CHAPTER IV

A KINETIC AND MECHANISTIC STUDY OF THE 
OXIDATION OF TYROSINE BY CHROMIUM (VI) IN 
AQUEOUS PERCHLORIC ACID MEDIUM
Chromium(VI) is a well-known oxidant in acidic media. The kinetics and mechanism of oxidation of chromium(VI) has been well studied, chromic acid being one of the most versatile available oxidizing agents, reacting with diverse substrates\(^1\). In acid solution, the reported reduction potential\(^2\) of the couple Cr(VI)/Cr(III) is 1.33V. The literature survey reveals that the oxidation of tyrosine by different oxidants is limited. We are particularly interested to see the mechanism of the oxidation of tyrosine by chromium(VI) in acidic media. The reaction mechanism is of great interest because of its non-complementary nature and the possibility of a variety of mechanisms involving the reactive intermediates such as chromium(V), chromium(IV), etc., all of which have been encountered in chemical reactions\(^3\). Hence we have investigated the kinetics of oxidation of tyrosine by chromium(VI) in perchloric acid medium in order to understand the behavior of intermediates of chromium(VI) and to arrive at a suitable mechanism in this chapter.

**EXPERIMENTAL**

**Materials**

The solutions were prepared in water, which had been twice distilled in an all-glass unit in the presence of potassium permanganate. Reagent grade chemicals were used. The stock solution of the oxidant, chromium(VI) was obtained by dissolving K\(_2\)Cr\(_2\)O\(_7\) (AR) in water and appropriate dilution\(^4\). A stock solution of tyrosine was prepared by dissolving tyrosine (s.d.fine chem.) in 0.50 mol dm\(^{-3}\) hydrochloric acid. The chromium(III) solution was prepared by dissolving chromic potassium sulphate (Cr\(_2\)(SO\(_4\))\(_3\)K\(_2\)SO\(_4\).24H\(_2\)O) (BDH,
AR) in water. NaClO₄ (AR) and HClO₄ (70% , E. Merck) were used to provide the required ionic strength and acidity respectively.

**Kinetic studies**

Kinetic measurements were performed under pseudo-first order conditions with tyrosine concentration greater than the chromium(VI) concentration at constant ionic strength of 3.10 mol dm⁻³. The reaction was initiated by mixing thermally equilibrated (at 30.0 ± 0.1 °C) solutions of chromium(VI) and tyrosine which also contained the required quantities of HClO₄ and NaClO₄. The reaction was followed by monitoring the decrease in the absorbance of chromium(VI) concentration in the reaction mixture at 360 nm in a 1cm cell placed in the thermostatted compartment of a Varian Cary-50 Bio UV -vis spectrophotometer as a function of time. Application of Beer’s law under the reaction conditions had been verified between 1.0 x 10⁻⁴ and 1.0 x 10⁻³ mol dm⁻³ of chromium(VI) at 360 nm and extinction coefficient, ε was found to be 1200 ± 12 dm³ mol⁻¹ cm⁻¹(Fig. IV (i) (p. 93)). The spectral changes during the chemical reaction for the standard condition at 30 °C are shown in (Fig. IV (ii) (p. 93)). The kinetic runs were followed more than 80% completion of the reaction and good first order kinetics were observed. The example run is given in Table IV (i) (p. 94) The pseudo-first order rate constants, kₒbs were obtained from the slope of the plots of log( absorbance) versus time. The pseudo-first order plots were linear over three half-lives (Fig. IV (iii) (p. 95)). The rate constants, kₒbs were reproducible to within ±5% and are the average of atleast three independent kinetic runs (Table IV (ii) (p.100)).
Fig. IV (i)
Verification of Beer’s law for chromium(VI) concentration at 360 nm in 3.0 mol dm$^{-3}$ aqueous perchloric acid and at 30 °C.

