

- 1933 (1976)
- (6) R.M. Golding and L.C. Stubbs, *Proc. Roy. Soc.*, **A354**, 223 (1977).
- (7) R.M. Golding and L.C. Stubbs, *J. Magn. Reson.*, **33**, 627 (1979).
- (8) R.M. Golding, R.O. Pascual and S. Ahn, *J. Magn. Reson.*, **46**, 406 (1982).
- (9) J. Reuben, *J. Magn. Reson.*, **50**, 233 (1982).
- (10) H.M. McConnell and R.E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).
- (11) R.J. Kurland and B.R. McGravey, *J. Magn. Reson.*, **2**, 286 (1970).
- (12) A.D. Buckingham and P.J. Stiles, *Mol. Phys.*, **24**, 99 (1972).
- (13) P.J. Stiles, *Mol. Phys.*, **27**, 501 (1974).
- (14) P.J. Stiles, *Mol. Phys.*, **29**, 1271 (1975).
- (15) W.B. Lewis, J.A. Jackson, J.F. Lemon and H.J. Taube, *J. Chem. Phys.*, **36**, 694 (1962).
- (16) R.M. Golding and P. Pyykko, *Mol. Phys.*, **26**, 1389 (1973).
- (17) B. Bleaney, *J. Magn. Reson.*, **8**, 91 (1972).
- (18) R.M. Golding, *Mol. Phys.*, **8**, 561 (1964).
- (19) B.R. McGravey, *J. Magn. Reson.*, **33**, 445 (1979).
- (20) J.W.M. De Boer, P.J. Sabers, C.W. Hilbers and E. De Boer, *J. Magn. Reson.*, **25**, 455 (1977).
- (21) H.A. Bergen and R.M. Golding, *Aust. J. Chem.*, **30**, 2361 (1977).
- (22) L.C. Stubbs, Unpublished Thesis (Ph. D. The University of New South Wales, 1978).
- (23) R.M. Golding, "Applied Wave Mechanics", Van Nostrand, London, 1969.
- (24) L.A. Boudreaux and L.N. Mulay, "Theory and Applications of Molecular Paramagnetism", John Wiley and Sons, N.Y., 1979.
- (25) S. Ahn, H.C. Suh and K.H. Lee, *Bull. Korean Chem. Soc.*, **4**, 17 (1983).
- (26) J.S. Griffith, "The Theory of Transition Metal Ions", Cambridge University Press, London, 1961.

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

Oh Cheun Kwun¹ and Jin Burm Kyong

Department of Chemistry, Hanyang University, Seoul 133, Korea (Received March 19, 1985)

Rate constants for the solvolysis of *p*-methylbenzyl chloride in various ethanol-water mixtures were studied at 30 and 40°C under various pressures up to 1600 bar. The rates of reaction were increased with increasing temperature and pressure, and decreased with increasing solvent composition of ethanol mole fraction. From the rate constants, the values of the activation parameters (ΔV^\ddagger , $\Delta\beta^\ddagger$, ΔH^\ddagger and ΔS^\ddagger) were evaluated. The values of ΔV^\ddagger and $\Delta\beta^\ddagger$ exhibit the extremum behavior at about 0.30 mole fraction of ethanol. This behavior is discussed in terms of solvent structure variation (electrostriction). From the relation between the reaction rate and the dielectric constant of solvent or the number of water molecule participated in the transition state, it could be postulated that the reaction proceeds through S_N1 mechanism.

Introduction

In recent years, the effect of pressure on the rates of organic reactions in binary solvent mixtures has been extensively studied¹⁻⁴. Rate measurements of reactions under high pressure allow us to estimate activation volumes, ΔV^\ddagger , by means of the following expression;

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\Delta V^\ddagger/RT \quad (1)$$

where ΔV^\ddagger is the difference in partial molal volume between initial state and transition state. 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 measurement and the interpretation of activation volumes have become a useful tool in the study of reaction mechanisms in binary solvent mixtures⁵. Whally⁶ 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, ΔG^\ddagger , ΔH^\ddagger

and ΔS^\ddagger .

Laidler and Martin⁷ have been concentrated on the effect of the change in solvent composition on the activation volumes for the solvolysis of *p*-methylbenzyl chloride in acetone-water mixtures under high pressure.

The results are interpreted on the view that the mechanisms are $S_N2(1)$. However, since the solvolysis considered in our analysis were carried out in ethanol-water mixtures, a direct comparison cannot be made with the acetone-water results.

