CHAPTER VII

OXIDATION OF ALLYL ALCOHOL BY QUINOLINIUM DICHROMATE - A KINETIC AND MECHANISTIC STUDY

Allyl alcohol (AA) finds a number of industrial applications in the preparation of resins, plasticizers, pharmaceuticals and many organic compounds. Kinetic studies of the oxidation of allyl alcohol with different oxidants, such as potassium permanganate, chromic acid, vanadium(V), chloramine-T, diperiodatonicelate(IV) and so on have been reported. Kinetics and mechanism of oxidation reactions of chromium(VI) are fairly well studied, with chromic acid as one of the most versatile of the available oxidising agents, reacting with diverse kinds of substrates. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be a subject of interest. The reagent employed in this investigation, quinolinium dichromate, \((C_9H_7NH^+)_2Cr_2O_7^-\), has been found to be a useful and versatile oxidant that deserves further evaluation. We are particularly interested to see the mechanism involved in the oxidation of organic substances by this new oxidant, quinolinium dichromate. Since the chromium(VI) exhibits different oxidation states during oxidation, such as chromium(V), chromium(IV), chromium(III), etc, the present reaction might involve several complexities. In view of the lack of literature on the oxidation of allyl alcohol by quinolinium dichromate in perchloric acid medium, we have undertaken this study to understand the plausible mechanism in such media.
EXPERIMENTAL

Reagent grade chemicals and double distilled water were used throughout. Quinolinium dichromate was prepared by a reported method\(^9\), as in Chapter VI (p.169), and its purity was checked with I.R. spectra. The quinolinium dichromate (QDC) solution was prepared by dissolving QDC in water and its concentration was determined iodometrically\(^9\). The allyl alcohol (Koch Light) was purified by a reported method\(^10\) and used to prepare a stock solution. The stock solution was standardised by addition of an excess of chloramine-T, followed by iodometric titration\(^11\). The chromium(III) solution needed was prepared by dissolving chromic potassium sulphate, \(\text{Cr}_2(\text{SO}_4)_3\cdot\text{K}_2\text{SO}_4\cdot24\text{H}_2\text{O}\) (BDH), in water. The concentration of chromium(III) was determined by oxidising it to chromium(VI) with excess persulphate in presence of one or two drops of \(1.0 \times 10^{-2}\) mol dm\(^{-3}\) silver nitrate. The excess persulphate was boiled off and the chromium(VI) thus obtained was determined against iron(II) ammonium sulphate solution. Perchloric acid (Merck) and sodium perchlorate (BDH) were used to keep the required acidity and to maintain the ionic strength, respectively.

KINETIC STUDIES

Kinetics was followed at \(25 \pm 0.1^\circ\text{C}\) and \(I = 1.30\) mol dm\(^{-3}\). The reaction was initiated by mixing previously thermostatted reactant solutions. The allyl alcohol solution contains the required amounts of sodium perchlorate and QDC solution contains perchloric acid. The kinetics was followed under pseudo-first
order conditions by taking allyl alcohol concentration much in excess of that of
the QDC concentration. The reaction was followed by measuring absorbance
of QDC in the reaction mixture at 440 nm in a 1 cm cell placed in the
thermostatted compartment of a Hitachi 150-20 spectrophotometer. Beer’s law
under the reaction conditions had earlier been tested between $1.0 \times 10^{-4}$ and
$2.0 \times 10^{-3}$ mol dm$^{-3}$ of QDC at 440 nm with $\varepsilon$ resulting as $380 \pm 10$ dm$^3$ mol$^{-1}$ cm$^{-1}$
(Fig. VII(i) (p.211)). An example run is shown in Table VII(i) (p.212). The
pseudo-first order rate constants, $k_{obs}$, were obtained from the plots of $\log (a / (a-x))$
versus time (Fig. VII(ii) (p.213)). The first order plots were linear up to 90% completion of the reaction. Rate constants were reproducible within $\pm 5\%$.