Fig. IV (ii)
Spectral changes during the oxidation of tyrosine by chromium(VI) in aqueous perchloric medium at 30°C

(Conditions as in Table IV (i) (p.94))
Table IV (i)

Oxidation of tyrosine by chromium(VI) in aqueous perchloric acid medium at 30°C

**Example run**

\[ [\text{Cr(VI)}] = 2.0 \times 10^{-4}; \quad [\text{tyrosine}] = 2.0 \times 10^{-2}; \]

\[ [\text{H}^+] = 3.0; \quad I = 4.60 \text{ /mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Absorbance (360 nm)</th>
<th>Concentration ( \times 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.259</td>
<td>21.6</td>
</tr>
<tr>
<td>0.4</td>
<td>0.221</td>
<td>18.4</td>
</tr>
<tr>
<td>0.8</td>
<td>0.190</td>
<td>15.9</td>
</tr>
<tr>
<td>1.2</td>
<td>0.165</td>
<td>13.7</td>
</tr>
<tr>
<td>1.6</td>
<td>0.143</td>
<td>11.9</td>
</tr>
<tr>
<td>2.0</td>
<td>0.129</td>
<td>10.8</td>
</tr>
<tr>
<td>2.4</td>
<td>0.116</td>
<td>9.68</td>
</tr>
<tr>
<td>2.8</td>
<td>0.106</td>
<td>8.80</td>
</tr>
<tr>
<td>3.2</td>
<td>0.090</td>
<td>7.48</td>
</tr>
<tr>
<td>3.6</td>
<td>0.079</td>
<td>6.56</td>
</tr>
<tr>
<td>4.0</td>
<td>0.071</td>
<td>5.92</td>
</tr>
<tr>
<td>4.4</td>
<td>0.064</td>
<td>5.33</td>
</tr>
<tr>
<td>4.8</td>
<td>0.058</td>
<td>4.83</td>
</tr>
<tr>
<td>5.2</td>
<td>0.052</td>
<td>4.33</td>
</tr>
<tr>
<td>5.6</td>
<td>0.045</td>
<td>3.75</td>
</tr>
<tr>
<td>6.0</td>
<td>0.040</td>
<td>3.33</td>
</tr>
</tbody>
</table>
Fig. IV (iii)

First order plots of the oxidation of tyrosine by chromium(VI) in aqueous perchloric acidic medium at 30°C

(Conditions as in Table IV (i) (p. 94))

[Chromium (VI)] x 10^4 / mol dm^-3 = (1) 0.5, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0 and (6) 5.0
RESULTS

Stoichiometry and product analysis

Different sets of concentrations of reactants in 3.0 mol dm\(^{-3}\) HClO\(_4\) and at constant ionic strength, I = 4.60 mol dm\(^{-3}\) were kept in a closed container under a nitrogen atmosphere at 30°C. After 1 hour chromium(VI) concentration was assayed by measuring the absorbance at 360nm. The results indicates that two moles of chromium(VI) reacts with three moles of tyrosine, as shown in equation (1). The main reaction products were identified as chromium(III) and 4-hydroxy phenyl acetaldehyde.

\[
2\text{H}_2\text{CrO}_4 + 3 \text{OH} \rightarrow 3 \text{CO}_2 + 3 \text{NH}_3 + 2\text{H}^+ + \text{H}_2\text{O} \quad (1)
\]

LC-ESI-MS analysis was carried out using reverse phase high performance liquid chromatography (HPLC) system with a phenomenes C-18 column, UV/Visible detector and series mass analyzer. 12 µL of acidified reaction mixture was injected. The mobile phase consisted of acetonitrile (eluent A) and methanol (Containing 0.1% CH\(_3\)COOH) at a flow rate of 1 cm\(^3\)/min. Gradient elution was run to separate substrate and reaction products. Gradient 0 min/ 95% A - 15 min/ 35% A - 25 min/ 35% A - 30 min/ 95% A - 35 min/ 35% A. LC-ESI-MS analysis of tyrosine reaction indicated the presence of product with molecular ion of m/z 136 (Yield 90%). The molecular
ion of tyrosine is m/z 182. The m/z 136 corresponds to 4-hydroxyphenylacetaldehyde (Fig.IV (iv) (p.98)). The other products were identified as ammonia and carbon dioxide. Ammonia was identified by Nessler's reagent test. The liberated carbon dioxide was qualitatively detected by bubbling N₂ gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water.