Hyne and his co-workers⁸ have investigated the behavior of the activation volume, ΔV^\ddagger , and the temperature dependence of the activation volume, $(\partial \Delta V^\ddagger / \partial T)_P$.

In this study, we calculated various pseudo thermodynamic quantities from the rate constants and discussed in terms of solvent structure variation of initial state 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*-methylbenzyl 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 mixtures and the number of water molecule participated in the transition state.

Experimental

Materials; The *p*-methylbenzyl chloride (GR grade, Tokyo Kasei, Japan) was dried over calcium chloride and doubly-distilled using a 100cm column packed with glass helices; the middle fraction of the first distillation was redistilled, and only the resulting middle fraction was used in the experiments. The purity of *p*-methylbenzyl chloride was established by a gas chromatographic analysis.

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 \cdot cm $^{-1}$ at 25°C.

Apparatus; The high pressure apparatus is shown in Figure 1. The high pressure vessel is equipped with an electrical head which is replaceable, if necessary, by a sampling assembly. The pressure-transmitting fluid was mineral oil and pressure was applied by means of a hand-operated pressure pump (Swiss NOVA). The high pressure vessel was maintained at the desired temperature 30° and 40°C. by a thermostat within $\pm 0.02^\circ\text{C}$ (Haake, Germany).

The electroconductivity cell is shown in Figure 1 (B). It is composed of two parts; One is made of pyrex glass cylinder of 4.2cm 3 in volume in which two platinum plate electrodes are sealed, the other two branched teflon tubes of 7cm long and 0.4cm in diameter. The former acts as conducting cell, the latter as pressure-transmitting equipment. The electroconductivity cell was supported by a stainless steel holder which was suspended

ed from the head of the pressure vessel by wire attached to hooks screwed into the head.

The electric conductivity of the solution was then measured by means of capacitance (Cardwell NO.1626391)-conductivity bridge (Fisher Model 31, Magic eye type) and oscilloscope.

Kinetics; The rates of solvolysis of *p*-methylbenzyl 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 9.4×10^{-3} mole \cdot l $^{-1}$. The electroconductivity cells were well rinsed with distilled water and the kinetic solution, and filled with this solution and placed in the high pressure vessel. All solutions were degassed by the conventional freeze-pump thaw technique before being loaded into the electroconductivity cells. 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 plots⁹ using the method of least squares ($\ln(R_t - R_{\infty}) / (R_i - R_{\infty}) = -kt + \text{constants}$).

Results

Rates and Activation parameters; The pseudo first-order rate constants for the solvolysis of *p*-methylbenzyl chloride under various conditions of temperature, pressure and solvent composition are shown in Table 1. Each rate constant represents the average of two or more experiments. Estimated error was less than 2% of its value. In all cases, the rates of reaction increase with increasing temperature and pressure, and decrease with increasing solvent composition (ethanol mole fraction).

According to the transition state theory¹⁰, the volume of activation at a given temperature, pressure and solvent composition, ΔV^\ddagger , is related to the pressure dependence of rate constant by eq.(1). In order to determine 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 at length by various workers. Benson and Berson¹¹ made use of the Tait equation¹² for the pressure variation of the partial molal volume of the species; by expressing the partial molal volume of reactions and activated complexes in terms of eq. (2).

TABLE 1: Rate Constants for the Solvolysis of *p*-Methylbenzyl Chloride at 30° and 40°C in Aqueous Ethanol at Various Pressures

Temp. (°C)	Pressure (bar)	$k \times 10^3(\text{sec}^{-1})$ for mole fraction of ethanol				
		0	0.10	0.20	0.30	0.40
30	1	87.3	11.7	2.31	0.683	0.357
	200	91.4	13.3	2.66	0.867	0.404
	400	96.6	14.0	3.09	1.05	0.458
	800	105	16.5	3.77	1.27	0.563
	1200	111	18.5	4.45	1.53	0.646
	1600	115	19.8	4.91	1.85	0.736
40	1	290	32.5	7.01	2.29	1.22
	200	305	36.9	8.08	2.87	1.39
	400	326	39.0	9.42	3.45	1.56
	800	356	46.1	11.5	4.14	1.92
	1200	378	51.7	13.6	4.97	2.19
	1600	396	55.3	15.1	5.97	2.47