RESULTS

Stoichiometry

Different sets of concentrations of reactants in 1.0 mol dm$^{-3}$ perchloric
acid at constant ionic strength, 1.30 mol dm$^{-3}$, were kept for over 4 h at 25°C in
a closed container. When $[\text{QDC}] > [\text{allyl alcohol}]$, the remaining QDC was
assayed by measuring absorbance at 440 nm, whereas under the conditions
$[\text{allyl alcohol}] > [\text{QDC}]$, when QDC had fully reacted, the remaining allyl
alcohol concentration was determined by the addition of excess chloramine-T
followed by iodometric titration$^{11}$. One of the products, chromium(III). was
quantitatively determined by measuring its absorbance at 580 nm, the molar
absorptivity of chromium(III) at this wavelength being $15.4 \pm 0.4$ dm$^3$ mol$^{-1}$
cm$^{-1}$. Another product acrolien was identified by a spot test$^{12}$. The acrolien was
confirmed by its 2:4 DNP derivative (80% yield) and silver mirror test.
Fig. VII(i)

Verification of Beer's law for [QDC] at 440 nm in 1 mol dm$^{-3}$ perchloric acid at 25$^0$C.
Table VII(i)

Oxidation of allyl alcohol by quinolinium dichromate at 25°C.

**Example run**

\[ [\text{QDC}] = 5.0 \times 10^{-4} ; \]
\[ [\text{AA}] = 5.0 \times 10^{-2} ; \]
\[ [\text{HClO}_4] = 1.0 ; \]
\[ I = 1.3 / \text{mol dm}^{-1} \]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Optical density at 440 nm</th>
<th>([\text{QDC}] \times 10^4 ) (a - x) (mol dm(^3))</th>
<th>( \log \frac{a}{(a - x)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.189</td>
<td>4.974</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5</td>
<td>0.142</td>
<td>3.737</td>
<td>0.124</td>
</tr>
<tr>
<td>1.0</td>
<td>0.140</td>
<td>3.684</td>
<td>0.130</td>
</tr>
<tr>
<td>2.0</td>
<td>0.109</td>
<td>2.868</td>
<td>0.239</td>
</tr>
<tr>
<td>3.0</td>
<td>0.082</td>
<td>2.158</td>
<td>0.363</td>
</tr>
<tr>
<td>4.0</td>
<td>0.063</td>
<td>1.658</td>
<td>0.477</td>
</tr>
<tr>
<td>5.0</td>
<td>0.048</td>
<td>1.263</td>
<td>0.595</td>
</tr>
<tr>
<td>6.0</td>
<td>0.037</td>
<td>0.974</td>
<td>0.708</td>
</tr>
<tr>
<td>7.0</td>
<td>0.029</td>
<td>0.763</td>
<td>0.814</td>
</tr>
<tr>
<td>8.0</td>
<td>0.021</td>
<td>0.553</td>
<td>0.954</td>
</tr>
<tr>
<td>9.0</td>
<td>0.016</td>
<td>0.421</td>
<td>1.072</td>
</tr>
<tr>
<td>10.0</td>
<td>0.013</td>
<td>0.342</td>
<td>1.163</td>
</tr>
<tr>
<td>11.0</td>
<td>0.010</td>
<td>0.263</td>
<td>1.285</td>
</tr>
<tr>
<td>12.0</td>
<td>0.007</td>
<td>0.184</td>
<td>1.431</td>
</tr>
</tbody>
</table>
**Fig. VII(ii)**

Oxidation of allyl alcohol by quinolinium dichromate in aqueous perchloric acid at 25°C.

(Conditions as in Table VII(i) (p.212))

![Graph showing the relationship between log a/(a-x) and time (min.)](image-url)
The results were in agreement with two moles of QDC being required for three moles of allyl alcohol.

$$2\text{QDC} + 3\text{CH}_2\text{CH}_2\text{OH} \rightarrow 2\text{Cr(III)} + 3\text{CH}_2\text{=CHCHO} + 6\text{H}^+ \quad (1)$$

**REACTION ORDERS**

The reaction orders were determined from the slopes of $\log k_{\text{obs}}$ versus $\log(\text{concn.})$ plots by varying the concentrations of oxidant, reductant and acid in turn while keeping the other concentrations, ionic strength and other conditions constant.

**Effect of [QDC]**

The QDC concentration was varied in the range of $1.0 \times 10^{-4}$ to $1.0 \times 10^{-3}$ mol dm$^{-3}$, and the linearity of plots of $\log a / (a - x)$ versus time indicates a unit order in [QDC] (Fig.VII(ii) (p.213)). This was also confirmed by the fact that the variation of [QDC] did not influence the pseudo-first order rate constants (Table VII(ii) (p.215)).

**Effect of [allyl alcohol]**

The concentration of allyl alcohol was varied in the range of $5.0 \times 10^{-4}$ to $6.0 \times 10^{-2}$ mol dm$^{-3}$, keeping oxidant and acid concentrations constant at constant ionic strength as in Table VII(ii) (p.215). The order in [allyl alcohol] was determined by the slope of the plot of $\log k_{\text{obs}}$ versus $\log(\text{concn.})$ and was found to be less than unity (Fig. VII(iii) (p.217)).
Table VII(ii).