Reaction order

The orders were determined from the slopes of log $k_{obs}$ versus log (concentration) plots by varying the concentrations of tyrosine, HClO₄, in turn, while keeping the others constant.

Effect of [chromium(VI)]

At constant concentrations of tyrosine, perchloric acid and other conditions constant, the chromium(VI) concentration was varied between $5.0 \times 10^{-5}$ to $5.0 \times 10^{-4}$ mol dm⁻³. The plot of log (absorbance) versus time, was linear over three half lives of the reaction for different initial chromium(VI) concentration (Fig. IV(iii) (p.95)) which indicates the unit order with respect to chromium(VI) concentration. This was also confirmed by the almost constant values of pseudo-first order rate constant, $k_{obs}$ for different chromium(VI) concentrations (Table IV( ii)(p.100)).

Effect of [tyrosine]

The tyrosine concentration was varied in the concentration range $5.0 \times 10^{-3}$ to $5.0 \times 10^{-2}$ mol dm⁻³ at constant acidity, 3.0 mol dm⁻³ and constant ionic
Fig. IV (iv)

LC-ESI-MS Spectra of oxidation product (4-hydroxyphenylacetaldehyde) of tyrosine by chromium(VI)

(1) Total ion chromatogram (TIC)

(2) Molecular ion peak of oxidation product (4-hydroxyphenylacetaldehyde)
strength, 4.60 mol dm$^{-3}$. As the tyrosine concentration increases the rate of reaction also increases (Table IV( ii)(p.100)). The order with respect to tyrosine concentration was found to be less than unity (ca 0.678)(Fig. IV (v) (p.101)).

**Effect of acid**

At fixed concentrations of chromium (VI), tyrosine and at constant ionic strength, the perchloric acid concentration was varied between 2.0 to 4.50 mol dm$^{-3}$ and the pseudo-first order rate constant, $k_{obs}$ was found to increase with increase in acid concentration (Table IV( ii)(p.100)). The order with respect to acid concentration was found to be two (ca 1.26)(Fig. IV (v) (p.101)).

**Effect of added product**

The effect of initially added product, chromium (III) was studied in the $5.0 \times 10^{-5} - 5.0 \times 10^{-4}$ mol dm$^{-3}$ concentration range, keeping the ionic strength, reactant concentrations and other conditions constant. No significant effect on the reaction rate was observed.

**Effect of dielectric constant and ionic strength**

At constant concentrations of reactants and with other conditions constant, the ionic strength was varied between 3.1 to 5.0 mol dm$^{-3}$ by varying the concentration of NaClO$_4$. Similarly, at constant concentrations of reactants and at other conditions constant, the acetic acid was varied from 0 - 50% (V/V) in the reaction medium. The results indicate that the ionic strength and dielectric constant of the medium did not have any significant effect on the rate of reaction.
**Table IV (ii)**

Effect of variation of chromium(VI), tyrosine and perchloric acid concentrations on the oxidation of tyrosine by chromium(VI) in aqueous perchloric acid medium at 30°C

