Kinetics of the Alkaline Solvolysis of Trichloroacetate Ion in Water-Ethanol Solutions

I. M. Issa, E. M. Diefallah, M. R. Mahmoud, and A. M. El-Nady

Chem. Dept. Faculty of Science, Assiut University, Assiut, Egypt

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Alkaline Solvolysis, Trichloroacetate Ion

The alkaline solvolysis of trichloroacetic acid in water-ethanol mixtures have been studied in the presence of 0.40–0.80 M sodium hydroxide within the temperature range 35–70 °C. The rate constant increased with progressive addition of the organic solvent. The dielectric constant effect on the reaction rate was investigated. The radius of the activated complex at different temperatures was calculated. The isocomposition and isodielectric energies as well as the thermodynamic parameters of activation were calculated and their significance in terms of solvent composition has been discussed. It was concluded that the reactant state is extensively higher solvated than the transition state by the highly polar (water) solvent.

Introduction

The kinetics and mechanisms of solvolysis reactions involving α-halo-acids and their salts were previously described. Wagner reported the results of a study of the alkaline hydrolysis and other substitution reactions with iodoacetate ion in aqueous solution. Brooks and Dawson studied the progressive elimination of bromine in the aqueous hydrolysis of sodium bromoacetate and concluded that the course of reaction is approximately unimolecular. The reaction of α-bromo-propionate ion with methoxide ion follows second-order kinetics and yields α-methoxy-propionate with inversion of configuration.

In the present investigation the alkaline solvolysis of trichloroacetic acid in water-ethanol solutions of different compositions is studied. This is made with the aim to clarify the effect of solvent on the kinetics and mechanism of this reaction and to collect some information concerning the nature of the transition state.

Experimental

Materials

Chemicals of the purest grade available (A. R. products) were used in all experiments. Ethyl alcohol used in this investigation was purified according to recommended methods.

Solutions

All solutions of trichloroacetic acid, sodium chloride and ammonium thiocyanate were prepared by dissolving the accurate amount in bidistilled water. The silver nitrate solution was standardized using Moira’s and Volhard’s methods. Sodium hydroxide solution free of carbonate was prepared from the A. R. product and stored in a well steamed waxed tall glass tube for several days. Solutions of the required molarity were prepared by dilution of the clear solution, then standardized against A. R. potassium hydrogen phthalate.

Rate measurements

The rate of alkaline solvolysis of trichloroacetate ion in aqueous and water-ethanol solutions was measured in the temperature range 35–70 °C. The initial concentrations of trichloroacetic acid were in the range 0.1 to 0.05 mole/litre, while the initial concentrations of the base were in the range 0.80 to 0.40 mole/litre. Reaction mixtures were prepared by mixing known amounts of trichloroacetic acid, measured volumes of aqueous sodium hydroxide, the proper amounts of bidistilled water and/or ethanol in a volumetric flask. The solutions and solvents were previously brought to the desired temperature before mixing. After suitable time intervals 5 ml portions of the reaction mixture were withdrawn by the aid of a calibrated pipette and analysed for their chloride ion content with standard silver nitrate solution following Volhard’s method.
Results and Discussion

Effect of medium composition

The rate of alkaline solvolysis of trichloroacetate ion at all concentrations used and in water-ethanol solutions covering the composition range 0.30 to 1.0 water mole fractions was found to be first order with respect to trichloroacetate ion. On the other hand, the rate of the reaction was found to be independent of sodium hydroxide concentration within the range of 0.40 to 0.80 M. The rate constants were evaluated from the slopes of the straight lines obtained when log(a-x) was plotted against t, where (a) is the initial concentration of trichloroacetate ion and (x) is the decrease in its concentration after the lapse of time t. Fig. 1 shows typical plots in water-ethanol solutions obtained at 35 °C. The rate-determining step of this reaction is expected to be the step involving the cleavage of the C-C bond to yield the carbanion $^{6}$

\[ \text{CCl}_3\text{COO}^- \rightarrow \cdot\text{CCl}_3^- + \text{CO}_2 \]

The carbanion intermediate is presumably stabilized by d-orbital resonance.$^{7,8}$

From the data shown in Table I and represented graphically in Fig. 2, it is readily seen that the rate constant increases gradually with increase of ethanol concentration in solution. Generally, an increase in ethanol concentration will result in:

(a) the decrease in water concentration and (b) the decrease in the fraction of free water molecules due to the fact that addition of ethanol leads to a destruction of the tetrahedral structure of water, whereby the hydrogen bonding between water molecules is replaced by stronger hydrogen bonding between water and alcohol molecules.$^{9,10}$ On the other hand, it is expected that the transition state is more voluminous than the reactant state as it involves a net loosening of the bonds to release the neutral CO$_2$ molecule, and thus it exhibits a de-localization of charge. This can be represented as follows:

Table I. Specific first order rate constant values, $k'$, energy of activation and thermodynamic parameters of activation for the solvolysis reaction of trichloroacetic acid.