Effect of variation of [QDC], [AA] and [HClO₄] on the oxidation of allyl alcohol by quinolinium dichromate at 25°C.

\[ I = 1.30 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[QDC] (\times 10^4) (mol dm(^{-3}))</th>
<th>[AA] (\times 10^2) (mol dm(^{-3}))</th>
<th>[HClO₄] (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>5.0</td>
<td>1.0</td>
<td>4.52</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>1.0</td>
<td>4.50</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>1.0</td>
<td>4.51</td>
</tr>
<tr>
<td>8.0</td>
<td>5.0</td>
<td>1.0</td>
<td>4.54</td>
</tr>
<tr>
<td>10.</td>
<td>5.0</td>
<td>1.0</td>
<td>4.51</td>
</tr>
<tr>
<td>5.0</td>
<td>0.5</td>
<td>1.0</td>
<td>0.52</td>
</tr>
<tr>
<td>5.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.05</td>
</tr>
<tr>
<td>5.0</td>
<td>2.0</td>
<td>1.0</td>
<td>1.89</td>
</tr>
<tr>
<td>5.0</td>
<td>4.0</td>
<td>1.0</td>
<td>3.50</td>
</tr>
<tr>
<td>5.0</td>
<td>6.0</td>
<td>1.0</td>
<td>5.28</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>0.06</td>
<td>0.31</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>0.24</td>
<td>1.26</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>0.42</td>
<td>1.98</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>0.72</td>
<td>3.18</td>
</tr>
<tr>
<td>5.0</td>
<td>5.0</td>
<td>1.20</td>
<td>5.20</td>
</tr>
</tbody>
</table>
Effect of acidity

At constant concentrations of oxidant, reductant and other constant conditions, the concentration of perchloric acid was varied between 0.06 and 1.20 mol dm$^{-3}$. The rate of reaction increased with increase in concentrations of perchloric acid (Table VII(ii) (p.215)). The order with respect to [HClO$_4$], was found from the plot of log $k_{obs}$ versus log(concn.), and was less than unity (Fig. VII(iii) (p.217)).

Effect of added products

The effect of initially added products, chromium(III) and acrolein, was studied in the $1.0 \times 10^{-4} - 1.0 \times 10^{-3}$ and $5.0 \times 10^{-5} - 4.0 \times 10^{-4}$ mol dm$^{-3}$ concentration ranges respectively, while keeping the reactant concentrations and all other conditions constant. It was observed that, both the chromium(III) and acrolein products, did not have any significant effect on the reaction rate.

Effect of added ions

When reactant concentrations and other conditions were kept constant, ions such as Cl$^-$, SO$_4^{2-}$, CH$_3$COO$^-$ did not have any effect on the rate of the reaction, while added Mn$^{2+}$ decreases the rate.

Effect of the dielectric constant and ionic strength

The effect of dielectric constant(D) was studied by varying the ethanoic acid content (v/v) in the reaction medium, keeping the reactant concentrations...
Fig. VII(iii)

Order in [AA] and [HClO₄]

Effect of variation of [AA] and [HClO₄] on the oxidation of allyl alcohol by quinolinium dichromate at 25°C.

(Conditions as in Table VII(ii) (p.215))

\[
3 + \log [AA]
\]

\[
2 + \log [HClO₄]
\]
and other conditions constant, the reaction rate increases (Table VII(iii) (p.219)). Since the dielectric constants of aqueous ethanoic acid are not available in the literature, they were computed by interpolation from the values for the pure liquids\textsuperscript{13}. The values of dielectric constants for different percentages of ethanoic acid-water (v/v) were calculated as in Chapter II (p.47). No reaction of the solvent with the oxidant occurred under the experimental conditions employed. A plot of log \( k_{\text{obs}} \) versus \( 1/D \) was linear with a positive slope (Fig. VII(iv) (p.220)). Variation of the ionic strength between 1.3 and 3.0 mol dm\(^{-3} \) using sodium perchlorate, caused marginal increase in the rate of the reaction.

Test for free radicals

The intervention of free radicals were examined as follows. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for one hour. Upon diluting the reaction mixture with methanol, a precipitate resulted, suggesting the participation of free radicals in the reaction.