<table>
<thead>
<tr>
<th>[Cr(VI)] x $10^4$ (mol dm$^{-3}$)</th>
<th>[tyrosine] x $10^2$ (mol dm$^{-3}$)</th>
<th>[HClO$_4$] (mol dm$^{-3}$)</th>
<th>$k_{obs} \times 10^3$ (s$^{-1}$)</th>
<th>$k_{cal} \times 10^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.0</td>
<td>3.0</td>
<td>5.10</td>
<td>5.24</td>
</tr>
<tr>
<td>1.0</td>
<td>2.0</td>
<td>3.0</td>
<td>4.85</td>
<td>5.24</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>3.0</td>
<td>5.03</td>
<td>5.24</td>
</tr>
<tr>
<td>3.0</td>
<td>2.0</td>
<td>3.0</td>
<td>4.89</td>
<td>5.24</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
<td>3.0</td>
<td>5.00</td>
<td>5.24</td>
</tr>
<tr>
<td>5.0</td>
<td>2.0</td>
<td>3.0</td>
<td>4.90</td>
<td>5.24</td>
</tr>
<tr>
<td>2.0</td>
<td>0.5</td>
<td>3.0</td>
<td>1.98</td>
<td>1.83</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>3.0</td>
<td>3.35</td>
<td>3.21</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>3.0</td>
<td>5.03</td>
<td>5.15</td>
</tr>
<tr>
<td>2.0</td>
<td>3.0</td>
<td>3.0</td>
<td>6.73</td>
<td>6.60</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>3.0</td>
<td>8.72</td>
<td>8.70</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>*2.0</td>
<td>3.20</td>
<td>3.20</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>2.5</td>
<td>4.20</td>
<td>4.20</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>3.0</td>
<td>5.03</td>
<td>5.07</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>3.5</td>
<td>6.20</td>
<td>6.20</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>4.0</td>
<td>6.80</td>
<td>6.80</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>4.5</td>
<td>8.00</td>
<td>8.00</td>
</tr>
</tbody>
</table>

* $I = 4.60 \text{ mol dm}^{-3}$
Order with respect to tyrosine and H\(^+\) ion concentrations on the oxidation of tyrosine by chromium(VI) in aqueous perchloric acid medium at 30\(^\circ\) C

(Conditions as in the Table IV (ii) (p. 100))
Test for free radicals (polymerization study)

The intervention of free radicals was examined as follows: The reaction mixture (10 cm$^3$), to which a known quantity of acrylonitrile (2 cm$^3$) (scavenger) had been added initially, was kept in an inert atmosphere for 1 hour at room temperature. When the reaction mixture was diluted with methanol no precipitate resulted, suggesting that there was no participation of free radicals in the reaction.

Effect of temperature

The influence of temperature on the reaction was studied at 15, 20, 25 and 30 °C by varying tyrosine and H$^+$ ion concentrations. The rate constant, $k$ of the slow step of Scheme 1 were obtained from the intercepts of the plots of $1/k_{obs}$ versus $1/[\text{tyrosine}]$ at four different temperatures. The rate constants were found to increase with increase in temperature (Table IV (iii) (p.103)). The data were subjected to least square analysis as in Chapter II (p.45) and are tabulated in Table IV (iii) (p.103). The energy of activation was obtained by the plot of log $k(Y_{\text{calc}}^*)$ versus $1/T$ (Fig. IV (vi) (p.104), from which the activation parameters were calculated (Table IV (iii)(p.103). The formation constant of the complex, $K_2$ of the second step, and the ionization constant, $K_1$, of the first step of Scheme 1 (p.106) were calculated from intercept and slope of the plot of $1/k_{obs}$ versus $1/[H^+]^2$ and $1/k_{obs}$ versus $1/[\text{tyrosine}]$ (Fig. IV (vii) (p.110)) at four different temperatures and the values are given in Table IV (iv)(p.111). The Van’t Hoff plots, log $K_1$ versus $1/T$ and log $K_2$ versus $1/T$ were drawn for the values of $K_1$ and $K_2$. The thermodynamic quantities were calculated and are given in Table IV (iv)(p.111).
Table IV (iii)

Activation parameters of the oxidation of tyrosine by chromium(VI) in aqueous perchloric acid medium with respect to slow step of Scheme 1

