Chapter IV

Oxidation Of Dimedone By Acidified Quinolinium dichromate, A New Oxidant - A Kinetic And Mechanistic Study

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, quinoliniumdichromate, (QDC), \((\text{C}_9\text{H}_7\text{NH}^+)_2\text{Cr}_2\text{O}_7^2-\); 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 QDC. Since the chromium exhibits different oxidation states during oxidation, such as chromium (V), chromium (IV), chromium (III), etc, the reaction might involve several complexities. Dimedone (5,5-dimethyl cyclohexane-1, 3-dione) finds a number of applications in organic syntheses. It is a well-known complexing agent, which forms varieties of co-ordination complexes with various metal ions. It also finds its application in medicine. To the best of our knowledge there are no reports on mechanistic studies of dimedone oxidation, except with permanganate and diperiodatonicelate (IV). In view of the lack of literature on the oxidation of dimedone by QDC, and in order to explore the mechanistic aspects of QDC.
oxidation in acid medium, we have chosen dimedone as a substrate. The present study deals with the title reaction to investigate the redox chemistry of QDC in such media.

**EXPERIMENTAL**

Since the initial reaction was too fast to monitor by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12).

**Materials and Methods**

Reagent grade chemicals and doubly distilled water were used throughout. Quinolinium dichromate was prepared by the reported method as follows: Quinoline (12.9 gms, 0.1 mol) was slowly added with stirring to a cooled solution of chromium trioxide (10 gms, 0.1 mol) in water (10 cm$^3$). After 30 min. the solution was diluted with acetone (40 cm$^3$) and cooled to -20 °C. The orange solid which separated out was filtered, washed with acetone, dried in vacuum and then recrystallised from water yielding 9 gms of quinolinium dichromate (QDC), m.p. 160-161 °C. Its purity was checked with I.R. and NMR spectroscopy. Further QDC solution was prepared by dissolving QDC in water and its concentration was determined iodometrically. Solution of dimedone (A.R) (DM) was prepared by dissolving appropriate amount of sample in hot distilled water. The chromium (III) solution was prepared by dissolving chromium sulphate Cr$_2$(SO$_4$)$_3$.K$_2$SO$_4$.24H$_2$O (BDH), in water. The concentration of chromium (III) was determined by oxidizing it to chromium (VI) with excess persulphate in presence of one or two drops of 1.0
x $10^2$ 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 (E.Merek) and sodium perchlorate (BDH) were used to keep the required acidity and to maintain the ionic strength, respectively.

**KINETIC MEASUREMENTS**

All kinetic measurements were performed under pseudo first-order conditions where dimedone used was at least 10 fold excess over [QDC] at a constant ionic strength of 1.70 mol dm$^{-3}$. The reaction was initiated by mixing previously thermostatted solutions of QDC and dimedone, which also contained required quantities of HClO$_4$ and NaClO$_4$ to maintain required acidity and ionic strength respectively. The temperature was maintained at $28 \pm 0.1^\circ$C. The course of the reaction was followed by monitoring the decrease in the absorbance of QDC in a 1cm quartz cell of Hitachi 150-20 spectrophotometer at its absorption maximum 440 nm. Application of Beer's Law under the reaction conditions had been verified earlier between $2.0 \times 10^{-4}$ and $2.0 \times 10^{-3}$ mol dm$^{-3}$ for QDC at 440 nm with $\varepsilon$ resulting as $380 \pm 10$ dm$^3$ mol$^{-1}$ cm$^{-1}$ as shown in Figure IV (i) (p.135). The first - order rate constants $k_{obs}$ were evaluated by the plots of log [QDC] versus time, an example run is given in Table IV (i) (p.136). The first order plots in almost all cases were found to be linear upto 85% of the reaction and $k_{obs}$ were reproducible within $\pm 5\%$. During the course of measurements the colour of the solution changed from yellow to green. The spectrum of green solution was identified to that of chromium (III). The formation of chromium (III) was also
Figure IV (i)

