

고압하에서 염화벤질의 가용매분해반응에 대한 속도론적 연구

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A Kinetic Study on the Solvolysis of Benzyl Chloride under High Pressure

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요 약. 염화벤질의 가용매분해반응에 대한 속도론 1~1600 bar 압력범위까지 변화시켜 가면서 온도 30 및 40°C에서 측정하였다. $\ln k$ 대 압력의 실험결과는 압력에 따라 이차함수형으로 변화하였으며, 이로부터 활성화부피 (ΔV^\ddagger)와 활성화 압축율 ($\Delta\beta^\ddagger$)의 값을 얻었다. $\ln k$ 를 용매파라미터 (Q_w) 및 $\ln C_w$ 의 함수로 도식한 결과 이들 사이의 관계는 본 연구의 반응이 S_N1 메카니즘으로 진행됨을 나타내었다. 이 전에 연구된 결과들과 비교한 결과 $|\Delta V_0^\ddagger|$ 와 n 값의 증가 순은 각각 $p\text{-Cl} > p\text{-H} > p\text{-CH}_3$ 와 $p\text{-CH}_3 > p\text{-H} > p\text{-Cl}$ 이었다. 이로부터 $p\text{-CH}_3$ 치환체는 $S_N1(1)$ 성격이 강하며, 반면 $p\text{-Cl}$ 는 $S_N1(2)$ 성격이 나타남을 알았다.

ABSTRACT. Rates of solvolysis of benzyl chloride in ethanol-water mixtures have been measured at 30 and 40°C under various pressures up to 1.6 kbar. The plots of $\ln k$ as a function of pressure are fitted to a second order function in P , and values of ΔV^\ddagger and $\Delta\beta^\ddagger$ are obtained from the results. Also the values of various pseudo thermodynamic quantities were evaluated from the rate constants. The relationships of the $\ln k$ to Q_w or $\ln C_w$ indicate that the reaction proceeds through S_N1 mechanism. A comparison between the present and the previous results gives that the increasing order of $|\Delta V_0^\ddagger|$ and n -values are $p\text{-Cl} > p\text{-H} > p\text{-CH}_3$ and $p\text{-CH}_3 > p\text{-H} > p\text{-Cl}$, respectively. From these results, it is believed substituent such as the $p\text{-CH}_3$ group favors the $S_N1(1)$ character, while the $p\text{-Cl}$ group leads to the $S_N1(2)$ character.

INTRODUCTION

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 studying solvolytic reaction mechanisms is well recognized recently.¹⁻⁴

Whalley⁵ has reviewed the significance of

activation volume in the determination of reaction mechanism, and has suggested that the volume of activation, ΔV^\ddagger , is probably easier to rationalize in terms of reaction mechanism than the other important parameters of activation, ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger . Hynes and his co-workers⁶ have also investigated the behavior of the activation volume and the temperature dependence of the activation volume, $(\partial\Delta V^\ddagger/\partial T)_p$.

Laidler and Martin⁷ have been concentrated on the effect of the change in solvent composition on the activation volume for the solvolysis of benzyl chloride in acetone-water mixture (0.1407 mole fraction of acetone) under high pressure. The mechanisms are interpreted on the view of $S_N2(1)$ or $S_N2(2)$ solvolyses. However, since the solvolysis in the present work were carried out in ethanol-water mixtures, a direct comparison cannot be made with the results in acetone-water mixtures,

In a previous report⁸ we proposed a relation between the activation volumes and the compressibilities in various ethanol-water mixtures on the basis of the electrostriction theory. Also, we compared the rate constants of solvolysis with the dielectric constants of aqueous ethanol and the number of water molecule participated in the transition state.

In this paper we investigated the solvolytic behavior of *p*-substituted benzyl chlorides in ethanol-water mixtures under various pressures. In order to determine the reaction mechanism of benzyl chloride various pseudo thermodynamic

quantities were calculated from the rate constants and discussed in terms of solvent structure variation of initial state and transition state, because these parameters are essential for getting detailed information about the transition states of the solvolysis reactions.

EXPERIMENTAL

Materials. Benzyl chloride (GR grade, Kanto, Japan) used was purified by doubly-distilled using a 100cm column packed with glass helices. The purity of benzyl chloride was established by a gas chromatographic analysis. Ethyl alcohol (GR grade, Merck, Germany) was used without further purification.

Water from an ion exchange column was distilled over $KMnO_4$ and then twice in a pyrex apparatus from which carbon dioxide was excluded. The specific conductance of the distilled water was about $9 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ at 25°C.