Effect of temperature

The rate of reaction was measured at four different temperatures, by varying [AA] keeping other conditions constant. The rate was found to increase with increase in the temperature. The rate constant, \( k \), of the slow step of Scheme 1 were obtained from the intercept of plots of \( 1/k_{\text{obs}} \) versus \( 1/[\text{AA}] \) at different temperatures (Fig. VII(vi) (p.226)). The data are subjected to a least
Table VII(iii)

Effect of variation of dielectric constant (D) on the oxidation of allyl alcohol by quinolinium dichromate at 25°C

\[ [\text{QDC}] = 5.0 \times 10^{-4}; \quad [\text{AA}] = 5.0 \times 10^{-2}; \]

\[ [\text{HClO}_4] = 1.0; \quad I = 1.3/\text{mol dm}^3 \]

<table>
<thead>
<tr>
<th>% of ethanoic acid - water (v/v)</th>
<th>D</th>
<th>( k_{\text{obs}} \times 10^2 ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.4</td>
<td>0.45</td>
</tr>
<tr>
<td>10</td>
<td>71.22</td>
<td>0.65</td>
</tr>
<tr>
<td>20</td>
<td>64.04</td>
<td>0.92</td>
</tr>
<tr>
<td>30</td>
<td>56.81</td>
<td>1.44</td>
</tr>
<tr>
<td>40</td>
<td>49.58</td>
<td>2.55</td>
</tr>
<tr>
<td>50</td>
<td>42.35</td>
<td>5.31</td>
</tr>
</tbody>
</table>
Fig. VII(iv)

Effect of variation of dielectric constant ($D$) on the oxidation of allyl alcohol by quinolinium dichromate at 25° C.

(Conditions as in Table VII(iii) (p.219))
square analysis as in Chapter II (p.50), have been tabulated in Table VII(iv) (p.222). The energy of activation corresponding to these constants was evaluated from log k versus 1 / T plot (Fig. VII(v) (p.223)) and other activation parameters were obtained as in Chapter II (p.54) and are listed in Table VII(iv) (p.222).

DISCUSSION

Variation of the concentrations each of the oxidant (QDC), substrate (AA) and acid, while keeping the others fixed showed that the reaction exhibits first order in oxidant, less than unit order each in substrate and acid concentrations (Table VII(ii) (p.215)). The reaction between allyl alcohol and QDC in perchloric acid has a stoichiometry of 3:2. No effect of initially added products was observed. The increase in the oxidation rate with acidity suggested the involvement of a protonated chromium(VI) species in the prior equilibrium step. There have been earlier reports of the involvement of such species in chromic acid oxidation\textsuperscript{14}. Here QDC in presence of acid forms a protonated species. The protonated species of QDC reacts with allyl alcohol to form a complex, which then decomposes in a rate-determining step to give the acrolein product, the intermediate chromium(IV) being generated. This intermediate chromium(IV) reacts in a fast step with another molecule of allyl alcohol to give a free radical derived from allyl alcohol and chromium(III) product. In further fast step, the free radical of allyl alcohol reacts with protonated QDC species to give acrolein product and another intermediate chromium(V). This intermediate chromium(V) reacts in a further fast step to give the products, acrolein and Cr(III). The initiation of polymerisation of
Table VII(iv)

Effect of temperature on the oxidation of allyl alcohol by quinolinium dichromate with respect to slow step of Scheme 1.

\[ [\text{QDC}] = 5.0 \times 10^{-4}; \]  
\[ [\text{AA}] = 5.0 \times 10^{-2}; \]  
\[ [\text{HClO}_4] = 1.0; \]
\[ I = 1.3/\text{mol dm}^3 \]

(a) Activation parameters with respect to slow step of Scheme 1.

<table>
<thead>
<tr>
<th>T* (K)</th>
<th>( k \times 10^2 ) (s(^{-1}))</th>
<th>1/( T \times 10^3 ) (x)</th>
<th>( \log k ) (y)</th>
<th>( y_{\text{cal}**} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>2.5</td>
<td>3.356</td>
<td>-1.602</td>
<td>-1.556</td>
</tr>
<tr>
<td>303</td>
<td>3.6</td>
<td>3.300</td>
<td>-1.444</td>
<td>-1.419</td>
</tr>
<tr>
<td>308</td>
<td>5.0</td>
<td>3.247</td>
<td>-1.301</td>
<td>-1.306</td>
</tr>
<tr>
<td>313</td>
<td>6.7</td>
<td>3.195</td>
<td>-1.174</td>
<td>-1.168</td>
</tr>
</tbody>
</table>