<table>
<thead>
<tr>
<th>Mole fraction of water</th>
<th>$D_{at}$ at 35°C</th>
<th>35°C</th>
<th>45°C</th>
<th>50°C</th>
<th>56°C</th>
<th>70°C</th>
<th>$\Delta E^*$ kcal/mole</th>
<th>$\Delta H^*$ kcal/mole</th>
<th>$\Delta F^*$ kcal/mole</th>
<th>$-\Delta S^*$ e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>75.00</td>
<td>0.04</td>
<td>0.18</td>
<td>0.40</td>
<td>0.88</td>
<td>7.68</td>
<td>31.03</td>
<td>31.42</td>
<td>31.39</td>
<td>28.50</td>
</tr>
<tr>
<td>0.964</td>
<td>71.02</td>
<td>0.10</td>
<td>0.42</td>
<td>0.85</td>
<td>1.49</td>
<td>9.59</td>
<td>27.91</td>
<td>27.30</td>
<td>27.27</td>
<td>27.89</td>
</tr>
<tr>
<td>0.932</td>
<td>66.86</td>
<td>0.14</td>
<td>0.51</td>
<td>1.17</td>
<td>2.13</td>
<td>12.05</td>
<td>26.54</td>
<td>25.93</td>
<td>25.90</td>
<td>27.29</td>
</tr>
<tr>
<td>0.889</td>
<td>62.53</td>
<td>0.21</td>
<td>0.54</td>
<td>1.49</td>
<td>2.98</td>
<td>14.39</td>
<td>25.63</td>
<td>25.01</td>
<td>24.98</td>
<td>27.47</td>
</tr>
<tr>
<td>0.840</td>
<td>57.97</td>
<td>0.28</td>
<td>0.85</td>
<td>1.81</td>
<td>3.41</td>
<td>16.00</td>
<td>24.25</td>
<td>23.64</td>
<td>23.61</td>
<td>27.29</td>
</tr>
<tr>
<td>0.709</td>
<td>48.44</td>
<td>0.35</td>
<td>1.41</td>
<td>2.52</td>
<td>5.12</td>
<td>18.40</td>
<td>22.88</td>
<td>22.27</td>
<td>22.24</td>
<td>27.14</td>
</tr>
<tr>
<td>0.505</td>
<td>37.75</td>
<td>0.58</td>
<td>1.79</td>
<td>3.19</td>
<td>5.76</td>
<td>20.80</td>
<td>21.05</td>
<td>20.44</td>
<td>20.41</td>
<td>26.84</td>
</tr>
<tr>
<td>0.353</td>
<td>32.07</td>
<td>0.70</td>
<td>2.05</td>
<td>3.68</td>
<td>6.39</td>
<td>25.60</td>
<td>20.13</td>
<td>19.52</td>
<td>19.49</td>
<td>26.72</td>
</tr>
</tbody>
</table>
According to the above facts, the slow rate of solvolysis observed in the presence of a lower percentage of ethanol in the medium can be mainly ascribed to the significantly higher solvation of the reactant state as compared with the transition state by the highly polar solvent (water).

**Effect of dielectric constant**

The dielectric constant values for the ethanol-water mixtures in the temperature range 35–70 °C were adopted from Akerlof's data\(^1\) by interpolation from large scale plots. Plots of log k against 1/D shown in Fig. 3 (D = dielectric constant of the medium) exhibit a linear portion in the low dielectric region that agrees with the electrostatic theory. The deviation from linearity in the region of high dielectric constant is probably due to higher preferential solvation of the reactant ion by the more polar solvent component (which is water with its high D value).