Apparatus and Kinetics. The high pressure apparatus described previously was used without further modification⁸.

The high pressure vessel was maintained at

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

Temp. (°C)	Pressure (bar)	$k \times 10^5 (\text{sec}^{-1})$ formole fraction of ethanol				
		0	0.10	0.20	0.30	0.40
30	1	2.52	0.865	0.236	0.0876	0.0485
	200	2.70	0.962	0.274	0.102	0.0555
	400	2.82	1.07	0.311	0.122	0.0621
	800	3.31	1.32	0.402	0.161	0.0777
	1200	3.79	1.58	0.510	0.204	0.0963
	1600	4.27	1.83	0.615	0.250	0.115
40	1	7.53	2.42	0.692	0.270	0.151
	200	8.08	2.70	0.803	0.314	0.173
	400	8.47	3.02	0.918	0.377	0.194
	800	10.0	3.74	1.19	0.497	0.244
	1200	11.5	4.49	1.51	0.636	0.305
	1600	13.0	5.22	1.83	0.782	0.363

a constant temperature (30 and 40°C) by a thermostat within $\pm 0.02^\circ\text{C}$. The reactions were followed by a conductometric method described in previous investigations.

The rates of solvolysis of benzyl chloride were studied in ethanol-water mixtures at 30 and 40°C over the pressure range from 1 to 1600 bar. 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 $5.4 \times 10^{-3} \text{ mole} \cdot \text{l}^{-1}$. All rate constants were determined by following the change in conductivity of the reaction mixture due to HCl formation as a function of time. The pseudo first-order rate constants were determined by the Guggenheim plots⁹ using the least-squares method.

RESULTS

Rates; The first-order rate constants for the solvolysis of benzyl chloride under various conditions of temperature, pressure and solvent composition are listed in Table 1. Each rate constant represents the average of two or more experiments. The experimental error in the determination of the rate constants was $\leq 2\%$. In all cases, the rates of reaction increase with

increasing temperature and pressure, and decrease with increasing solvent composition.

Activation Parameters. The activation volume, ΔV^\ddagger , defined as difference in the partial molal volumes between the transition and the initial states, can be determined experimentally from the rate data under pressure by means of the following equation;

$$\Delta V^\ddagger = -RT(\partial \ln k / \partial P)_T \quad (1)$$

In order to evaluate the volume of activation it is necessary to ascertain the functional dependence of $\ln k$ upon pressure. The problem of deriving an analytical expression for this dependence has been discussed by various workers.

Hyne *et al.*⁶ have examined the relative merits of various methods and concluded that the quadratic function of eq. (2) give the best representation of the dependence of $\ln k$ upon pressure for some organic reactions.

$$\ln k = a + bP + cP^2 \quad (2)$$

This method has been described in detail in a previous paper⁸. Substituting eq. (2) into eq. (1) we obtain the following equation for the evaluation of the activation volume.

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

Temp. (°C)	Mole fraction of ethanol	$-\Delta V^\ddagger (\text{ml} \cdot \text{mole}^{-1})$					$-\Delta \beta^\ddagger \times 10^3 (\text{ml} \cdot \text{bar}^{-1} \cdot \text{mole}^{-1})$	
		1 bar ($-\Delta V^\ddagger_0$)	200	400	800	1200		1600
30	0	8.65	8.60	8.55	8.46	8.37	8.27	0.23
	0.10	14.9	14.2	13.4	11.9	10.4	8.95	3.71
	0.20	18.7	17.8	16.9	15.1	13.4	11.6	4.44
	0.30	22.0	20.6	19.3	16.6	13.9	11.2	6.77
	0.40	16.3	15.6	14.9	13.6	12.2	10.9	3.44
40	0	9.37	9.29	9.21	9.05	8.90	8.74	0.39
	0.10	15.9	15.1	14.2	12.6	11.0	9.42	4.03
	0.20	19.7	18.7	17.8	15.9	14.0	12.1	4.74
	0.30	22.8	21.4	20.1	17.4	14.7	12.0	6.74
	0.40	17.2	16.5	15.8	14.3	12.9	11.4	3.64

$$\Delta V^* = -RT(b + 2cP) \quad (3)$$

The values of ΔV^* and $\Delta\beta^*$ were determined by b and c . The results are given in Table 2. Experimental plots of $\ln k$ vs. P usually curve towards the pressure axis with increasing pressure, i.e. the numerical value (the absolute value) of ΔV^* falls as the pressure is raised.

