Kinetics and Solvent Effect in Hydrolysis of Ethyl Cinnamate in Water-Methanol Mixture

Singh AK*
Department of Chemistry, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh, India

Abstract

The solvent effect of ethanol on the alkali catalyzed solvolysis reaction was studied by carrying out the hydrolysis of ester namely ethyl cinnamate in water-methanol media of varying composition consisting of 30 to 70% of methanol (v/v) at different Temperature ranging from 20°C to 70°C. The Specific rate constant values of the reaction were found to depleted with increasing concentration of methanol in reaction media. Enhancement in ∆G* with simultaneous depletion in ∆H* and ∆S* of the reaction, it has been concluded that reaction is enthalpy stimulating and entropy inhibiting and specific salivation take place in water- methanol media. From the evaluated value of Iso kinetic temperature, which is less than 300 indicates that this reaction in water-methanol media obey Barclay-Butler rule and there is weak but considerable solvent –solute interaction taking place in reaction media. However, the possible rate depleting factors in the rate can be enlisted as follows:

1. Decrease in bulk dielectric constant value of medium,
2. Decrease in the polarity of the reaction media by adding less polar methanol to it.

The above noted two depleting factors are quite in operation and are with good agreement with theory of Hughes and Ingold[4] that rate ought to decrease with decreasing dielectric constant of the reaction media. Such decrease in rate constant with increasing proportion of organic co-solvent like methanol have also reported by Elsemomy[5], and recently by Singh[6].

Solvent effect on iso-composition activation energy of the reaction

From Table 4, (Figure 2) it is found that the values of Iso-composition Activation Energy goes on increasing [52.16 to 57.37 kJ/mole] with increasing concentration of MEOH from 30% to 70% (v/v) in reaction media. The increasing trend in the E_exp values can be explained by any of the following three situations.

1. Transition state is desolvated less than Initial state
2. Transition state is solvated more than the initial state
3. Transition state is solvated and initial state desolvated.

The transition state being large cat ion (ester+H+) is available more for solvation by ethanol molecule than the initial state, so third factor seem to operative in my case and is also supported by decrease in entropy of activation (∆S°). This conclusion is also supported recently by Singh et al. [7].

Keywords: Solvent effect; Ethyl cinnamate; Hydrolysis water-methanol mixture; Specific rate constant; Iso-dielectric activation energy; Activated complex

Introduction

The effect of solvent on the rate and mechanism of alkali catalyzed hydrolysis of ester have received continued attention, but the explanation put forward is not satisfactory [1-3]. So, in order to explore the above idea, it was thought essential and useful to investigate about the fact that how ethyl cinnamate is useful as flavor and fragrance agent in cigarettes and cut tobacco. This compound is also used as food additive for human beings.

Experimental

Kinetic of alkali catalyzed solvolysis of ethyl cinnamate was studied by adding different concentrations of the protic organic co solvent(Ethanol) from 30 to 70% (v/v) in reaction media at five different temperature i.e., 20°C, 25°C, 30°C, 35°C and 40°C using volumetric method. All chemicals used were either of BDH or Merck grades. The strength of the solution was kept 0.1M with respect to NaOH and 0.05 M with respect to ester. The reaction rates were determined by titrating the sample at different time interval using phenolphthalein indicator. The specific rate constant value was calculated using second order reaction and tabulated in Table 1. Variation of specific rate constant with different mole% and different temperature are inserted in Table 2. The value of slopes of Arrhenius plot of logk versus 1/T (Table 3) (Iso-composition activation energy (E*) and plots of logk verse D(Iso-dielectric activation energy) were evaluated and inserted in Tables 4 and 5 respectively. From the plots of Logk versus Log [H₂O] Table 6, the value of slopes were evaluated and tabulated in Table 7. Thermodynamic Activation Parameter were also calculated and inserted in Table 8.

Results and Discussion

Solvent effect on specific rate

In order to highlight the effect of the solvent on specific rate constant values (Table 1) of the reaction, the logk values were plotted against the mole% of organic co-solvent (their values from Table 2 as shown in Figure 1) and were found to show decreasing trend. The plots show, that with increase in the temperature of the reaction, the degree of depletion in the rate constant of the reaction becomes slower.

*Corresponding author: Singh AK, Department of Chemistry, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh, India, Tel: 07351318000; E-mail: anilkumar2_singh@yahoo.com

Received July 25, 2017; Accepted August 07, 2017; Published August 14, 2017


Copyright: © 2017 Singh AK, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Journal of Physical Chemistry & Biophysics

Research Article

Open Access
Solvent effect and iso-dielectric activation energy

From the slope of Arrhenius plot of logkD values against 1/T, the value of iso-dielectric activation energy has been evaluated and recorded in Table 5. From the Table 5 (Figures 3 and 4), it is inferred that E_D value goes on increasing from 55.45 to 65.09 kJ/mole with increasing D values. This trend of variation is similar as E_c values (62.31 to 64.88 KJ/mole) (Table 5) with gradual addition of more solvent in reaction media. This interpretation was supported by past view of Wolford [8] recently supported by Singh et al. [9].

Effect of concentration of water molecules [H_2O], associated with the activated complex on mechanistic path of the reaction

The effect of water concentration [H_2O] of the water-ethanol mixture, on rate and mechanism of alkali catalysed hydrolysis of ethyl cinnamate has been studies. For this, the number of water molecule associated with activated complex was determined by plotting Log k against Log[H_2O]. According to Robertson [10] relation

\[ \log k = \log k_0 + n \log [H_2O] \]

Here n is the solvation number and decide the criteria about the mechanism of reaction.