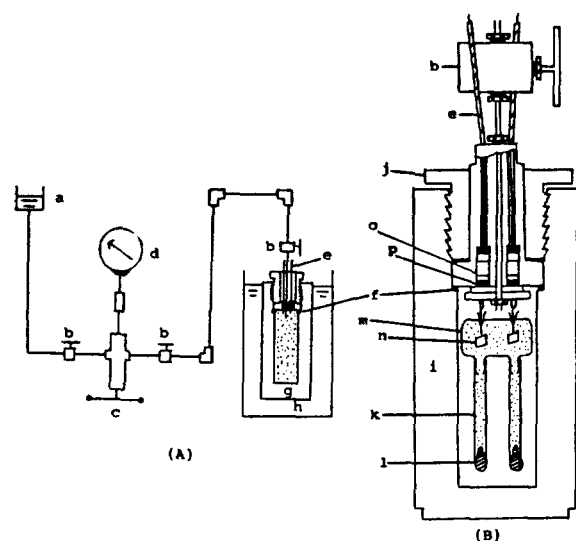


Figure 1. High pressure apparatus. (A) Schematic diagram of hydrostatic system a: reservoir, b: ventilator, c: hand pump, d: gauge, e: electrical leads to bridge, f: O-ring, g: high pressure vessel, h: thermostatted bath. (B) Sketch of conductivity cell and pressure vessel. i: stainless steel vessel, j: gland nut, k: teflon tube, l: stopper, m: conductivity cell, n: platinum electrodes, o: teflon rod, p: bakelite.

$$(1/P) \ln(k_p/k_0) = A + BP^{0.52} \quad (2)$$

where P is the pressure and B is a complex expression containing the volume of activation. This equation fits the data satisfactorily for certain reaction, but it has been criticized on various grounds.

Golinkin and his co-workers¹³ made a careful examination of various methods and concluded that their data were best represented by the quadratic function (eq.(3)), since the standard deviations were smaller for the quadratic function than for the other functions.

$$\ln k = A + BP + CP^2 \quad (3)$$

Figure 2 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 eq. (3).

Substitution of eq. (3) into eq. (1) gives

$$\Delta V^* = -RT(B + 2CP) \quad (4)$$

The volume of activation at atmospheric pressure (zero applied pressure), ΔV_0^* , is therefore given by eq. (5).

$$\Delta V_0^* = -RTB \quad (5)$$

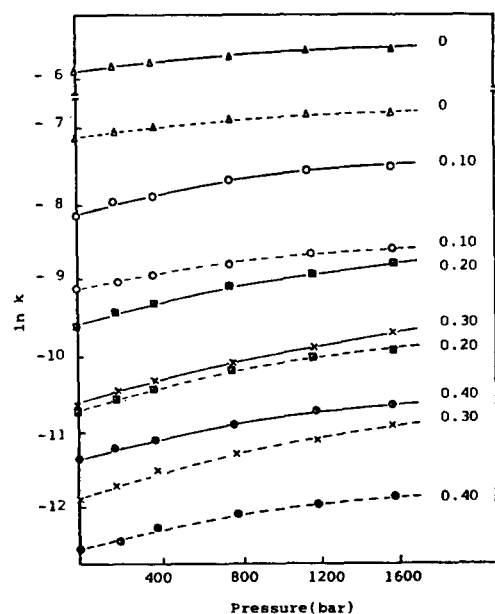


Figure 2. Pressure dependence of $\ln k$ for the solvolysis of *p*-methylbenzyl chloride in various mole fractions of ethanol-water mixture (--- : 30°C, — : 40°C).

TABLE 2: Activation Volume Parameters for the Solvolysis of *p*-methylbenzyl Chloride in Aqueous Ethanol at 30° and 40°C

Temp. (°C)	Mole fraction of ethanol	$-\Delta V^*$ (ml·mole ⁻¹)						$-\Delta\beta^* \times 10^3$ (ml·bar ⁻¹ ·mole ⁻¹)
		1 bar (- ΔV_0^*)	200	400	800	1200	1600	
30	0	7.33	6.66	5.99	4.64	3.30	1.95	3.36
	0.10	13.0	11.8	10.5	8.09	5.63	3.17	6.14
	0.20	19.5	17.7	15.8	12.1	8.40	4.70	9.25
	0.30	23.4	21.2	19.0	14.7	10.3	5.96	10.9
	0.40	16.4	15.1	13.7	11.0	8.35	5.66	6.71
40	0	8.30	7.40	6.51	4.71	2.91	1.12	4.49
	0.10	13.8	12.4	11.0	8.30	5.54	2.79	6.88
	0.20	20.3	18.3	16.4	12.5	8.56	4.65	9.78
	0.30	23.0	20.9	18.9	14.8	10.6	6.52	10.3
	0.40	17.5	16.0	14.5	11.4	8.40	5.37	7.58