![Fig. 3. Variation of log k vs. 1/D at different temperatures.](image)

The variation of log k with 1/D within the linear portion was applied for the determination of the radius of the activated complex making use Amis' equation\(^2\)

\[
\ln k_D = \ln k_\infty + \frac{Ze \mu}{KTDr^*^2}
\]

Thus, the slope of the linear portion is equal to \(Ze \mu/KTDr^*^2\), where \(r^*\) is the radius of the activated complex, \(Ze\) is the ionic charge and \(\mu\) is the dipole moment of trichloroacetic acid which amounts to 1.78 debye. The latter value was calculated using the following equations\(^3\):

\[
dipole\ moment = 0.0127 \sqrt{P'} T \times 10^{-18}
\]

\[
D = \frac{\varepsilon - 1}{\varepsilon + 2}
\]

\[
\mu = \frac{\varepsilon}{\varepsilon + 2} \cdot \text{density of trichloroacetic acid}
\]

\[
\varepsilon = \text{dielectric constant of trichloroacetic acid}
\]

\[
R = \text{molar refraction} = \Sigma R_A
\]

\[
R_A = \text{atomic or ionic refraction}
\]

The values of the radius of the activated complex (\(r^*\)) within the temperature range 35–70 °C were obtained and compiled in Table II. It is evident that the values of \(r^*\) are all within a reasonable range and change from 2.67 to 3.10 Å on increasing the temperature from 35 to 70 °C. This is presumably due to the stronger loosening of the bonds of the activated complex as the temperature increases, i.e. larger volumes.

<table>
<thead>
<tr>
<th>°C</th>
<th>35</th>
<th>45</th>
<th>50</th>
<th>56</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r^*)</td>
<td>2.67</td>
<td>2.78</td>
<td>2.85</td>
<td>2.93</td>
<td>3.10</td>
</tr>
</tbody>
</table>

**Energy of activation**

The activation energies for the solvolysis reactions in ethanol-water solutions were calculated from the slopes of the straight line plots of log k versus 1/T. Fig. 4 indicates that good straight lines were obtained showing that the reaction strictly follows the Arrhenius equation. The results obtained are given in Table I. The decrease in the activation energy by increasing alcohol percentage may be attributed to the higher solvation of the reactants relative to that of the activated complex by water molecules. Thus increasing the alcohol concentration will result in an increase of the potential energy of the reactant and consequently a decrease of the activation energy.

The energy of activation calculated by plotting log k against 1/D (isocomposition energy) comprises the effect due to changes in the dielectric constant of solvent with change of temperature. This effect faints away when the activation energies are
calculated from the rate constants in isodielectric solutions and the contribution due to solvation phenomena will be mostly or partly eliminated. Table III shows that the isodielectric energy of activation for the solvolysis reaction of trichloroacetic acid changes from 4.814 to 4.80 kcal mole\(^{-1}\) in the dielectric constant range of 40-70 and passes through a minimum at \(D = 50\). This behaviour may presumably be due to the preferential solvation of the reactant in the water rich side.

Table III. Values of isodielectric energies of activation (\(E_d\)), in ethanol-water mixtures.

<table>
<thead>
<tr>
<th>Dielectric constant</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_d) kcal/mole</td>
<td>4.80</td>
<td>4.666</td>
<td>4.733</td>
<td>4.814</td>
</tr>
</tbody>
</table>

**Thermodynamic parameters of the activation**

The role of the effect of change in solvent composition on the rate and mechanism of the reaction is conveniently expressed in terms of the thermodynamic parameters of activation, namely, the free energy of activation \(\Delta F^*\), enthalpy \(\Delta H^*\) and entropy \(\Delta S^*\). Furthermore these parameters provide suitable means for studying the properties of the activated complex. These parameters were calculated making use of the transition state theory\(^1\). The results of these calculations at 35 °C and 50 °C are recorded in Table I. Examination of the data given in this Table indicates that \(\Delta F^*\) increases gradually with increase of water concentration. According to the theory of absolute reaction rates, the increase in \(\Delta F^*\) is a sign of solvation of the reacting species. Therefore solvation is expected to be more pronounced in the presence of higher concentrations of water. The variation of \(\Delta S^*\) with solvent composition does not follow a linear relationship (c.f. Fig. 5). This non-linear behaviour is a criterion\(^2\) of specific solvation and shows that the random orientation of the two component is not valid. It is worth mentioning that the positive \(\Delta S^*\) values observed in pure aqueous medium indicate the more extensive solvation of the reactant state relative to the transition state.

**Fig. 4.** Arrhenius plot of \(\log k\) vs. \(1/T\).

**Fig. 5.** Variation of \(\Delta S^+\) vs. water mole fraction.

Plotting of \(\Delta H^*\) versus \(\Delta S^*\) (at 50 °C) gives rise to a straight line as shown in Fig. 6. This should be taken to indicate that there is no change in the mechanism of this reaction in the different water-ethanol mixtures used in the present study.

**Fig. 6.** Linear relation of \(\Delta S^+\) vs. \(\Delta H^*\) at 50 °C.

\(^1\) A. STREITWIESER, Chem. Rev. 56, 571 [1956].
\(^2\) C. WAGNER, Z. Phys. Chem. 115, 121 [1925].