Verification of Beer’s law for [QDC] at 440 nm in 10 mol dm$^{-3}$ perchloric acid.
### Table IV (i)

An Example run for the oxidation of dimedone by aqueous acidic quinolinium dichromate at 28 °C

\[
[\text{QDC}] = 1.10 \times 10^{-3}; \quad [\text{DM}] = 1.10 \times 10^{-2};
\]
\[
[\text{H}^+] = 1.0; \quad I = 1.70 / \text{mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Optical density (440 nm)</th>
<th>Log [QDC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.405</td>
<td>-2.9723</td>
</tr>
<tr>
<td>0.4</td>
<td>0.385</td>
<td>-2.9943</td>
</tr>
<tr>
<td>0.8</td>
<td>0.339</td>
<td>-3.0495</td>
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<td>1.2</td>
<td>0.313</td>
<td>-3.0842</td>
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<td>1.6</td>
<td>0.288</td>
<td>-3.1203</td>
</tr>
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<td>2.0</td>
<td>0.264</td>
<td>-3.1581</td>
</tr>
<tr>
<td>2.4</td>
<td>0.242</td>
<td>-3.1959</td>
</tr>
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<td>2.8</td>
<td>0.223</td>
<td>-3.2314</td>
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<tr>
<td>3.2</td>
<td>0.203</td>
<td>-3.2722</td>
</tr>
<tr>
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<td>0.179</td>
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</tr>
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<td>4.4</td>
<td>0.159</td>
<td>-3.3783</td>
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<td>5.0</td>
<td>0.137</td>
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</tr>
<tr>
<td>5.6</td>
<td>0.124</td>
<td>-3.4863</td>
</tr>
<tr>
<td>6.2</td>
<td>0.106</td>
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<tr>
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<td>-3.6207</td>
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<tr>
<td>7.8</td>
<td>0.079</td>
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</tr>
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<td>0.072</td>
<td>-3.7224</td>
</tr>
<tr>
<td>9.0</td>
<td>0.070</td>
<td>-3.7346</td>
</tr>
</tbody>
</table>

Error ± 5%.
confirmed by decreasing absorbance of QDC at 380 nm and an increasing absorbance of chromium (III) at 580 nm during the course of the reaction. The spectral changes during the redox reaction are shown in Figure IV (ii) (p.138). Earlier it was verified that there is no interference from other reagents at this wavelength.

Fresh solutions were used while conducting the experiments. Regression analysis of experimental data to obtain the regression coefficient, $r$ and the standard deviation, $s$ of points from the regression line was performed using a Pentium computer.

RESULTS

Stoichiometry and Product Analysis

The reaction mixture containing excess QDC concentration over dimeredone were mixed in presence of 1mol dm$^{-3}$ HClO$_4$, adjusted to a constant ionic strength of 1.70 mol dm$^{-3}$ and allowed to react for about 4h at 28 ± 0.1°C. The remaining QDC was then analysed spectrophotometrically. The results indicated that three moles of dimeredone were consumed by four moles of QDC according to equation (1). The results are in agreement with 3:4 stoichiometry, as shown in Table IV (ii) (p.139).

$$\begin{align*}
3 \text{QDC (Cr V I)} + 9 \text{H}_2\text{O} & \rightarrow 3 \text{C} \quad + 3 \text{HCHO} + 4\text{Cr(III)} + 12\text{H}^+ \\
& \quad \text{C} \quad \text{OH} \\
& \quad \text{C} \quad \text{OH}
\end{align*}$$
Figure IV (ii)

Spectroscopic changes occurring during the oxidation of QDC by aqueous acidic quinolinium dichromate at 28 °C, scanning time interval = 1 min.

\[ [\text{QDC}] = 1.10 \times 10^{-3}; \quad [\text{DM}] = 1.10 \times 10^{-2}; \]

\[ [\text{H}^+] = 1.0; \quad 1 = 1.70/\text{mol dm}^{-3}. \]
**Table IV (ii)**

Stoichiometry of oxidation of dimedone by aqueous acidic quinolinium dichromate at 28° C.