The pressure dependence of ΔV^* is given by differentiation of eq. (4) with respect to pressure.

$$\begin{aligned} \Delta\beta^* &= -(\partial\Delta V^*/\partial P)_T \\ &= -\{(\partial\bar{V}_i/\partial P)_T - (\partial\bar{V}_i/\partial P)_T\} = -2RTC \end{aligned} \quad (6)$$

where $\Delta\beta^*$ represents the pressure dependence of the volume of activation. The coefficients A , B and C in eq. (3) were obtained by the method of least squares, and the values of ΔV^* and $\Delta\beta^*$ were calculated by B and C . The results are shown in Table 2 and Figure 3.

The activation enthalpies (ΔH^*) and entropies (ΔS^*) used in this work were all calculated using eqs. (7) and (8).

$$\Delta H^* = R(T_1T_2/T_2 - T_1) \ln(k_2T_1/k_1T_2) \quad (7)$$

$$\Delta S^* = \Delta H^*/T + R \ln(hk/kT) \quad (8)$$

The calculated values of ΔH^* and ΔS^* for the solvolysis of *p*-methylbenzyl chloride in ethanol-water mixtures as various pressures at 30° and 40°C are presented in Table 3.

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

$$\begin{aligned} \ln k &= \ln \left(\kappa \frac{\kappa T}{h} k_0^* \right) - \frac{1}{\kappa T} \frac{D-1}{2D+1} \left(\frac{\mu_a^2}{a_a^3} + \frac{\mu_b^2}{a_b^3} - \frac{\mu_{ab}^2}{a_{ab}^3} \right) \\ &\quad + \frac{\phi_A + \phi_B - \phi_{AB}}{\kappa T} \end{aligned} \quad (9)$$

can be obtained.^{14,15} In this equation, D is the 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. a and μ are the radius of the molecule and the dipole moment, respectively. The first term on the right of the eq. (9) gives the values of gaseous phase, and the last term the nonelectrostatic term. Provided the nonelectrostatic terms are negligibly small, the plot of $\ln k$ vs. $(D-1)/(2D+1)$ should give a straight line.^{16,17} The results are shown in Figure 4. Here, the dielectric constants of ethanol-water mixture under various pressures were taken from the literature.¹⁸⁻²⁰

If the water molecules in the transition state would have relation to the solvolysis reactions, the rates would be taken as the following equation, *i.e.* Rate = $k_2[\text{CH}_3-\text{C}^{\oplus}(\text{H}_2\text{O})-\text{CH}_2\text{Cl}][\text{H}_2\text{O}]^n$. Putting $k = k_2[\text{H}_2\text{O}]^n$, we can write it as follows; $\ln k = n \ln[\text{H}_2\text{O}] + \text{const}$. Where n is the number of water molecule participated in the transition state. The plots of $\ln k$ vs. $\ln[\text{H}_2\text{O}]$ are shown in Figure 5.

TABLE 3: Dependence of ΔH^\ddagger (ΔS^\ddagger) on Pressure and Solvent Composition

Press. (bar)	ΔH^\ddagger kcal·mole ⁻¹ (ΔS^\ddagger e.u.)				
	mole fraction of ethanol				
	0	0.10	0.20	0.30	0.40
1	22.0	18.6	20.3	22.2	22.5
	(-0.12)	(15.0)	(12.7)	(8.94)	(9.04)
200	22.1	18.6	20.3	22.0	27.7
	(-0.50)	(14.8)	(12.4)	(9.26)	(8.37)
400	22.3	18.7	20.4	21.8	22.7
	(-1.30)	(14.4)	(11.9)	(9.34)	(8.28)
800	22.4	18.8	20.4	21.7	22.8
	(-1.76)	(14.0)	(11.4)	(9.46)	(7.56)
1200	22.5	18.8	20.5	21.6	22.8
	(-2.14)	(13.7)	(11.0)	(9.31)	(7.26)
1600	22.4	18.7	20.6	21.5	22.7
	(-2.70)	(13.6)	(10.4)	(9.34)	(7.31)

*All entropies negative.