The activation enthalpies (ΔH^*) and entropies (ΔS^*) used in this work are the same equation that described in a previous paper. The calculated values of ΔH^* and ΔS^* for the solvolysis of benzyl chloride in ethanol-water mixtures under various pressures at 30 and 40°C are listed in Table 3.

Correlations involving solvent effects; Using the reaction $A + B \rightarrow X^* \rightarrow \text{products}$, the equation for the rate constant,

$$\ln k = \ln k_0 + \frac{1}{k_B T} \left(\frac{\mu^2_{X^*}}{r^3_{X^*}} - \frac{\mu^2_A}{r^3_A} - \frac{\mu^2_B}{r^3_B} \right) \frac{D-1}{2D+1} + \frac{\Sigma\phi}{k_B T} \quad (4)$$

can be obtained.¹⁰ In this equation, D is the

Table 3. Dependence of ΔH^* (ΔS^*) on pressure and solvent composition

Press. (bar)	ΔH^* kcal·mole ⁻¹ (ΔS^* e. u)				
	Mole fraction of ethanol				
	0	0.10	0.20	0.30	0.40
1	20.0	18.8	19.7	20.6	20.8
	(13.5)	(19.7)	(19.4)	(18.2)	(18.8)
200	20.1	18.9	19.7	20.6	20.8
	(13.3)	(19.3)	(19.1)	(18.0)	(18.5)
400	20.1	19.0	19.8	20.7	20.9
	(13.0)	(18.8)	(18.4)	(17.4)	(18.1)
800	20.2	19.0	19.9	20.7	21.9
	(12.3)	(18.1)	(17.7)	(17.0)	(17.3)
1200	20.3	19.1	19.9	20.8	21.2
	(11.7)	(17.6)	(17.3)	(15.9)	(16.4)
1600	20.4	19.2	20.0	20.9	21.1
	(11.3)	(17.0)	(16.6)	(15.3)	(16.2)

*All entropies negative.

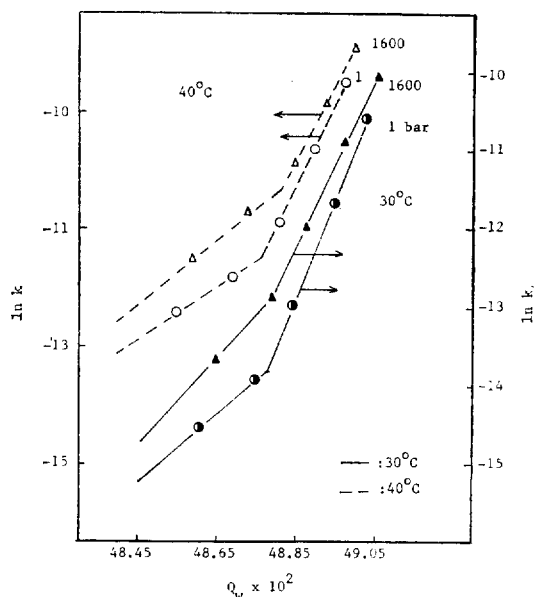


Fig. 1. Plots of the first-order rate constants as a function of the solvent parameter Q_w for the solvolysis of benzyl chloride under various pressures: 30°C, 40°C.

dielectric constant of the final solution formed, and for dilute solutions D is effectively the dielectric constant of the pure solvent or the binary solvent. r and μ are the radius of the molecule and the dipole moment, respectively. The first term on the right of the eq. (4) gives the rate in a solvent $D=1$, and the last term is the nonelectrostatic term. Provided the nonelectrostatic terms are negligibly small, the plot of $\ln k$ vs. $Q_w \equiv (D-1)/(2D+1)$ should give a straight line.¹²⁻¹³ The results are shown in Fig. 1. Here, the dielectric constants of ethanol-water mixture under various pressures were taken from the literature.¹⁴⁻¹⁶

If the water molecules in the transition state are related to the solvolysis reactions, the rates would be taken as the following equation, i.e. Rate = $k_2[\rho\text{-X-C}_6\text{H}_4\text{CH}_2\text{Cl}][\text{H}_2\text{O}]^n$. Putting $k = k_2[\text{H}_2\text{O}]^n$, we can write it as follows;

$$\ln k = n \ln [\text{H}_2\text{O}] + \text{const.} = n \ln C_w + \text{const.} \quad (5)$$