From noted value of slope mention in Table 7, it may be seen that with rise of temperature from 20 to 70°C, the value of slope (number of water molecule associated with activated complex) goes on increasing from (2.08 to 2.56). This observation may be attributed to the fact that with addition of ETOH in reaction media, the equilibrium of water component reaction media shifted from its dense form to its bulky form with rise of temperature.
Figure 4: Variation of 3+log\(k\) against log[H\(_2\)O] water-methanol system.

Table 5: Values of Iso-Dielectric Activation Energy (water-methanol).

<table>
<thead>
<tr>
<th>% of Acetone</th>
<th>% of H(_2)O</th>
<th>Log [H(_2)O]</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>70%</td>
<td>1.5660</td>
<td>0.890</td>
<td>1.075</td>
<td>1.210</td>
<td>1.70</td>
<td>1.570</td>
</tr>
<tr>
<td>40%</td>
<td>60%</td>
<td>1.5229</td>
<td>0.820</td>
<td>0.989</td>
<td>1.145</td>
<td>1.290</td>
<td>1.500</td>
</tr>
<tr>
<td>50%</td>
<td>50%</td>
<td>1.4437</td>
<td>0.735</td>
<td>0.895</td>
<td>1.045</td>
<td>1.190</td>
<td>1.390</td>
</tr>
<tr>
<td>60%</td>
<td>40%</td>
<td>1.3468</td>
<td>0.650</td>
<td>0.819</td>
<td>0.965</td>
<td>1.090</td>
<td>1.280</td>
</tr>
<tr>
<td>70%</td>
<td>30%</td>
<td>1.2218</td>
<td>0.565</td>
<td>0.730</td>
<td>0.880</td>
<td>0.980</td>
<td>1.160</td>
</tr>
</tbody>
</table>

Table 6: Variation of 3+Log \(k\) with log [H\(_2\)O] (water – methanol) at different temperature.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>2.08</td>
<td>2.16</td>
<td>2.21</td>
<td>2.29</td>
<td>2.56</td>
</tr>
</tbody>
</table>

Table 7: Calculated values of slopes (Plot of log \(k\) versus log[H\(_2\)O]) of water-methanol media.

<table>
<thead>
<tr>
<th>% of MEOH</th>
<th>Mole %</th>
<th>(\Delta H) in KJ/Mole</th>
<th>(\Delta G)</th>
<th>(\Delta S)</th>
<th>(\Delta G)</th>
<th>(\Delta S)</th>
<th>(\Delta G)</th>
<th>(\Delta S)</th>
<th>(\Delta G)</th>
<th>(\Delta S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>16.03</td>
<td>53.31</td>
<td>93.64</td>
<td>137.64</td>
<td>94.27</td>
<td>137.44</td>
<td>94.98</td>
<td>137.52</td>
<td>95.60</td>
<td>137.30</td>
</tr>
<tr>
<td>40%</td>
<td>22.90</td>
<td>52.95</td>
<td>94.20</td>
<td>140.78</td>
<td>94.91</td>
<td>138.42</td>
<td>95.65</td>
<td>140.89</td>
<td>96.31</td>
<td>140.77</td>
</tr>
<tr>
<td>50%</td>
<td>30.82</td>
<td>52.87</td>
<td>94.68</td>
<td>142.6</td>
<td>95.44</td>
<td>140.30</td>
<td>96.23</td>
<td>143.10</td>
<td>96.96</td>
<td>143.14</td>
</tr>
<tr>
<td>60%</td>
<td>40.06</td>
<td>51.28</td>
<td>95.16</td>
<td>149.76</td>
<td>95.88</td>
<td>147.24</td>
<td>96.72</td>
<td>149.96</td>
<td>97.43</td>
<td>149.83</td>
</tr>
<tr>
<td>70%</td>
<td>50.97</td>
<td>50.51</td>
<td>95.64</td>
<td>154.02</td>
<td>96.39</td>
<td>151.44</td>
<td>97.19</td>
<td>154.05</td>
<td>97.96</td>
<td>152.56</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[H(<em>2)O]</em>(_d)</th>
<th>(\Delta [H(_2)O]_b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Finally, it is inferred that with rise of temperature, the number of water molecule associated with activated complex increases as the proportion of bulky form of water molecule increase with increase in MEOH content in the water-ethanol mixture and it explain that when MEOH is added to water, the mechanistic path of reaction is changed from biomolecular to unimolecular in similar way as observed by parker and Tomilinson [11] and recently by Singh [12].

Conclusion

In hydrolysis of Ethyl cinnamate, the decreasing trend of specific rate constant at all temp with increasing mole % of co-solvent which show that the decrease is either due to bulk dielectric constant value of medium or decrease in the polarity of the reaction media by adding less polar methanol to it. The values of Iso-composition Activation Energy goes on increasing [52.16 to 57.37 kJ/mole] with increasing concentration of MEOH from 30% to 70%(v/v) in reaction media indicate Transition state is solvated and initial state desolveted. Increase in the value of and \(\Delta G\) with simultaneous increase in \(\Delta H\) and\(\Delta S\) for the hydrolysis ethyl cinamate in water- Methanol is enthalpy dominating and Enthalpy control. The linear plots obtained by plotting log\(k\) as function of D represent the different electrostatic interaction for the ion-dipole as well as dipole - dipole reaction. Solvating power of MEOH change the mechanism of the reaction from bio-molecular to unimolecular due to increase in number of water molecule associated with activated complex (2.08 to 2.56).

References