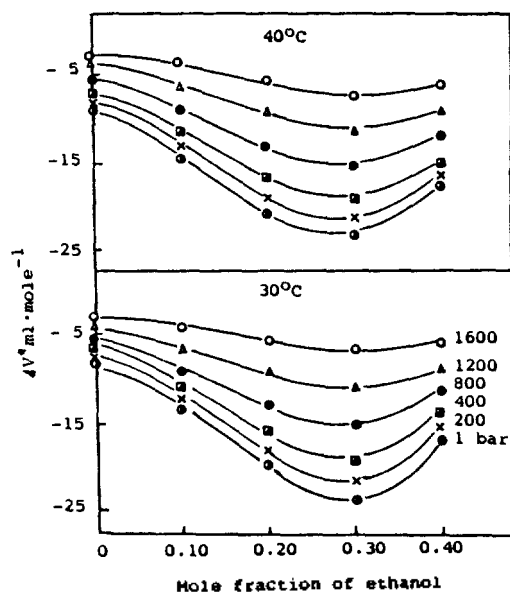


Figure 3. Solvent dependence of activation volume under various pressures.

Discussion

The volumes of activation presented in Table 2 are all 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. 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 initial state and the transition state ($\Delta V^\ddagger = \bar{V}_r - \bar{V}_i$). Namely, we could know that the electrostrictive effect decreases with increasing pressure.

Figure 3. shows the solvent dependence of activation volume under various pressures. Here, the values of ΔV^\ddagger and $\Delta\beta^\ddagger$ ex-

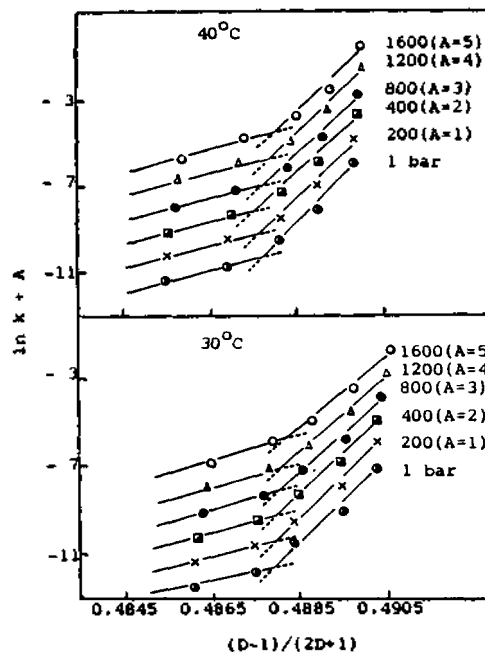


Figure 4. Plots of $\ln k$ vs. $(D-1)/(2D+1)$ under various pressures

TABLE 4: n -Values Obtained for the Solvolysis of *p*-Methylbenzyl Chloride under Various Pressures

Temp. (°C)	n -value					
	1 bar	200	400	800	1200	1600
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

hibit the extremum behavior at about 0.30 mole 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 composition¹³.

From Table 2 and 3, extremum behavior of the ΔV^\ddagger dependence on solvent composition is the higher ethanol concentration than that of ΔH^\ddagger and ΔS^\ddagger . If the reason for the existence of these extrema is the same for all three activation parameters, it must be concluded that the factors leading to the extremum in ΔV^\ddagger have a different dependence on solvent composition from those responsible for the extremum in ΔH^\ddagger and ΔS^\ddagger . The existence of such a situation is not hard to envision since ΔV^\ddagger behavior is probably more directly related to solvent structure than either ΔH^\ddagger or ΔS^\ddagger . And also, activation parameters in Table 2 and 3 are characterized by the large values of ΔH^\ddagger (18.6–22.8 kcal·mole⁻¹), $-\Delta V^\ddagger$ (-7.33–-23.4 ml·mole⁻¹) and the small negative values of ΔS^\ddagger (2.70–-15.0 e.u.). These values are general characteristics of the S_N1 mechanism in ethanol-water mixtures^{5,16,21}.