* Temperature, ** Calculated

(b) Activation parameters with respect to slow step of Scheme 1.

\[ E_a = 52 \pm 2 \text{ kJ mol}^{-1} \]
\[ \Delta H^\# = 49.7 \pm 1.5 \text{ kJ mol}^{-1} \]
\[ \log A = 7.5 \pm 0.4 \]
\[ \Delta S^\# = -109 \pm 6 \text{ JK}^{-1}\text{mol}^{-1} \]
\[ \Delta G^\# = 82 \pm 4 \text{ kJ mol}^{-1} \]
Fig. VII(v)

Effect of temperature on the oxidation of allyl alcohol by quinolinium dichromate, with respect to slow step of Scheme 1

(Conditions as in Table VII(iv) (p.222))
acrylonitrile, indicated the presence of a free radical intermediate. A free radical mechanism has been proposed\textsuperscript{15} for the oxidation of 2-propanol by chromium(VI) in aqueous acetic acid medium. A chromate ester which is formed in the second step of Scheme 1 is also in accordance with earlier work\textsuperscript{15} and then followed a series of rapid steps which involve intermediate oxidation states of chromium, Cr(IV) and Cr(V). The intermediate formation of the chromate ester was confirmed by a study of the oxidation of sterically hindered alcohols by chromic acid\textsuperscript{16}. The results can be accommodated by Scheme 1

\[
\begin{align*}
\text{CH}_2 = \text{CH}_2 \text{OH} + \text{Cr}^{\text{IV}} &\xrightarrow{\text{fast}} \text{CH}_2 = \text{CHO} + \text{Cr}^{\text{III}} + \text{H}^- \\
\text{CH}_2 = \text{CH} - \text{CHO} + \text{Cr}^{\text{V}} &\xrightarrow{\text{fast}} \text{CH}_2 = \text{CHO} + \text{Cr}^{\text{III}} + 2\text{H}^-
\end{align*}
\]

Scheme 1
Attempts to obtain uv-vis. spectral evidence for the complex formation between QDC and allyl alcohol were not successful at room temperature which might be due to a weak interaction. However, at a lower temperature (nearly 2°C), the evidence for complex formation was obtained from uv-vis. spectrum of both allyl alcohol and QDC-allyl alcohol mixtures, in which a bathochromic shift of QDC from 313 to 317 nm and a hyperchromicity at 317 nm occurred. This was also evident from the Michaelis-Menten plot (1 / $k_{obs}$ versus 1 / [AA] plot), Fig. VII(vi) (p.226) and such complex formation between substrate and oxidant has also been observed in other studies\textsuperscript{17}. Since the oxidation of allyl alcohol by QDC is a non-complementary reaction, it may occur by the intervention of reactive chromium(IV) and chromium(V) species. The intervention of chromium(IV) is evident from a progressive rate decrease in the presence of increasing amounts of added manganese(II), the decrease reaching a limit of approximately 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\textsuperscript{18}. The intervention of chromium(V) is evident from the induction experiment with iodide\textsuperscript{14}. The induced oxidation of iodide yields two equivalent of iodine for each equivalent of the inductor oxidised. In any induced oxidation, the “induction factor” is defined as the ratio of the number of equivalents of reducing agent oxidised to the number of equivalents of inductor oxidised. The induction factor for iodide oxidation is nearly two, which indicates that the active oxidising agent is pentavalent chromium.
Fig. VII(vi)

Verification of rate law (8) on the oxidation of allyl alcohol by quinolinium dichromate.

(Conditions as in Table VII(ii) (p.215))

\[
\frac{1}{[\text{AA}]} \text{ dm}^3 \text{ mol}^{-1}
\]

\[
\frac{1}{k_{\text{obs}}} \times 10^{-2} \text{ s}
\]

\[
\frac{1}{[\text{H}^+]} \text{ dm}^3 \text{ mol}^{-1}
\]
From the Scheme 1, the rate law (8) is derived as follows:

\[
\text{Rate} = k [C] \tag{2}
\]

But, from the second equilibrium step of Scheme 1, we get,

\[
C = K_2[AA] [QH^+] \tag{2}
\]

Substituting the value of 'C' in equation (2), we have,

\[
\text{Rate} = kK_2[AA] [QH^+] \tag{3}
\]

Similarly, from the first equilibrium step of Scheme 1,

\[
[QH^+] = K_i[QDC] [H^+] \tag{3}
\]

\[C = K_iK_2[QDC] [AA] [H^+] \tag{4}
\]

