‘Learning to let go should be learned before learning to get’

Buddha

CHAPTER 6

APPLICATION OF THE COMPETITION TECHNIQUE TO STUDY THE RAPID REACTION

\[ \text{ICl} + \text{I}^- \rightarrow \text{I}_2 + \text{Cl}^\cdot \]

IN AQUEOUS SOLUTION
A] INTRODUCTION

Halogen displacement reactions in aqueous solution are very rapid and the kinetics of most of these reactions have been studied$^{1,2}$. The formation of interhalogen compounds in the intermediate steps of most of these reactions is significant since these compounds are highly reactive and undergo displacement reactions. Besides, molecular halogens in aqueous solution undergo hydrolysis and the hypohalous acids formed complicate the displacement reaction mechanism. Presently, the displacement of iodine from aqueous iodide solution by iodine monochloride, ICl has been kinetically investigated avoiding the complication of formation of interhalogen compounds as intermediates.

The reaction

\[
\text{ICl} + I^{-} \rightarrow \text{I}_{2} + \text{Cl}^{-}
\]

in aqueous solution is found to be very rapid necessitating a special technique for this kinetic study.

The competition technique employed is a relatively simpler technique used to study rapid reactions. It is based on a competition between two reactants that do not react with another but compete with each other to react with a reagent that is present in an insufficient amount. In the present study, KI and anthranilic acid (AA) do not react with each other but compete to react with ICl fulfilling the prime requirement of competition. The competition between KI and AA is complete once ICl is fully consumed. The amount of I$_2$ liberated in the competition when compared to that formed in the displacement reaction alone, provides the basis of estimating the kinetics of the reaction under study. The competition is governed by the relative reactivities of KI and AA towards ICl. In radical clock reactions, a free radical is the “internal clock”. In the present kinetic study, AA may be considered an internal clock which facilitates convenient determination of $k_1$ in terms of the iodine liberated in the competition.

The two competition reactions that take place simultaneously are,
The specific reaction rate, $k_2$ for the reaction between ICl and AA in aqueous solution has been independently estimated using the rotating platinum electrode. The conditions under which this reaction was studied are maintained in the present study.
B] EXPERIMENTAL

i) Preparation of solutions

Stock solutions of 0.01M sodium thiosulphate; 0.0016 M potassium hydrogen phthalate 0.25 M potassium chloride, 0.01 M hydrochloride acid and 0.016 M AA are prepared in double distilled water. A solution of 0.00186 M ICl (Merck-CAS No. 7790-99-0) is prepared in double distilled water from a stock solution of 0.01 M ICl. The exact strength of ICl solution is determined by treating its known quantity with an excess of potassium iodide solution and estimating the amount of iodine liberated by titrating with 0.01 M of sodium thiosulphate. All the solutions are maintained in a thermostat at the desired temperature.

ii) Determination of the specific rate of the reaction.

First, 25 cm$^3$ of ICl are added to a 225 cm$^3$ buffered solution of potassium iodide and potassium chloride but not AA. The resulting 250 cm$^3$ solution is titrated with 0.01 M sodium thiosulphate, V cm$^3$ being the titre value. In the competition experiment, 25 cm$^3$ of ICl maintained at the desired temperature and containing the buffer components are slowly added, with stirring, to 225 cm$^3$ of the competitors, potassium iodide and AA, which are also buffered at the same temperature. Subsequently, this 250 cm$^3$ reaction mixture is titrated with 0.01 M sodium thiosulphate. The end point V cm$^3$ represents the extent of ICl reacting with potassium iodide in terms of the iodine liberated during the competition and (V-v) cm$^3$ correspond to that reacted with AA. \( \frac{v}{(V-v)} \) represents the competition ratio. Any error in the titre value will consequently cause an error in the competition ratio which affects the accuracy of the determination of the specific rate of the reaction. The error in this ratio would be minimum when this ratio is unity. Hence the concentrations of potassium iodide and AA are so chosen that the competition ratio is close to unity. The experiments are repeated several times to obtain concordant results. During the competition experiment, the ratio \( \frac{v}{(V-v)} \) slightly exceeds unity because the conditions leading to unity cannot be rigorously maintained due to the following. (a) The AA concentration cannot be increased beyond a certain value due to the limitations of its solubility in aqueous solution and (b) the reduction in the potassium iodide concentration is not possible below a certain limit because a minimum of tenfold that
of potassium iodide relative to that of ICl has to be maintained, being one of the two competitors.