As shown in Figure 4, the plots of $\ln k$ vs. $(D-1)/(2D+1)$ 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 constant¹⁷. Also, from Figure 4, 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. $(D-1)/(2D+1)$ indicates a change of mechanism

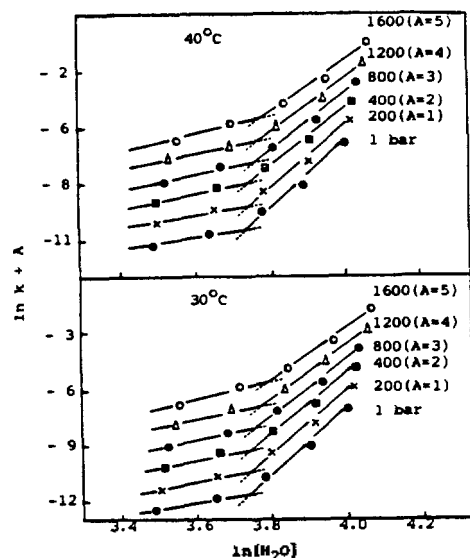


Figure 5. Plots of $\ln k + A$ vs. $\ln [H_2O]$ under various pressures.

in a solvolytic reaction in binary solvent mixtures²². But this conclusion does not seem justified when the more extensive graph is considered. Accordingly, as has been pointed out by Kivinen,²³ the use of the relation between $\ln k$ vs. $\ln[H_2O]$ as a criterion of reaction mechanism is discussed. According to Kivinen, it has been found that the value of the slope (n -value) is 6–7 for S_N1 reactions, but much lower, 2–3, for S_N2 reactions. In this study, we could know that the n -values are 6.01–6.68 for 0.20–0.40 mole fraction of ethanol and 7 or more value for 0 (pure water)–0.20 mole fraction of ethanol (see Table 4 and Figure 5). In view of these facts, the solvolysis of *p*-methylbenzyl chloride in ethanol–water mixtures takes place by the S_N1 mechanism. 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.

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), a solvent molecule slightly makes a nucleophilic attack on the *p*-methylbenzyl chloride forming partially a covalent bond.

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References

- (1) W. J. LeNoble and A. Shurpik, *J. Org. Chem.*, **35**, 3588 (1970).
- (2) M. L. Tonnet and E. Whalley, *Can. J. Chem.*, **53**, 3414 (1975).
- (3) H. Kelm (Ed.), "High Pressure Chemistry," Proceedings of NATO Advanced Study Institute, Reidel, Amsterdam, 1978.
- (4) J. G. Jee and O. C. Kwun, et al., *Bull. Korean Chem. Soc.*, **5**, 112 (1984).
- (5) N. S. Isaacs, "Liquid Phase High Pressure Chemistry," John Wiley & Sons, 1981.
- (6) E. Whalley, "Advances in Physical Organic Chemistry," Vol. 2, Academic Press, N.Y., 1964.
- (7) K. J. Laidler and R. Martin, *Inter. J. Chem. Kinetics*, **1**, 113 (1969).
- (8) M. J. Mackinnon and J. B. Hyne, *Can. J. Chem.*, **49**, 3840 (1971)
- (9) E. A. Guggenheim, *Phill. Mag.*, **2**, 538 (1926).
- (10) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, 1941.
- (11) S.W. Benson and J.A. Berson, *J. Amer. Chem. Soc.*, **84**, 152 (1962).
- (12) P. G. Tait, "Physics and Chemistry of the Voyage of H.M.S. Challenger," Vol. 2, Part 4, 1888.
- (13) H. S. Golinkin, I. Lee and J. B. Hyne, *J. Amer. Chem. Soc.*, **89**, 1307 (1967).
- (14) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934).
- (15) J. K. Laidler and H. Eyring, *Ann. N.Y. Acad. Soc.*, **39**, 303 (1940).
- (16) D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 3352 (1953).
- (17) E. S. Amis and J. F. Hinton, "Solvent Effect on Chemical Phenomena," Academic Press, 1973.
- (18) Jeffries Wyman, *J. Amer. Chem. Soc.*, **53**, 3292 (1931).
- (19) Gösta Akerlöf, *ibid.*, **54**, 4125 (1932).
- (20) B.B. Owen, R.C. Miller and C.E. Milner, *J. Phys. Chem.*, **65**, 2065 (1961).
- (21) O. C. Kwun, et al., *J. Korean Chem. Soc.*, **25**, 152 (1981).
- (22) V. J. Hilton and E. G. Jefferson, *J. Chem. Soc.*, 2756 (1954)
- (23) A. Kivinen, *Acta Chem. Scand.*, **19**, 845 (1965).