(a) Effect of temperature with respect to slow step of Scheme 1

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>k x 10^3 (sec^{-1})</th>
<th>log k (y)</th>
<th>1/T x 10^3</th>
<th>Log k(Y_cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>4.96</td>
<td>0.696</td>
<td>3.472</td>
<td>0.672</td>
</tr>
<tr>
<td>293</td>
<td>6.25</td>
<td>0.796</td>
<td>3.413</td>
<td>0.835</td>
</tr>
<tr>
<td>298</td>
<td>10.0</td>
<td>1.000</td>
<td>3.356</td>
<td>0.992</td>
</tr>
<tr>
<td>303</td>
<td>14.2</td>
<td>1.150</td>
<td>3.300</td>
<td>1.144</td>
</tr>
</tbody>
</table>

(b) Activation Parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_a (kJ mol^{-1})</td>
<td>52.3</td>
</tr>
<tr>
<td>ΔH^# (kJ mol^{-1})</td>
<td>49.8</td>
</tr>
<tr>
<td>ΔS^# (J K^{-1} mol^{-1})</td>
<td>-58.8</td>
</tr>
<tr>
<td>ΔG^# (kJ mol^{-1})</td>
<td>53.9</td>
</tr>
<tr>
<td>logA</td>
<td>10.2</td>
</tr>
</tbody>
</table>
Fig. IV (vi)

Effect of temperature on the oxidation of tyrosine by chromium(VI) in aqueous perchloric acid medium with respect to the slow steps of Scheme 1.
DISCUSSION

The reaction between chromium (VI) and tyrosine has stoichiometry 2 : 3, with an apparent unit order in tyrosine and chromium (VI) concentrations. As the perchloric acid concentration increased in the reaction medium, the rate of reaction also increased. The order with respect to perchloric acid concentration was found to be two. No effect of initially added products, ionic strength and dielectric constants were observed. It is well known fact that in aqueous acid solution, chromium(VI) exists mainly in the form of acid chromate, $\text{H}_2\text{CrO}_4$. The results suggest that $\text{H}_2\text{CrO}_4$ reacts with tyrosine forming a complex, which decomposes in the rate determining step to give an intermediate chromium(IV) and a product 4-hydroxyphenylacetaldehyde. In the next step another molecule of acid chromate reacts with one molecule of tyrosine producing another molecule of an intermediate, chromium(IV) and 4-hydroxyphenylacetaldehyde. In further fast step, two molecules of chromium(IV) reacts with one more molecule of tyrosine giving final products chromium(III) and 4-hydroxy phenylacetaldehyde. The results can be accommodated in the form of Scheme 1.

$$\text{CrO}_4^{2-} + 2 [\text{H}^+] \rightleftharpoons K_1 \text{H}_2\text{CrO}_4$$

$$\text{H}_2\text{CrO}_4 + \text{Complex (C)} \rightleftharpoons K_2 \text{H}_2\text{CrO}_4$$
The results indicate the formation of a complex between the substrate, tyrosine and the oxidant, chromium(VI) in the perchloric acid medium. The formation of complex was proved kinetically by Michaelis – Menten plot i.e., a non zero intercept of the plot $1/k_{obs}$ versus $1/[\text{tyrosine}]$ (Fig. IV (vii) (p.110)). The evidence for complex formation was also obtained in perchloric acid media from the UV-vis. spectrum of both chromium(VI) and tyrosine and chromium(VI) - tyrosine mixtures in which a bathochromic shift of 4 nm from 270 nm to 274 nm and hyperchromicity at 274 nm was observed. The complex formation between oxidant and substrate was also observed in literature $^{3,7}$. 
Since the oxidation of tyrosine by chromium(VI) may occur by the intervention of chromium(V) and chromium(IV) species. In the present investigation, the negative test for free radicals was observed, which itself rule out the formation of an intermediate species, chromium(V). The intervention of chromium(IV) is evident from the progressive rate decrease in the presence of increasing amounts of added manganese(II), the decrease reaching a limit of ca. one half of the rate found in the absence of manganese(II). Such results have also been obtained for chromium(VI) oxidation of 2-propanol in aqueous acetic acid and QDC oxidation of thallium(I) in aqueous acetic acid–chloride media.