\[ [H^+] = 1.0; \quad I = 1.70/\text{mol dm}^3. \]

<table>
<thead>
<tr>
<th>Taken</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>[QDC] x 10³</td>
<td>[DM] x 10²</td>
</tr>
<tr>
<td>(mol dm⁻³)</td>
<td>(mol dm⁻³)</td>
</tr>
<tr>
<td>4.0</td>
<td>3.0</td>
</tr>
<tr>
<td>9.0</td>
<td>6.0</td>
</tr>
<tr>
<td>10.0</td>
<td>4.0</td>
</tr>
<tr>
<td>8.0</td>
<td>3.0</td>
</tr>
<tr>
<td>8.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Error ± 5%.
The reaction products were eluted with ether, and organic products were submitted to spot test, which revealed the presence of an acid\(^{10}\) (a) and aldehyde\(^{10}\) (b). The presence of 3,3-dimethyl-1,5-pentanedioic acid, (β, β-dimethylglutaric acid) was also confirmed by finding m.p. \((102^\circ C)\)\(^{11}\) of recrystallised sample and by its IR\(^{12}\) and \(^{1}HNMR\)\(^{13}\) spectroscopy. IR showed bands at \((\nu)\) 1699 cm\(^{-1}\) (for carboxyl, C=O stretching) and 2962 cm\(^{-1}\) (for C-H and acid O-H stretching). \(^{1}HNMR\) (CDCl\(_3\)) showed chemical shifts (δ) at 1.1(s, 6H, 2CH\(_3\)), 2.54(s, 4H, 2CH\(_2\)) and 7.69(br, 1H, carboxylic OH), respectively. The other product formed was formaldehyde. Its presence was identified by spot test (silver mirror)\(^{10}(b)\). The products acid and aldehyde were quantitatively estimated to ca. 80%, evidence for which was provided by the corresponding cyclic anhydride and 2,4-DNP derivatives\(^{14}\). The concentration of chromium (III) was determined by measuring its absorbance at 580nm. It was further observed that the acid and the corresponding aldehyde do not undergo further oxidation under the present kinetic conditions.

**REACTION ORDERS**

The order each in dinedone and perchloric acid was investigated by varying one of these concentrations while keeping all other concentrations and conditions constant and studying the effect of its concentration on the rate of the reaction. The resulting data were employed to plot log \(k_{obs}\) versus log concentration graphs and the orders were obtained from such graphs.
Effect of [quinolinium dichromate]

The oxidant, QDC concentration was varied in the range of $2.0 \times 10^{-4}$ to $2.0 \times 10^{-3}$ mol dm$^{-3}$ and the linearity of plot of log [QDC] versus time (Fig. IV (iii) (p.142)) ($r > 0.9979$, $s < 0.0416$) indicates the order in [QDC] as unity. This was also confirmed by varying [QDC], which did not show any change in pseudo first order rate constants $k_{obs}$ (Table IV (iii) (p.143)).

Effect of [Substrate]

The substrate dimedone concentration was varied in the range of $2.0 \times 10^{-3}$ to $2.0 \times 10^{-2}$ mol dm$^{-3}$ at $28^\circ$C keeping all other reactants concentration and conditions constant (Table IV (iv) (p.144)). The apparent order in [Dimedone] was found to be less than unity (Fig. IV (iv) (p.145)).

Effect of [Acid]

The effect of increasing concentration of acid was studied on the reaction rate at constant concentration of dimedone and QDC at constant ionic strength of 1.70 mol dm$^{-3}$ at $28^\circ$C. The rate constants increased with the increase in acid concentration. (Table IV (iv) (p.144)). The order was found to be 0.88 (Fig. IV (iv) (p.145)).

Effect of Initially Added Reaction Products

The initially added products such as chromium (III), 3,3-dimethyl-1, 5-pentanedioic acid and formaldehyde did not show any significant effect on the rate of the reaction (Table IV (v) (p.146)).
Figure IV (iii)

First order plot of \([\text{QDC}]\) on oxidation of dimedone by aqueous acidic quinolinium dichromate at 28 °C.