In the actual competition experiment; 25 cm$^3$ of ICl maintained at the desired temperature and containing the buffer components is slowly added, with stirring, to 225 cm$^3$ of the competitors which are also buffered at the same temperature. Subsequently, this 250 cm$^3$ reaction mixture is titrated with 0.01 M sodium thiosulphate to obtain ‘v’, the end point, representing the extent of ICl reacting with potassium iodide in terms of the iodine liberated, during the competition.

iii) Determination of the energy of activation of the reaction

The experiment is repeated at the different temperatures in the range 27$^\circ$C to 50$^\circ$C keeping the competition ratio nearly unity. From the values of the specific reaction rates, $k_2$, for the iodination of AA at different temperatures, those for the reaction under study at each of these temperatures, $k_1$, are evaluated. A plot of log $k_1$ versus T$^{-1}$ is found to be linear from the slope of which the energy of activation for the reaction is evaluated.

iv) Determination of the order of the reaction

The special technique used to study this reaction necessitates the order to be determined in an unconventional way. The ratio of the concentrations of the two competing reagents is varied to ascertain the order of the reaction as shown in Table 6.01.
C] TABLES

TABLE 6.01

VOLUME COMPONENTS OF THE REACTION MIXTURE AT 27.5°C

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Components</th>
<th>cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Volume of buffered reaction mixture containing potassium iodide, AA, potassium chloride, potassium hydrogen phthalate and hydrochloric acid</td>
<td>225.0</td>
</tr>
<tr>
<td>2</td>
<td>Volume of buffered ICl solution containing potassium hydrogen phthalate and hydrochloric acid</td>
<td>25.0</td>
</tr>
<tr>
<td>3</td>
<td>Total volume of reaction mixture</td>
<td>250.0</td>
</tr>
</tbody>
</table>

TABLE 6.02

CONCENTRATIONS OF REACTANTS AND BUFFER COMPONENTS IN THE 250.0 CM³ REACTION MIXTURE

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Component</th>
<th>Concentration/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ICl</td>
<td>0.000186</td>
</tr>
<tr>
<td>2</td>
<td>Potassium iodide</td>
<td>0.0016</td>
</tr>
<tr>
<td>3</td>
<td>AA</td>
<td>0.016</td>
</tr>
<tr>
<td>4</td>
<td>Hydrochloric acid</td>
<td>0.0001</td>
</tr>
<tr>
<td>5</td>
<td>Potassium hydrogen phthalate</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td>Potassium chloride</td>
<td>0.005</td>
</tr>
</tbody>
</table>
TABLE 6.03

VARIATION OF THE COMPETITION RATIO WITH TEMPERATURE

<table>
<thead>
<tr>
<th>Temp/K</th>
<th>0.01M Na$_2$S$_2$O$_3$ required to titrate the I$_2$ liberated by 250.0 cm$^3$ of the buffered reaction mixture containing KI and AA, $v$/cm$^3$</th>
<th>0.01M Na$_2$S$_2$O$_3$ required to titrate the I$_2$ liberated by 250.0 cm$^3$ of the buffered reaction mixture containing only KI, $V$/cm$^3$</th>
<th>Competition ratio ${v/(V-v)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.5</td>
<td>5.40</td>
<td>9.30</td>
<td>1.416</td>
</tr>
<tr>
<td>305.7</td>
<td>5.15</td>
<td>9.30</td>
<td>1.247</td>
</tr>
<tr>
<td>310.5</td>
<td>5.00</td>
<td>9.30</td>
<td>1.163</td>
</tr>
<tr>
<td>315.6</td>
<td>4.90</td>
<td>9.30</td>
<td>1.114</td>
</tr>
<tr>
<td>320.8</td>
<td>4.85</td>
<td>9.30</td>
<td>1.090</td>
</tr>
</tbody>
</table>

TABLE 6.03

DETERMINATION OF THE ORDER OF THE REACTION

\[ \text{ICl} + I^- \rightarrow I_2 + Cl^- \]

Temperature $= 27.5^\circ C$
Rate constant of iodination of AA ($k_2$) $= 560.5$ M$^{-1}$ s$^{-1}$
Concentration of AA $= 0.016$ M

<table>
<thead>
<tr>
<th>I /10$^{-3}$ M</th>
<th>1.60</th>
<th>3.20</th>
<th>4.80</th>
<th>6.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Competition Ratio</td>
<td>1.46</td>
<td>2.83</td>
<td>4.22</td>
<td>5.70</td>
</tr>
<tr>
<td>Third order rate constant k /10$^6$M$^{-2}$s$^{-1}$</td>
<td>4.96</td>
<td>2.48</td>
<td>1.64</td>
<td>1.25</td>
</tr>
<tr>
<td>Second order rate constant k /10$^3$M$^{-1}$s$^{-1}$</td>
<td>7.94</td>
<td>7.95</td>
<td>7.88</td>
<td>7.99</td>
</tr>
</tbody>
</table>
TABLE 6.04