From Scheme 1, the rate law (7) can be derived as follows:

$$\text{Rate} = k \ [\text{Complex (C)}]$$

$$\text{Rate} = - \frac{d [\text{CrO}_4^{2-}]}{dt} = k K_1 K_2 [\text{tyrosine}] f [\text{CrO}_4^{2-}] f [\text{H}^+]^2 f$$  \hspace{1cm} (2)

The total concentration of CrO₄²⁻ is given by,

$$[\text{CrO}_4^{2-}]_t = [\text{CrO}_4^{2-}]_f + [\text{H}_2\text{CrO}_4] + [\text{Complex (C)}]$$

$$= [\text{CrO}_4^{2-}]_f + K_1 [\text{CrO}_4^{2-}]_f [\text{H}^+]^2 f + K_1 K_2 [\text{tyrosine}] [\text{CrO}_4^{2-}]_f [\text{H}^+]^2$$

$$= [\text{CrO}_4^{2-}]_f \{1 + K_1 [\text{H}^+]^2 f + K_1 K_2 [\text{tyrosine}] [\text{H}^+]^2 f\}$$

Therefore,

$$[\text{CrO}_4^{2-}]_f = \frac{[\text{CrO}_4^{2-}]_t}{1 + K_1 [\text{H}^+]^2 f + K_1 K_2 [\text{tyrosine}] [\text{H}^+]^2 f}$$  \hspace{1cm} (3)

where 't' and 'f' stands for total and free concentration of chromium(VI).
Similarly,

\[
[\text{tyrosine}]_k = [\text{tyrosine}]_f + [\text{Complex (C)}]
\]

\[
= [\text{tyrosine}]_f + K_1 K_2 [\text{CrO}_4^{2-}]_f [\text{tyrosine}] [H^+]^2
\]

\[
= [\text{tyrosine}]_f \{1 + K_1 K_2 [\text{CrO}_4^{2-}]_f [H^+]^2\}
\]

\[
[\text{tyrosine}]_f = \frac{[\text{tyrosine}]_k}{1 + K_1 K_2 [\text{CrO}_4^{2-}]_f [H^+]^2}
\]  \hspace{1cm} (4)

In view of the low concentration of chromium(VI) used in the experiment, in equation (4) the term \(K_1 K_2 [\text{CrO}_4^{2-}]_f [H^+]^2\) can be neglected in comparison with unity.

Hence,

\[
[\text{tyrosine}]_k = [\text{tyrosine}]_f
\]  \hspace{1cm} (5)

and \([H^+]_2 = [H^+]_2 + [\text{H}_2\text{CrO}_4] + [\text{Complex (C)}]\)

\[
= [H^+]_2 + K_1 [\text{CrO}_4^{2-}]_f [H^+]^2 + K_2 [\text{H}_2\text{CrO}_4] [\text{tyrosine}]
\]

\[
= [H^+]_2 + K_1 [\text{CrO}_4^{2-}]_f [H^+]^2 + K_1 K_2 [\text{tyrosine}] [\text{CrO}_4^{2-}]_f
\]

\[
[H^+]^2 = [H^+]_2 \{1 + K_1 [\text{CrO}_4^{2-}]_f + K_1 K_2 [\text{tyrosine}] [\text{CrO}_4^{2-}]_f\}
\]

Similarly,

\[
[H^+]_2 = [H^+]_2
\]  \hspace{1cm} (6)

Substituting equations (3), (5) and (6) in equation (2), and omitting subscripts we get equation (7), which explains all the experimentally observed orders with respect to different species of reaction.

\[
\text{Rate} = - \frac{d [\text{CrO}_4^{2-}]}{dt} = \frac{k K_1 K_2 [\text{CrO}_4^{2-}] [\text{tyrosine}] [H^+]^2}{1 + K_1 [H^+]^2 + K_1 K_2 [\text{tyrosine}]}
\]  \hspace{1cm} (7)
The rate law (7) can be rearranged to equation (8), which is suitable for verification.

