The Influence of Solvent on the Solvolysis of Ethyl Cinnamate in Water-Acetone Mixed Solvent System

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Abstract
The kinetic of alkaline hydrolysis of ethyl cinnamate was investigated at different percentage of aqua-organic solvent mixture with Acetone (30 to 70% v/v) over the temperature range of 20°C to 40°C. The specific rate constant was found to be decreased with increasing proportion of solvent (Acetone) at all the temperature range. The Iso-composition Activation energy (E) was also evaluated which decreases with solvent composition in (water-Acetone) system. The number of water molecule associated with the activated complex is found to be increased (0.7003 to 0.786) in water-Acetone system. The thermodynamic activation parameter such as Enthalpy of Activation (Δ H), Entropy of Activation (Δ S) and Gibb's free energy of activation (Δ G) were also calculated.

Keywords: Solvolysis; Solvent-solute interaction; Iso composition energy; Activated complex; Activation parameters

Introduction
Although the solvent effect on the rate and mechanism of the various type of reaction has been reported [1-3] but very little attention has paid towards the study of the solvent effect on the thermodynamic activation parameter and the solvent-solute interaction, particularly for an ion-dipolar reaction. In order to highlight the above noted idea, it has been proposed to make the kinetic study of the solvent effect on the alkali catalyzed hydrolysis of ethyl cinnamate.

Experimental
All the chemical used were either of BDH (Analar) or Merck (CD) grades. The water used was doubly distilled. The specific rate constant value was calculated using second order reaction and tabulated in Tables 1 and 2, the Iso composition Activation energy (E) were evaluated and tabulated in Table 3. Thermodynamic activation parameter was also calculated inserted in Table 4. The number of water molecule evaluated by the slope of plot of log k and log (H₂O) and inserted in Table 5.

Results and Discussion
Solvent effect on rate of reaction
From Tables 1 and 2; Figure 1, it is clear that specific rate constant values of the reaction go on decreasing with increasing organic co-solvent in the solvent (Acetone). From the plot of log k with mole % of organic co-solvent, it was observed that plots follows trend at all temperature. From the plot (Figure 1) it is also apparent that the decrease is regular and follows linear trend at all the temperature in solvent. The trend of variation in the values of specific rate constant may be discussed in light of the Hughes and Ingold theory [4]. According to the theory of increase in dielectric constant values of the reaction media result in increase in the rate when there is concentration of charges on the transition state and cause a decrease in the rate when there is diffusion or destruction of charges on transition state. Acetone being poor anion solvate their increase in aqueous medium will facilitate the desolvation

<table>
<thead>
<tr>
<th>Temp in °C</th>
<th>30%</th>
<th>40%</th>
<th>50%</th>
<th>60%</th>
<th>70%</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>15.66</td>
<td>11.22</td>
<td>10</td>
<td>8.12</td>
<td>6.45</td>
</tr>
<tr>
<td>25°C</td>
<td>20.89</td>
<td>16.59</td>
<td>13.48</td>
<td>10.59</td>
<td>8.49</td>
</tr>
<tr>
<td>30°C</td>
<td>27.54</td>
<td>21.87</td>
<td>16.98</td>
<td>13.64</td>
<td>10.83</td>
</tr>
<tr>
<td>35°C</td>
<td>38.01</td>
<td>30.19</td>
<td>23.17</td>
<td>18.62</td>
<td>14.62</td>
</tr>
<tr>
<td>40°C</td>
<td>45.7</td>
<td>36.3</td>
<td>27.86</td>
<td>22.38</td>
<td>17.74</td>
</tr>
</tbody>
</table>

Table 1: Specific rate constant k × 10² (dm³/mole/min) values of alkali catalyzed hydrolysis of ethyl-cinnamate in water-acetone.

<table>
<thead>
<tr>
<th>Temp in °C</th>
<th>% of Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>1.569</td>
</tr>
<tr>
<td>25°C</td>
<td>1.5229</td>
</tr>
<tr>
<td>30°C</td>
<td>1.4437</td>
</tr>
<tr>
<td>35°C</td>
<td>1.3468</td>
</tr>
<tr>
<td>40°C</td>
<td>1.2218</td>
</tr>
</tbody>
</table>

Table 2: Variation 3+Log K value against 10^3/T, water-acetone System.

