The Effect of Pressure on the Solvolysis of Benzylchlorides (II).

*p*-Chlorobenzyl Chloride in Ethanol-Water Mixtures

Oh Cheun Kwun† and Jin Bum Kyong

Department of Chemistry, Hanyang University, Seoul 133, Korea

(Received October 8, 1985)

INTRODUCTION

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

The activation volume, \( \Delta V^e \), 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;

\[
\Delta V^e = -RT(\partial \ln k/\partial P)\tau \tag{1}
\]

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 studying solvolytic reaction mechanisms is well recognized.²
Whalley 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, $\Delta G^\ne$, $\Delta H^r$ and $\Delta S^r$.

Hyne and his co-workers have also investigated the study of the behavior of the activation volume, $\Delta V^a$, and the temperature dependence of the activation volume, $(\partial \Delta V^a/\partial T)_p$. 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 paper, 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 $9 \times 10^{-7}$ mho$\cdot$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.

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 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 $4.0 \times 10^{-3}$ mole$\cdot$1$^{-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 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, $\Delta V^a$, 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

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure (bar)</th>
<th>( \Delta \times 10^4 ) (sec(^{-1})) for mole fraction of ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td>0  0.10  0.20  0.30  0.40</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.67  0.523  0.138  0.0582  0.0354</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.77  0.584  0.167  0.0643  0.0392</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.89  0.679  0.194  0.0715  0.0452</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>2.39  0.878  0.252  0.0896  0.0543</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>2.77  1.07  0.339  0.114  0.0664</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>3.20  1.39  0.436  0.133  0.0778</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>0  0.11  0.20  0.30  0.40</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.02  1.48  0.410  0.130  0.111</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>5.33  1.67  0.498  0.200  0.123</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>5.71  1.98  0.571  0.223  0.140</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>7.05  2.47  0.745  0.277  0.169</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>8.44  3.01  0.990  0.351  0.206</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>9.81  3.87  1.24  0.408  0.242</td>
</tr>
</tbody>
</table>

\[ \ln k = A + BP + CP^2 \]  \( \text{(2)} \)

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

\[ \Delta V^\ast = -RT(B + 2CP) \]  \( \text{(3)} \)

The volume of activation at atmospheric pressure (zero applied pressure), \( \Delta V^\ast \) is therefore determined according to eq. (4).

\[ \Delta V^\ast = -RTB \]  \( \text{(4)} \)

The pressure dependence of \( \Delta V^\ast \) is given by differentiation of eq. (3) with respect to pressure.

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

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Mole fraction of ethanol</th>
<th>( -\Delta V^\ast ) (mL mole(^{-1}))</th>
<th>( -\Delta V^\ast \times 10^3 ) (mL bar mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 bar ((-\Delta V^\ast)) 200 400 800 1200 1600</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>11.8 11.4 11.2 10.7 10.3 9.83</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>17.6 17.3 17.0 16.4 15.9 15.3</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>21.2 20.4 19.6 17.9 16.2 14.5</td>
<td>4.13</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>15.0 14.6 14.2 13.4 12.6 11.8</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>15.3 15.5 15.9 15.2 11.1 9.63</td>
<td>3.58</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>11.2 11.1 11.1 11.0 10.9 10.8</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>17.4 16.9 16.4 15.4 14.4 13.4</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>21.4 20.5 19.6 17.8 16.0 14.2</td>
<td>4.48</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>15.7 15.2 14.7 13.7 12.7 11.7</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>15.3 14.6 14.6 13.7 12.7 10.2</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Journal of the Korean Chemical Society
The activation enthalpies ($\Delta H^\circ$) and entropies ($\Delta S^\circ$) used in this work were all calculated using eqs. (6) and (7).

\[
\Delta H^\circ = R(T_1/T_2 - T) \ln (k_2T_1/k_1T_2) \tag{6}
\]

\[
\Delta S^\circ = \Delta H^\circ / T + R \ln (kh/kT) \tag{7}
\]

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

Correlations involving solvent effects: Laidler and Eyris applied the continuum concept for the solvent to interpret the free energy of activation of reactions between dipole molecules:

\[
\Delta G^\circ = -RT \ln (kh/kT)
\]

\[
= \Delta G^\circ_0 - N \frac{D-1}{2D+1} \ln \frac{a_A^2}{a_B^2} + N \Sigma \phi_i \tag{8}
\]

Using the reaction $A + B \rightarrow M^+ \rightarrow$products and applying eq. (8), the equation for the rate constant,

\[
\ln k = \ln k_0 - \frac{1}{kT} \left(\frac{a_A^2}{a_B^2} + \frac{a_B^2}{a_A^2} - a_M^{2+}\right) \frac{D-1}{2D+1} \Sigma \phi_i \tag{9}
\]

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. Provided the nonelectrostatic terms are negligibly small, the plot of $\ln k$ versus the solvent parameter $q = (D-1)/(2D+1)$ 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 $= k_2[Cl] - (\square - CH_2Cl) [H_2O]^*$. Putting $k = k_2[H_2O]^*$, we can write it as follows: $\ln k = n \ln [H_2O] + \text{constants}$. $n$ is frequently iden-
DISCUSSION

As has been pointed out by Evans and Polanyi, $\Delta V^*$ may conveniently be regarded as being constituted of two terms; $\Delta_1 V^*$, which represents a change in the volume of a reacting molecule during an activation process, and $\Delta_2 V^*$, which is a corresponding change in the volume of the surrounding solvent molecules caused by their rearrangement. In a unimolecular ionization process, $\Delta_2 V^*$ is actually the dominating term².

All the activation volumes presented in Table 2 are negative. Negative values of $\Delta V^*$ 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. 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 $|\Delta V^*|$ 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 ($\Delta V^* = V_T - V_i$). 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 $\Delta V^*$ exhibit the extremum behavior at about 0.20 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 composition. 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 $\Delta H^\circ$ (18.7–20.9 kcal mol$^{-1}$), $-\Delta V^\circ$ (11.2–21.4 ml mol$^{-1}$) and the small negative values of $-\Delta S^\circ$ (11.5–20.1 e.u.). These values are general characteristics of the $S_N2$ mechanism in ethanol–water mixtures.$^4$15.

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 Jefferon 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. $q$ in $C_n$ 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 solvolytic 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.

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.

ACKNOWLEDGEMENT

This investigation was carried out with the grant from the Korean Science and Engineering Foundation in 1984. This financial support is gratefully acknowledged.

REFERENCES