(Conditions as in Table IV (iii) (p.143)).

\([\text{QDC}] \times 10^3 \text{moldm}^{-3}: (1) 0.20, (2) 0.4, (3) 0.7, (4) 1.10 \text{ and } (5) 2.0\)
Table IV (iii)

Effect of variation of [QDC], on the oxidation of dimedone by aqueous acidic quinolinium dichromate at 28° C.

\[ [\text{DM}] = 1.10 \times 10^{-2}; \quad [\text{H}^+] = 1.0 \;
\]
\[ I = 1.70 \text{ mol dm}^{-3} . \]

<table>
<thead>
<tr>
<th>[QDC] x 10^3 (mol dm(^{-3}))</th>
<th>( k_{\text{obs}} \times 10^3 ) (s(^{-1}))</th>
<th>Expt*</th>
<th>Cald.*</th>
</tr>
</thead>
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<tr>
<td>0.20</td>
<td>3.42</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
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<td>3.40</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
<td>0.70</td>
<td>3.44</td>
<td>3.49</td>
<td></td>
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<td>3.49</td>
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<tr>
<td>2.00</td>
<td>3.41</td>
<td>3.49</td>
<td></td>
</tr>
</tbody>
</table>

*Experimental and Calculated.

Error ± 5%.
Table IV (iv)

Effect of variation of [DM] and [H\(^+\)] on the oxidation of dimedone by aqueous acidic quinolinium dichromate at 28° C.

\[ \text{[QDC]} = 1.10 \times 10^{-3}; \quad I = 1.70 \text{ mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>[DM] x 10(^2) (mol dm(^{-3}))</th>
<th>[H(^+)] (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^3) (s(^{-1}))</th>
<th>Expt(^*)</th>
<th>Cald(^*)</th>
</tr>
</thead>
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<td>1.44</td>
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</tr>
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<td>2.38</td>
<td></td>
</tr>
<tr>
<td>1.10</td>
<td>1.0</td>
<td>3.40</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
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<td>4.50</td>
<td>4.45</td>
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<td>1.0</td>
<td>5.62</td>
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<td>0.67</td>
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<td>1.21</td>
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<td>4.30</td>
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<tr>
<td>1.10</td>
<td>1.60</td>
<td>5.27</td>
<td>5.00</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\)Experimental and Calculated.

Error ± 5%.
Figure IV (iv)

Order of reaction with respect to [DM] and [H+] on oxidation of dimedone by aqueous acidic quinolinium dichromate at 28° C.

(Conditions as in Table IV (iv) (p.144))
Table IV (v)

Effect of variation of [Cr$^{3+}$], [Acid] and [Aldehyde] on the oxidation of dimedone by aqueous acidic quinolinium dichromate at 28°C.

\[ [\text{QDC}] = 1.10 \times 10^{-3}; \]
\[ [\text{DM}] = 1.10 \times 10^{-2}; \]
\[ [\text{H}^+] = 1.0; \]
\[ I = 1.70/\text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>[Cr$^{3+}$] x 10$^{-3}$ (mol dm$^{-3}$)</th>
<th>[Acid] x 10$^{-2}$ (mol dm$^{-3}$)</th>
<th>[Aldehyde] x 10$^{-2}$ (mol dm$^{-3}$)</th>
<th>$k_{\text{obs}} \times 10^3$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>4.29</td>
</tr>
<tr>
<td>5.0</td>
<td>-</td>
<td>-</td>
<td>4.31</td>
</tr>
<tr>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>4.24</td>
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<td>12.0</td>
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<td>-</td>
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<td>3.33</td>
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<td>0.5</td>
<td>3.38</td>
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<td>3.34</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>3.34</td>
</tr>
</tbody>
</table>
**Effect of Ionic Strength**

The effect of ionic strength was studied by varying the sodium perchlorate concentration. The ionic strength of the reaction medium was varied from 1.0 to 2.2 mol dm\(^{-3}\) at constant concentrations of QDC, dimedone and acid. It was found that the rate constant did not change with increasing concentration of NaClO\(_4\), Table IV (vi) (p.148)).

