenzyl chloride in ethanol-water mixtures takes place by the $S_N1(2)$ mechanism, *i.e.* is towards the S_N2 end of the S_N1 spectrum of behavior. And also, the n-value increases with increasing pressure and decreasing mole fraction of ethanol. We can therefore know that the S_N1 character of the reaction increases with increasing pressure and slightly decreases with increasing mole fraction of ethanol.

Table 4. n-values obtained for the solvolysis of p-chlorobenzyl chloride under various pressures.

Temp. (°C)	n-value					
	1 bar	200	400	800	1200	1600
30	4.67	4.92	5.00	5.22	5.55	5.82
40	4.49	4.87	4.78	5.14	5.41	5.59

From these results, at high pressure and water-rich solvent mixture, the binary solvent molecules merely solvate the ions produced, without forming a covalent bond, whereas, at low pressure and water-poor solvent mixture, a solvent molecule slightly makes a nucleophilic attack on the p-chlorobenzyl chloride forming partially a covalent bond.

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