Substituting the value of [QH^+] in equation (3), we have,

\[
\text{Rate} = kK_iK_2 [QDC] [AA] [H^+] \tag{4}
\]

The total concentration of QDC is given by

\[
[QDC]_T = [QDC]_f + QH^+ + C
\]

\[= [QDC]_f + K_i[QDC]_f [H^+] + K_iK_2[QDC]_f [AA][H^+] \tag{4}
\]

\[= [QDC]_f \{1+K_i[H^+] + K_iK_2[AA][H^+]\}
\]

Therefore,

\[
[QDC]_f = \frac{[QDC]_T}{1 + K_i[H^+] + K_iK_2[AA][H^+]} \tag{5}
\]
Similarly,

\[
[AA]_T = [AA]_f + C
\]

\[
= [AA]_f + K_1K_2[AA]_f[QDC][H^+]
\]

\[
= [AA]_f \{1+K_1K_2[QDC][H^+])\}
\]

\[
\therefore [AA]_f = \frac{[AA]_f}{1+K_1K_2[QDC][H^+]}
\]  (6)

where subscripts 'T' and 'f' stand for total and free respectively.

Substituting for [QDC]_f and [AA]_f from equations (5) and (6) in equation (4) and omitting the subscripts, we have,

\[
\text{Rate} = kK_1K_2[QDC][AA][H^+] \frac{1}{(1 + K_1[H^+] + K_1K_2[AA][H^+])}
\]  (7)

The concentration of QDC is very very less in comparison with the concentration of allyl alcohol, hence, the term \(1+K_1K_2[QDC][H^+]\) in the denominator of equation (7) approximates to unity.

\[
\therefore \text{Rate} = \frac{-d[QDC]}{dt} = \frac{kK_1K_2[QDC][AA][H^+]}{1 + K_1[H^+] + K_1K_2[AA][H^+]} \]  (8)

OR

\[
\frac{\text{Rate}}{[QDC]} = k_{obs} = \frac{kK_1K_2[AA][H^+]}{1 + K_1[H^+] + K_1K_2[AA][H^+]} \]  (8)
The rate law (8) may be rearranged to equation (9), which is suitable for verification.

\[
\frac{1}{k_{\text{obs}}} = \frac{1}{kK_1K_2[AA][H^+]} + \frac{1}{kK_2[AA]} + \frac{1}{k} \quad (9)
\]

According to equation (9), the plots of \(1/k_{\text{obs}}\) versus \(1/[\text{AA}]\) and \(1/k_{\text{obs}}\) versus \(1/[\text{H}^+]\) should be linear, and is found to be so (Fig. VII(vi) (p.226)). The slopes and intercepts of such plots lead to the values of \(K_1, K_2\) and \(k\) as \(5.51 \pm 0.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}, 80 \pm 3 \text{ dm}^3 \text{ mol}^{-1}\) and \(2.5 \pm 0.1 \times 10^3 \text{ s}^{-1}\) respectively. Using these values, rate constants under different experimental conditions were calculated and compared with experimental data (Table VII(ii) (p.218)). Experimental and calculated values agree reasonably well. The negative value of the entropy of activation indicated that the complex is more ordered than the reactants. The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction.

The ionic strength has negligible effect on the rate of reaction, which is in the right direction, since an ion and a neutral molecule are involved in Scheme 1. However, increase in the content of acetic acid in the reaction medium leads to the increase in the reaction rate. This suggested an interaction between a positive and dipole\(^{20}\) and was in consonance with the observation that in the presence of acid a protonated Cr(VI) species and allyl alcohol is involved in the reaction scheme (Scheme 1).
FINDINGS

Quinolinium dichromate (QDC) oxidation of allyl alcohol (AA) has been studied in aqueous perchloric acid medium at a constant ionic strength of 1.30 mol dm$^{-3}$ and at 25$^\circ$ C. The rate of reaction is first order dependent in oxidant and less than unit order in each of the substrate and acid concentrations. The added products, chromium(III) and acrolein do not significantly affect the reaction rate. A free radical mechanism involving the intermediates of chromium(IV) and chromium(V) is proposed. The reaction constants involved in the mechanism have been evaluated.

IMPORTANCE OF CHAPTER VII

The main products of the reaction were found to be chromium(III) and acrolein. A mechanism in terms of active species of oxidant and catalyst is proposed and the rate law is derived and verified.
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