**Effect of Solvent Polarity**

The relative permittivity (D) effect was studied by varying acetic acid - water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivity were not successful. Since the dielectric constant of aqueous acetic acid are not available in the literature, they were computed from the values of pure liquids\(^{15}\) as given in chapter II (p.50). It was also confirmed that there was no reaction between acetic acid and dimedone at the experimental conditions employed. There is no reaction of the solvent with the oxidant under the experimental conditions. The rate constant \(k_{\text{obs}}\) decreased with the decrease in the dielectric constant of the medium, (Table IV (vi) (p.148)). The plot of log \(k_{\text{obs}}\) versus 1/D (\(r > 0.9992, s \leq 0.02660\)) was linear with negative slope (Fig. IV (v) (p.149)).

**Test for Free Radicals**

The intervention of free radicals in the reaction was examined as follows. The reaction mixture to which a known quantity of acrylonitrile scavenger had been added initially was kept for one hour in an inert atmosphere. On diluting the
Table IV (vi)

Effect of variation of ionic strength (I) and solvent polarity (D) on the oxidation of dimedone by aqueous acidic quinolinium dichromate at 28° C.

\[
\text{[QDC]} = 1.10 \times 10^{-3}; \quad \text{[DM]} = 1.10 \times 10^{-2};
\]

\[
\text{[H}^+\text{]} = 1.0; \quad I = 1.70 \text{ /mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>I (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^3)</th>
<th>% of Acetic acid*</th>
<th>D</th>
<th>(k_{\text{obs}} \times 10^3)</th>
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</thead>
<tbody>
<tr>
<td>1.0</td>
<td>3.42</td>
<td>5</td>
<td>74.90</td>
<td>2.84</td>
</tr>
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<td>1.4</td>
<td>3.41</td>
<td>10</td>
<td>71.20</td>
<td>2.66</td>
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<td>1.7</td>
<td>3.40</td>
<td>15</td>
<td>67.60</td>
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<td>3.46</td>
<td>20</td>
<td>64.10</td>
<td>1.92</td>
</tr>
<tr>
<td>2.2</td>
<td>3.44</td>
<td>25</td>
<td>60.40</td>
<td>1.60</td>
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</tbody>
</table>

*Acetic acid-water (v/v)

Error ± 5%.
Figure IV (v)

Effect of solvent polarity (D) on the oxidation of dimedone by aqueous acidic quinolinium dichromate at 28° C.

(Conditions as in Table IV (vi) (p.148))
reaction mixture with methanol, a precipitate resulted, suggesting the possibility of free radical intervention.

**Effect of Temperature**

The rate of reaction was measured at different temperatures under varying [DM]. The rate of reaction increased with the increase of temperature. The rate constants, k of the slow step of scheme 1 were obtained from intercept and slope of $1/k_{obs}$ versus $1/[DM]$ and used to calculate the activation parameters. The values of k (s$^{-1}$) were incorporated in the Table IV (vii a) (p.151). The energy of activation was calculated from the plot of $\log k$ (Y and $T$) versus $1/T$ ($r>0.9686$ $s<0.06662$) (Fig. IV (vi) (p.152)). The activation parameters were evaluated as given in chapter II (p.52) and are tabulated in Table IV (vii b) (p.151).

**DISCUSSION**

Variation of the concentrations each of the oxidant (QDC), substrate (DM) and acid, while keeping the others constant showed that the reaction exhibits first-order in oxidant, and less than unit order each in substrate and acid concentrations (Table IV (iv) (p.144). The reaction between dimedone and QDC in perchloric acid has a stoichiometry of 3:4. 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$^{16}$. Here QDC in presence of acid forms a protonated species. The protonated species of QDC reacts with dimedone to form a complex, which then decomposes in a rate-
Table IV (vii)
Effect of temperature on the slow step of the mechanism of oxidation of dimedone
by acidic quinolinium dichromate.