<table>
<thead>
<tr>
<th>Temp in °C</th>
<th>% of acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>0.700</td>
</tr>
<tr>
<td>25°C</td>
<td>0.732</td>
</tr>
<tr>
<td>30°C</td>
<td>0.746</td>
</tr>
<tr>
<td>35°C</td>
<td>0.759</td>
</tr>
<tr>
<td>40°C</td>
<td>0.786</td>
</tr>
</tbody>
</table>

Table 3: Values of Iso-composition activation energy (Water-Acetone) media.

References:

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of ions already solvated by water molecule. Since initial and transition state (both being anions differing in size and charge) cannot be equally desolated, the rate will be affected by such specific salvation changes. Depletion in the rate of the reaction in different reaction with change temperature and constants of acetone of reaction media partly due to dielectric effect and partly due to salvation change to different degree in the initial and translated of reaction. Our interpretation has also been supported recently by Singh [5]. Effect of solvent on activation energy (Iso-composition) of the reaction

From Table 3 and Figure 2, it is found that the value of Iso-composition Activation Energy is goes on decreasing trend with gradual addition of organic content In case of Acetone the value of Activation Energy decreases from 41.64 to 37.39 Kj/mole with increase proportion of Acetone in water-acetone media. The depleting trend in the $E_{\text{exp}}$ values can be explained by any of the following three situations.

(i) The transition state is less desolvated than the initial state.

(ii) The initial state is less solvated than the transition state.

(iii) The initial state is desolvated and the transition state is solvated.

Out of three situation the third factor seems to be operative as both $\Delta H^*$ and $\Delta S^*$ values of the reaction were found with decreasing with increasing concentration acetone in water-acetone media. Our this inference has also been in favor of the finding of Singh [5].

On the basis of depletion (water-Acetone) media, it is inferred that acetone has the solvating power to solvate the initial state and to desolated the transition state. Our this finding is also supported by Singh [6].

Effect of solvating power on the number of water molecules associated with the activated complex and on mechanistic path of the reaction

The effect of water concentration $[H_2O]$ of water-Acetone media on rate and mechanism of alkaline hydrolysis of ethyl cinnamate has been studied in light of guideline and observation render by Tommil [7], Lane [8], Elsmongy et al. [9] they have established an idea of the number of water molecule associated with activated complex has been determined by plotting log $k$ against $[H_2O]$, according to the relation proposed by Robertson [10].

$$\log k = \log n \log [H_2O]$$

Here, $n$ is the salvation number which tells about the criteria for studying about the mechanism of reaction.

It is obvious from the plots of log $k$ versus log $[H_2O]$ that at all the five temperature at which kinetics were studied, straight lines shown in Figure 2. From the value of slope as mentioned in Table 5 and Figure 2 the number of water molecules associated with Activated complex varies from (0.700 to 0.786) in case of water-Acetone media with rise of temperature.

From the above values of slope mentioned in Table 3 it is inferred that equilibrium shifted from dense form (d) of water to bulk form (b) in case of water-Acetone media, with rise of temperature.

$$[H_2O]_d \approx [H_2O]_b$$

In the light of finding of Robertson [10] and Singh and from above noted trend, it is concluded that solvating power of Acetone change the mechanism of the reaction from bi-molecular to unimolecular, the resent report of Singh has been support of our finding.

Thermodynamic activation parameters

Thermodynamic activation parameters are shown in Table 6.

Conclusion

The result of this work indicate that the rate of hydrolysis of ethyl

Table 6: Thermodynamics activation parameters of the reaction in Water- Acetone media ($\Delta H^*$ and $\Delta G^*$ in Kj/Mole, $\Delta S^*$ in J/K/Mole).
cinnamate decreasing trend at all temperature which appear that depletion in rate of reaction with change in temperature and concentration is probably due to dielectric effect and partly due to salvation change to different degree in transition state of reaction. Decrease in value of activation energy with gradual increasing proportion of acetone indicates that initial state is desolvated and transition state is solvated. The number of water molecule associated with Activated complex indicates the solvating power of acetone change the mechanism of reaction from bimolecular to unimolecular.

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References