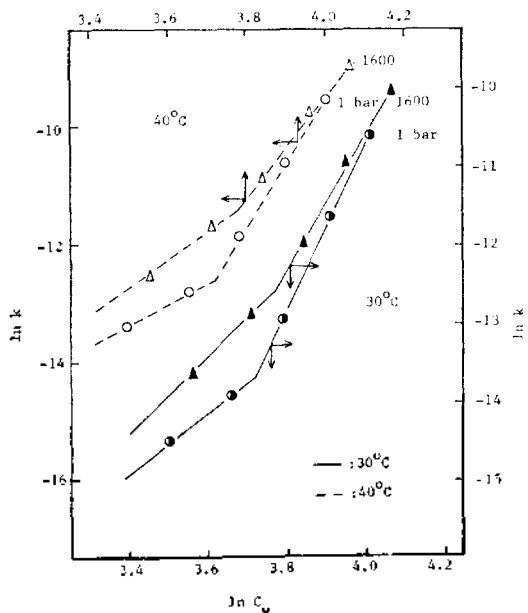


Fig. 2. Plots of $\ln k$ vs. $\ln C_w$ for the solvolysis of benzyl chloride in various mole fractions of ethanol-water mixture.

n is frequently identified with the number of water molecules that are needed to solvate the transition state.¹⁷⁻¹⁹ The plots of $\ln k$ versus $\ln C_w$ are shown in Fig. 2.

DISCUSSION

All the activation volumes presented in Table 2 are negative. Negative values of ΔV^\ddagger in this study correspond to increased electrostriction of the kinetically important immediate solvent environment around the more polar transition state compared with the initial state. 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. Generally, ΔV^\ddagger has been treated as the sum of the two terms;²⁰

$$\Delta V^\ddagger = \Delta V^\ddagger_{\text{intr.}} + \Delta V^\ddagger_{\text{solv.}} \quad (6)$$

Where $\Delta V^\ddagger_{\text{intr.}}$ is the change in volume of the

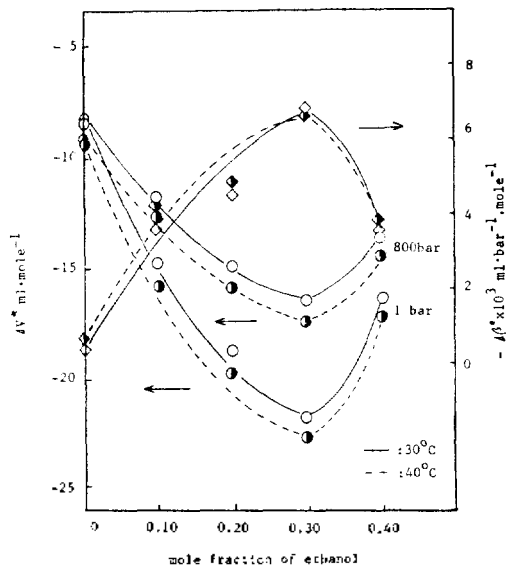


Fig. 3. Solvent dependence of ΔV^\ddagger and $\Delta\beta^\ddagger$ under various pressures.

reacting molecules themselves, when they form the transition state, and $\Delta V_{\text{solv.}}$ is the accompanying volume change due to interaction of the surrounding solvent molecules with the newly-formed transition state. The results in Table 2 clearly indicate the solvent dependence of the activation volumes. Since the $\Delta V^\ddagger_{\text{intr.}}$ term is insensitive to the solvent change²¹, the different behavior of ΔV^\ddagger in the five solvents (0-0.40 mole fraction) may be thought to be a reflection of differences in the electrostrictive effect.

And the variation of $|\Delta V^\ddagger|$ with pressure decrease 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 transition and the initial state ($\Delta V^\ddagger = \bar{V}_i - \bar{V}_j$). Namely, we could know that the electrostrictive effect decreases with increasing pressure.

Fig. 3 shows a solvent dependence of activation volume under various pressures, in which the values of ΔV^\ddagger and $\Delta\beta^\ddagger$ exhibit the

extremum behavior at about 0.30 mole fraction of ethanol. This 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 composition²². Also, in pure water (0 mole fraction of ethanol) $\Delta\beta^\ddagger$ is approximately zero. This phenomenon indicates that the partial molal volumes of the transition and the initial states responded similarly to pressure, i. e. $(\partial\bar{V}_i/\partial P)_T \doteq (\partial\bar{V}_i/\partial P)_T$.