\[ [QDC] = 1.10 \times 10^{-3}, \quad [DM] = 1.10 \times 10^{-2}; \]
\[ [H^+] = 1.0; \quad 1 = 1.70 \text{ mol dm}^{-3}. \]

(a) Values of rate constants

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>( k \times 10^2 ) (s(^{-1}))</th>
<th>( 1/T \times 10^3 )</th>
<th>Log k</th>
<th>( Y_{\text{calcd}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>1.83</td>
<td>3.32</td>
<td>-1.737</td>
<td>1.752</td>
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<tr>
<td>306</td>
<td>2.50</td>
<td>3.26</td>
<td>-1.602</td>
<td>1.586</td>
</tr>
<tr>
<td>311</td>
<td>3.63</td>
<td>3.21</td>
<td>-1.440</td>
<td>1.427</td>
</tr>
<tr>
<td>313</td>
<td>4.50</td>
<td>3.19</td>
<td>-1.346</td>
<td>1.348</td>
</tr>
</tbody>
</table>

*Calculated.

(b) Values of Thermodynamic Parameters

<table>
<thead>
<tr>
<th>Activation parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) (kJ mol(^{-1}))</td>
<td>53.6 ± 2</td>
</tr>
<tr>
<td>Log A</td>
<td>7.6 ± 0.4</td>
</tr>
<tr>
<td>( \Delta S^* ) (JK(^{-1}) mol(^{-1}))</td>
<td>-108 ± 6</td>
</tr>
<tr>
<td>( \Delta H^* ) (kJ mol(^{-1}))</td>
<td>51.2 ± 1.5</td>
</tr>
<tr>
<td>( \Delta G^* ) (kJ mol(^{-1}))</td>
<td>83.8 ± 4.0</td>
</tr>
</tbody>
</table>

Error ± 5%.

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Figure IV (vi)
Effect of temperature on the slow step of the mechanism of oxidation of dimedone by aqueous acidic quinolinium dichromate.
(Conditions as in Table IV (vii) (p. 151)).
determining step to give the free radical, derived from dimedone and the intermediate chromium (V) being generated. This intermediate chromium (V) reacts with free radical in a fast step to give a sec-alcohol of dimedone as intermediate with generation of chromium (IV). The sec-alcohol of dimedone intermediate further undergoes rearrangement to form a biradical intermediate and product, formaldehyde. This type of biradicals have been observed in the literature\textsuperscript{17}. This biradical in presence of chromium (IV) in a fast step gives another free radical intermediate with the formation of the product chromium (III). The free radical intermediate further reacts with one more molecule of QDC in a fast step to give the final product, dicarboxylic acid (3,3-dimethyl-1,5-pentanedioicacid) and intermediate chromium (V). This step is further followed by subsequent fast steps to give the products in order to satisfy the stoichiometry. The initiation of polymerization of acrylonitrile indicated the possibility of a free radical intervention. The results can be accommodated by scheme 1.

\[
\begin{align*}
\text{Cr}(\text{OH})_2 + H^+ & \rightleftharpoons K_1 \text{Cr(OH)} + \text{QH}^+ \\
\text{QDC} & \rightleftharpoons \text{Cr(OH)} + \text{QH}^+ \\
\text{H}_2\text{C} \quad \text{C} \quad \text{H}_2\text{C} & \rightleftharpoons \text{Cr(OH)} + \text{QH}^+ \\
\text{H}_2\text{C} \quad \text{C} \quad \text{H}_2\text{C} & \rightleftharpoons \text{Cr(OH)} + \text{QH}^+ \\
\end{align*}
\]