VARIATION OF THE SPECIFIC REACTION RATE WITH TEMPERATURE
FOR THE REACTION

\[ \text{ICl} + \text{I}^- \rightarrow \text{I}_2 + \text{Cl}^- \]

<table>
<thead>
<tr>
<th>T/ K</th>
<th>$T^{-1}/10^3$K$^{-1}$</th>
<th>$k_2$/M$^{-1}$s$^{-1}$</th>
<th>log $k_2$</th>
<th>$k_1$/ M$^{-1}$s$^{-1}$</th>
<th>log $k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.5</td>
<td>3.3271</td>
<td>560.5</td>
<td>2.75</td>
<td>7936</td>
<td>3.90</td>
</tr>
<tr>
<td>305.7</td>
<td>3.2711</td>
<td>824.8</td>
<td>2.92</td>
<td>10285</td>
<td>4.01</td>
</tr>
<tr>
<td>310.5</td>
<td>3.2206</td>
<td>1214.0</td>
<td>3.08</td>
<td>14118</td>
<td>4.15</td>
</tr>
<tr>
<td>315.6</td>
<td>3.1685</td>
<td>1930.5</td>
<td>3.29</td>
<td>21505</td>
<td>4.33</td>
</tr>
<tr>
<td>320.8</td>
<td>3.1162</td>
<td>2630.0</td>
<td>3.42</td>
<td>28667</td>
<td>4.46</td>
</tr>
</tbody>
</table>
FIGURE 6.01

ARRHENIUS PLOT FOR THE REACTION

$\text{ICl} + I^- \rightarrow I_2 + Cl^-$

Scale:
- on X-axis - 1 unit = 0.05
- on Y-axis - 1 unit = 0.1
- Slope = -2.73491

Fig.(1): Variation of the $\log k$ vs $T^{-1}$
**E] CALCULATIONS**

**Specific reaction rate of the reaction under study**
\[ k_1 = k_2 \times [\text{AA}]^{-1} \times [v/(V-v)] \]

**Slope of the plot**
\[ \log k_1 \text{Vs} T^{-1} = -2.734 \times 10^3 \text{ K} \]

**Energy of activation**
\[ E_a = -2.303 \times R \times \text{slope} = 52.37 \text{ kJ mole}^{-1} \]

**iv) Entropy change, \( \Delta S \)**

\[ \Delta S = 2.303R \log k - 2.303 R \log (ek*T/h) + \frac{E_a}{T} \]

\[ \Delta S = 19.15 \log k - 253.25 + \frac{E_a}{T} \]

where, \( e = 2.713 \), \( h = \text{Planck constant} \), \( k^* = \text{Boltzmann constant} \)

\[ \Delta S = -3.8 \text{ J K}^{-1} \text{ mol}^{-1} \]
RESULTS AND DISCUSSION

The rates $R_1$ and $R_2$ of the reactions (1) and (2) are respectively,

$$-d [AA] / dt = R_2 = k_2 [ICl] [AA]$$

$$-d [I^-] / dt = R_1 = k_1 [ICl] x [I^-]^y$$

where $k_1$ and $k_2$ are the specific rates.

In the reaction mixture, the concentrations of the competitors are much larger than that of ICl reacting with them. Hence their concentrations are virtually unchanged during the competition. The expressions for second order and third order for the reaction under study in terms of the competition ratio may be stated as,

$$v / (V_v) = k_1 x [I^-] / k_2 x [AA] \quad \ldots \ldots \text{second order}$$

$$v / (V_v) = k_1 x [I^-]^2 / k_2 x [AA] \quad \ldots \ldots \text{third order}$$

From Table 6.03 it is evident that the reaction under study is of the second order. The specific reaction rate at 27.5 °C is 7936 M⁻¹ s⁻¹ within limits of experimental error (+2 %). The energy of activation for the reaction is found to be 52.37 kJ mol⁻¹. Iodine monochloride undergoes hydrolysis in aqueous solution.

$$ICl + H_2O \rightleftharpoons HOI + H^+ + Cl^-$$

The equilibrium constant of the hydrolysis is of the order of 10⁻⁴. The choice of the acidic pH 4 in the present study ensures the suppression of the
hydrolysis. Further, the hundreded fold concentration of KCl used to maintain identical condition as in reaction 2, predominantly shifts this equilibrium to the left. The following probable mechanism for the reaction under study is proposed.

\[
\text{ICl} + \text{I}^- \rightarrow \text{I}_2 + \text{Cl}^-
\]

Iodine liberation in the above reaction in view of the high polarity of the ICl bond seems to predominate over the reaction,

\[
\text{HOI} + \text{H}^+ + \text{I}^- \rightarrow \text{I}_2 + \text{H}_2\text{O}.
\]

This is due to the very low concentration of HOI in the equilibrium for the hydrolysis of ICl in the present study.
REFERENCES