And also, activation parameters in Table 2 and 3 are characterized by the large values of ΔH^\ddagger (18.8–21.1 kcal·mole⁻¹), $-\Delta V^\ddagger_0$ (8.65–22.8 ml·mole⁻¹) and the small negative values of $-\Delta S^\ddagger$ (11.3–19.7 e.u.). These values are general characteristics of the S_N1 mechanism in ethanol-water mixtures.^{8,12}

As shown in Fig. 1, the plots of $\ln k$ vs. Q_w show a good linearity 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.¹¹ Also, in Fig. 1, deviation from linearity in the 0.20~0.30 mole fraction of ethanol indicates an alternation of mechanism and solvent structure. In fact, Hilton and Jefferson²³ have suggested that a deviation from the linearity between $\ln k$ and Q_w indicates a change of mechanism in a solvolytic reaction in

binary solvent mixtures. But this conclusion is doubtful in the more extensive graph is considered. Accordingly, as pointed out by Kivinen²⁴, the use of the relation between $\ln k$ and $\ln C_w$ as a criterion of reaction mechanism should be discussed. Kivinen proposed $n \leq 2$ for the S_N2 type of displacement reactions and $n > 5$ for the S_N1 type. In this study, we obtained the n -values with 5.25~5.80 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). These values suggest that the solvolysis of benzyl chloride in ethanol-water mixtures takes place by the S_N1 mechanism. And also, the n -value increases with increasing pressure, which indicates that the S_N1 character of the reaction increase with increasing pressure.

The activation volumes of these compounds (*p*-Cl, *p*-H, *p*-CH₃) in 0.10 mole fraction of ethanol are given in Table 5. The order of the increase of $|\Delta V^\ddagger_0|$ values with para substituents is *p*-Cl > *p*-H > *p*-CH₃.

In the case of the *p*-methylbenzyl chloride the induction and resonance effect of the CH₃ group will reduce the effective charge on the carbon atoms, causing the charge to be smeared over the aromatic part of the molecule (delocalization). No such effect occurs with the *p*-chlorobenzyl chloride. There will thus be more electrostriction of the solvent with the *p*-chlorobenzyl chloride. In general, the magnitude

Table 4. n -values obtained for the solvolysis of *p*-substituted benzyl chlorides under various pressures

substituent	Temp. (°C)	n -value					
		1 bar	200	400	800	1200	1600
<i>p</i> -Cl	30	4.67	4.92	5.00	5.22	5.55	5.82
	40	4.49	4.78	4.87	5.14	5.41	5.59
<i>p</i> -H	30	5.45	5.50	5.56	5.79	5.77	5.80
	40	5.25	5.31	5.37	5.48	5.55	5.60
<i>p</i> -CH ₃	30	6.36	6.48	6.57	6.59	6.64	6.68
	40	6.01	6.16	6.19	6.23	6.27	6.31

Table 5. Activation parameters (ΔV_0^\ddagger and ΔS^\ddagger) for the solvolysis of *p*-substituted benzyl chlorides in 0.10 mole fraction of ethanol at 30°C

Substituent	ΔV_0^\ddagger (ml·mole ⁻¹)	ΔS^\ddagger (e·u)
<i>p</i> -Cl	-17.6	-20.1
<i>p</i> -H	-14.9	-19.7
<i>p</i> -CH ₃	-13.0	-15.0

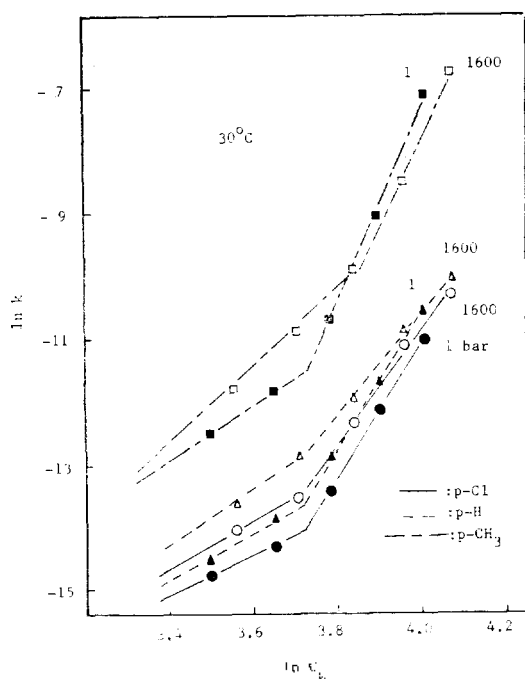


Fig. 4. Plots of $\ln k$ as a function of $\ln C_w$ for the solvolysis of benzyl chlorides under various pressures

of the electrostrictive term for solvolytic reaction depends on the degree of charge dispersion in the transition state; when the developed charge is dispersed more extensively over the whole molecule, the electrostrictive volume contraction becomes less significant, and hence a less negative value of ΔV^\ddagger appears^{25,26}