Complex (C)
Attempts to obtain UV/Vis spectral evidence for the complex formation between QDC and dimedone are not successful at room temperature, which might be due to weak interaction. However, at lower temperature (nearly 0 °C) the evidence for complex formation was obtained from UV/Vis. spectrum of both dimedone and QDC-dimedone mixtures, in which a hypsochromic shift of about 5nm from 208nm to 203nm and a hyperchromicity at 203 nm occurred. This was also evident from the Michaelis-Menten plot, (1/k<sub>obs</sub> versus 1/[DM] plot) and such complex formation between substrate and oxidant has also been observed in other studies. The observed modest enthalpy of activation and a relatively low value of the entropy of activation, as well as a higher rate constant for the slow step, indicates that the oxidation presumably occurs via inner-sphere mechanism. This conclusion is supported by the earlier observations. Since scheme 1 is in accordance with the generally well-accepted principle of non complementary oxidations taking place in sequences of one electron steps, the reaction between a
substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility (vide infra). This type of radical intermediate has also been observed in earlier work on the QDC oxidation of various organic substrates in acid medium.

Since the oxidation of dimedone by QDC is a noncomplementary reaction, it may occur by the intervention of reactive chromium (IV) and chromium (V) species. The intervention of chromium (IV) is evident from the progressive rate decrease in the presence of increasing amounts of added manganese (II). Such results have also been obtained for chromium (VI) oxidation of 2-propanol in aqueous acetic acid. The intervention of chromium (V) is evident from the induction experiment with iodide. 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.

According to scheme 1.

\[
\text{Rate} = - \frac{d[QDC]}{dt} = k [C] = kK_1K_2[QDC]_f[DM]_f[H^+]_f 
\]

The total concentration of dimedone is given by

\[
[DM]_t = [DM]_f + [C] = [DM]_f + K_1K_2[QDC]_f[DM]_f[H^+]_f = [DM]_f(1 + K_1K_2[QDC]_f[H^+])
\]
Therefore,

\[
[DM]_T = \frac{[DM]}{1 + K_1 K_2 [QDC] [H^+]} \tag{3}
\]

The subscripts T and f stand for total and free concentration.

Similarly,

\[
[QDC]_T = \frac{[QDC]}{1 + K_1 [H^+] + K_1 K_2 [DM] [H^+]} \tag{4}
\]

and

\[
[H^+]_T = \frac{[H^+]_T}{1 + K_1 [QDC] + K_1 K_2 [QDC][DM]} \tag{5}
\]

Substituting equations (3) to (5) in equation (2)

\[
\text{Rate} = \frac{k K_1 K_2 [QDC]_T [DM]_T [H^+]_T}{(1 + K_1 [H^+] + K_1 K_2 [DM][H^+]) (1 + K_1 K_2 [QDC][H^+]) (1 + K_1 [QDC] + K_1 K_2 [QDC][DM])}
\]

The terms \((1 + K_1 K_2 [QDC][H^+])\) and \((1 + K_1 [QDC] + K_1 K_2 [QDC][DM])\) in the denominator approximate to unity in view of the low concentration of quinolinium dichromate used.

Hence (omitting the subscripts T and f)

\[
\text{Rate} = \frac{\frac{d[QDC]}{dt}}{k K_1 K_2 [DM] [H^+]} = \frac{k K_1 K_2 [QDC] [DM] [H^+]}{1 + K_1 K_2 [QDC][H^+]}
\]

OR

\[
\frac{\text{Rate}}{[QDC]} = k_{obs} = \frac{k K_1 K_2 [DM] [H^+]}{1 + K_1 [H^+] + K_1 K_2 [DM] [H^+]} \tag{7}
\]

The rate law (7) may be rearranged to equation (8), which is suitable for verification.