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{K_1 K_2 [\text{tyrosine}] [H^+]^2} + \frac{1}{k K_2 [\text{tyrosine}]} + \frac{1}{k} \tag{8}
\]

According to equation (8), plots of \(1/k_{\text{obs}}\) versus \(1/[\text{tyrosine}]\) and \(1/k_{\text{obs}}\) versus \(1/[H^+]^2\) should be linear and are found to be so (Fig. IV (vii) (p.110)). From the slopes and intercepts of such plots lead to the values of \(K_1, K_2\) and \(k\) (Table IV (iv) (p.111)). The thermodynamic quantities for the first and second equilibrium steps of Scheme 1 can be evaluated as follows. The tyrosine and \(H^+\) ion were varied at four different temperatures. The plots of \(1/k_{\text{obs}}\) versus \(1/[\text{tyrosine}]\) and \(1/k_{\text{obs}}\) versus \(1/[H^+]^2\) should be linear (Fig. IV (vii) (p.110)). From the slopes and intercepts, the values of \(K_1\) and \(K_2\) were calculated at different temperatures and these values are given in Table IV (iv) (p.111).

For example at 30 °C:

i) **From the plot of \(1/k_{\text{obs}}\) versus \(1/[\text{tyrosine}]\)**

\[(\text{Intercept})_1 = \frac{1}{k}\]

Therefore, \(k = (\text{Intercept})_1 = 1.426 \times 10^{-2} \text{ sec}^{-1}\)

\[(\text{Slope})_1 = \frac{1}{k K_1 K_2 [H^+]^2} + \frac{1}{k K_2}\]
Verification of rate law (7) in the form of (8) on the oxidation of tyrosine by chromium(VI) in aqueous perchloric acid medium at 30 °C

(Conditions as in Table IV(ii) (p.100))
Table IV(iv)

Thermodynamic parameters of the oxidation of tyrosine by chromium(VI) in aqueous perchloric acid medium

(a) Effect of temperature on first and second equilibrium step of Scheme 1

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$K_1 \times 10^2$ dm$^6$ mol$^{-2}$</th>
<th>$K_2 \times 10^2$ dm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>7.39</td>
<td>1.42</td>
</tr>
<tr>
<td>293</td>
<td>5.43</td>
<td>1.60</td>
</tr>
<tr>
<td>298</td>
<td>3.00</td>
<td>1.86</td>
</tr>
<tr>
<td>303</td>
<td>1.84</td>
<td>2.10</td>
</tr>
</tbody>
</table>

(b) Thermodynamic quantities with respect to $K_1$ and $K_2$

<table>
<thead>
<tr>
<th>Quantities</th>
<th>Using $K_1$ values</th>
<th>Using $K_2$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>-70.1</td>
<td>19.4</td>
</tr>
<tr>
<td>$\Delta S$ (J K$^{-1}$mol$^{-1}$)</td>
<td>-226</td>
<td>108</td>
</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
<td>-1.5</td>
<td>-13.5</td>
</tr>
</tbody>
</table>
ii) From the plot of $1/k_{obs}$ versus $1/[H^+]^2$

$$\frac{\text{Intercept}}{k} = 87.68 = \frac{1}{k} + \frac{1}{k_2 [\text{tyrosine}]}$$

From (Intercept)$^1$, the value of $k = 1.426 \times 10^{-2} \text{ sec}^{-1}$

Hence,

$$87.68 = \frac{1}{1.426 \times 10^{-2} \times K_2 \times 2.0 \times 10^{-2}} + \frac{1}{1.426 \times 10^{-2}}$$

$$K_2 = 210.0 \text{ dm}^3 \text{ mol}^{-1}$$

(Slope)$^2 = 916.8 = \frac{1}{K_1 K_2 [\text{tyrosine}]}$

$$916.8 = \frac{1}{1.426 \times 10^{-2} \times 210 \times 2.0 \times 10^{-2} \times K_1}$$