Electrostriction is a phenomenon where a strong electrostatic interaction exerts between the reacting molecules and the surrounding solvent molecules. Therefore, the degree of freedom of

the solvent molecules is restricted resulting in a decrease in the entropy of the system. In fact, reactions which have large negative ΔV_0^\ddagger values are known to be characterized by large negative ΔS^\ddagger values (see Table 5).²⁷ Accordingly, one can anticipate the presence of a rough proportionality between ΔV_0^\ddagger and ΔS^\ddagger .

From Table 4 and Fig. 4, one may notice that the n -values are 4.49~6.69 and the order of the increase of n -values with *p*-substituents is *p*-CH₃ > *p*-H > *p*-Cl. Accordingly, this may be interpreted in terms of greater $S_{N1}(1)$ character in the *p*-CH₃ case and in terms of greater $S_{N1}(2)$ character in the *p*-Cl case.

From these results, at high pressure and water-rich solvent mixture (less alcoholic composition), the binary solvent molecules merely solvate the ions produced, without forming a covalent bond, whereas, at low pressure and water-poor solvent mixture (more alcoholic composition), the binary solvent molecules slightly make a nucleophilic attack on the *p*-substituted benzyl chlorides forming partially a covalent bond.

REFERENCES

1. W. J. le Noble, "Progress in Physical Organic Chemistry," Vol. 5, Interscience Pub., N. Y., 1967.
2. N. S. Isaacs, "Liquid Phase High Pressure Chemistry," John Wiley & Sons, 1981.
3. C. F. Wells, *J. Chem. Soc., Faraday Trans. I*, 73, 1851 (1977).
4. J. G. Jee, *et al.*, *Bull. Korean chem. Soc.*, 4, 237 (1983).
5. E. Whalley, "Advances in Physical Organic Chemistry," Vol. 2, Academic Press, N. Y., 1964.
6. (a) J. B. Hyne, H. S. Golinkin and W. G. Laidlaw, *J. Am. Chem. Soc.*, 88, 2104 (1966); (b) M. J. Mackinnon and J. B. Hyne, *Can. J. Chem.*, 49, 3840 (1971).

7. K. J. Laidler and R. Martin, *Inter. J. Chem. Kinetics*, **1**, 113 (1969).
8. O. C. Kwun and J. B. Kyong, *Bull. Korean Chem. Soc.*, **6**, 259 (1985).
9. E. A. Guggenheim, *Phill. Mag.*, **2**, 538 (1926).
10. J. K. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).
11. E. S. Amis and J. F. Hinton, "Solvent Effect on Chemical Phenomena," Academic Press, 1973.
12. R. F. Hudson and D. A. Brown, *J. Chem. Soc.*, 3352 (1953).
13. K. J. Laidler, *Suomen Kemistilehti A*, **33**, 44 (1960).
14. Jeffries Wyman, *J. Am. Chem. Soc.*, **53**, 3292 (1931).
15. Gösta Akerlöf, *ibid.*, **54**, 4125 (1932).
16. B. B. Owen, R. C. Miller, and C. E. Milner, *J. Phys. Chem.*, **65**, 2065 (1961).
17. A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **72**, 1536 (1968).
18. E. Tommila, *Acta Chem. Scand.*, **9**, 975(1955).
19. A. Kivinen, *Ann. Acad. Sci. Fenn. All Chem.*, **108**, 1(1960).
20. M. G. Evns and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935).
21. K. R. Brower, *J. Am. Chem. Soc.*, **85**, 1401 (1963).
22. S. J. Dickson and J. B. Hyne, *Can J. Chem.*, **49**, 2394 (1971).
23. V. J. Hilton and E. G. Jefferson, *J. Chem. Soc.*, 2756 (1954).
24. A. Kivinen, *Acta Chem. Scand.*, **19**, 845 (1965).
25. J. B. Hyne and R. Wills, *J. Am. Chem. Soc.*, **85**, 3650 (1963).
26. A. Sera, *et al.*, *Bull. Chem. Soc. Japan* **46**, 3490 (1973).
27. K. J. Laidler, *Trans. Faraday Soc.*, **51**, 1497 (1955).