Therefore,

$$K_1 = 1.842 \times 10^{-2} \text{ dm}^6 \text{ mol}^2$$

Hence, at $30 ^\circ \text{C}$:

$$k = 1.426 \times 10^{-2} \text{ sec}^{-1}$$

$$K_1 = 1.842 \times 10^{-2} \text{ dm}^6 \text{ mol}^2$$

$$K_2 = 210.0 \text{ dm}^3 \text{ mol}^{-1}$$

In the same way $k$, $K_1$ and $K_2$ values were calculated for remaining temperatures and are given in Table IV(iv)(p.111). Van’t Hoff plots were made for the variation of $K_1$ and $K_2$ with temperature (log $K_1$ versus $1/T$ and log $K_2$ versus $1/T$). The values of enthalpy of reaction, $\Delta H$, entropy of reaction, $\Delta S$ and free energy of reaction, $\Delta G$, were calculated for the first, and second...
equilibrium steps of Scheme 1(p.106). These values are given in Table IV(iv)(p.111). A comparison of latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step. Supporting the fact that the reaction before the rate determining step is fairly fast and involves high activation energy. The moderate values of $\Delta H^\#$ and $\Delta S^\#$ were both favorable for electron transfer processes. The negative value of $\Delta S^\#$ indicates that the complex(C) is more ordered than the reactants. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by literature. The ionic strength and dielectric constant of the medium does not have any significant effect on the rate of reaction, which indicates the reaction between ion and a neutral molecule.

**FINDINGS OF THE CHAPTER IV**

The reaction between tyrosine and chromium (VI) is very slow in the low perchloric acid concentration at room temperature. However, the reaction occurs in measurable quantities above 2.0 mol dm$^{-3}$ concentrations of perchloric acid. The oxidant, chromium (VI) in acid media exists as $\text{H}_2\text{CrO}_4$, which take part in the chemical reaction. The roles of hydrogen ions are crucial to the chemical reaction. The given mechanism consistent with all the experimental evidences both kinetic and product studies.
REFERENCES

1. S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor,
   Transition Met. Chem., 26, 662 (2001);
   K. B. Wiberg,
   "Oxidation in Organic Chemistry", Academic Press, New York, Part A,
   (1965) p.69

2. S. A. Chimatadar, T. Basavaraj and S. T. Nandibewoor,
   Polyhedron, 25, 2976 (2006);
   M. C. Day, Jr. and J. Selbin,
   "Theoretical Inorganic Chemistry", Reinhold Publishing Corporation,
   New York, (1964) p.226

3. S. A. Chimatadar, M. S. Salunke and S. T. Nandibewoor,

4. G. H. Jeffery, J. Bassett, J. Mendham and R. C. Denney,
   "Vogel's Textbook of Quantitative Chemical Analysis", 5th edn., ELBS,

5. A. K. Das and M. Das,

6. K. B. Wiberg and P. A. Lepse,
   J. Am. Chem. Soc., 86, 2612 (1964);
   P. A. Best, J. S. Littler and W. A. Waters,
   J. Chem. Soc., 822 (1962);
   F. Hasan and J. Rocek,
7. S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor,  
   *Oxid. Commun.*, 27, 81 (2004);  
   J. G. Mason and A. D. Kowalak,  

8. M. Rahaman and J. Rocek,  
   *J. Am. Chem. Soc.*, 93, 5462 (1971);  
   S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor,  

9. K. S. Rangappa, M. P. Ragavendra, D. S. Mahadevappa and D. Channegouda,  

10. E. S. Lewis,  

11. M. Martinez, M. A. Pitarque and R. V. Eldik,  
   *J. Chem. Soc., Dalton Trans.*, 2665(1996);  
   S. A. Farokhi and S. T. Nandibewoor,  