\[
\frac{1}{k_{obs}} = \frac{1}{k K_1 K_2 [DM] [H^+]} + \frac{1}{k K_2 [DM]} + \frac{1}{k} \tag{8}
\]
According to equation (8), the plots of $1/k_{obs}$ versus $1/[DM]$ and $1/k_{obs}$ versus $1/[H^+]$ should be linear, and is found to be so (Fig. IV (vii) (p.159)). The slopes and intercepts of such plots lead to the values of $K_1$, $K_2$ and $k$ as $4.12 (\pm 0.16) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$, $5.23 (\pm 0.15) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$ and $1.83 (\pm 0.05) \times 10^{-2} \text{ s}^{-1}$ respectively. Using these values, rate constants under different experimental conditions were calculated according to equation (8) and compared with experimental data (Table IV (iv) (p.144)). Experimental and calculated values agree reasonably well. The value of $K_1$ is in close agreement with the earlier reported value$^{22}$. 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 negligible effect of ionic strength on the rate of reaction is in the right direction, since an ion and a neutral molecule are involved$^{23}$ in scheme 1. The effect of solvent on the reaction kinetics has been described in earlier literature$^{24-28}$. For the limiting case of a zero angle approach between two dipoles or an ion-dipole system, Amis$^{29}$ has shown that a plot of log $k_{obs}$ versus $1/D$ is linear with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion-dipole interaction. However, in the present study, an increase in the content of acetic acid in the reaction medium leads to the decrease in the reaction rate, which is not in agreement with Amis theory$^{29}$. Applying the Born equation, Laidler and Eyring derived the equation (9).
Figure IV (vii)
Plots of $1/k_{obs}$ versus $1/[DM]$ and $1/k_{obs}$ versus $1/[H^+]$ (Verification of rate law (7)).

(Conditions as in Table IV (iv) (p. 144)
In $k = \ln k_0 + \frac{NZe^2}{2DRT} \left( \frac{1}{r} - \frac{1}{r^*} \right)$ (9)

where $k_0$ is the rate constant in a medium of infinite dielectric constant and $r$ and $r^*$ refer to the radius of the reacting species and the activated complex, respectively. It can be seen from the equation (9) that the rate should be greater in a medium of lower dielectric constant when $r^* > r$. Intermolecular hydrogen bonding, that could stabilise the transition state, increasing the size of the activated complex by attracting solvent molecules due to a solvation effect is possible. It is likely that $r^* > r$ for dimedone, thus explaining the experimental observation. Hence one can expect intermolecular hydrogen bonding in dimedone (A), as intermolecular hydrogen bonding can help to stabilize the enol form of dimedone.

Dimedone can not form intramolecular H-bond because the C=O group in the enol is too far from the OH group. However, infrared data show, that the compound exits largely as the enolic tautomer (B) and that it has a chelated enol structure similar to that in earlier studies.

\[
\text{(A)} \quad \text{CH}_3\text{C} - \text{C} - \text{CH}_2 \quad \text{CH}_2\text{C} - \text{C} - \text{CH}_2 \\
\text{(B)} \quad \text{O} - \text{H} \cdots \cdot \text{O} = \text{C} - \text{CH}_2 \\
\]
Importance of Chapter IV:

Since the oxidation of dimedone by QDC is a noncomplementary reaction, the intervention of Cr(V) and Cr(IV) intermediate species are evidenced in the reaction scheme. Various reaction constants involved in the different steps of scheme 1 are evaluated. The value of equilibrium constant in the first step of scheme 1 is in good agreement with earlier reported value. Activation parameters with respect to slow step of scheme 1 are evaluated.
References

1. E. J. Corey and G. Schmidt,  


3. E. J. Corey, E. P. Barette and P.A. Magriotis,  

4. F. Ciminale, M. Camporeale, R. Mello, L. Troisi and R. Curci,  

5. G. C. Sarma and M. K. Mahanti,  

6. K. Balasubramanian and V. Prathibha,  

7. S.A Chimatadar, S.B. Koujalagi and S.T. Nandibewoor,  

8. R.G. Panari and S.T. Nandibewoor,  

9. S.M. Desai, N.N. Halligudi and S.T. Nandibewoor,  
10. F. Feigl,
"Spot test in Organic Analysis", Elsevier, New York, (a) p.150 and
(b) p.132 (1975).

11. B.S. Furniss, A.J. Hannaford, V. Rogers, P.W.G. Smith and A.R.
Tatchell,
"Vogel's Text Book of Practical Organic Chemistry", ELBS, 4th

12. L. J. Bellamy,
"The IR Spectra of Complex Organic Molecules", 2nd Edn.Methuen
and Co., London, p. 425 (1958);
R.C. Aggarwal and A.K. Srivastava,

13. R.M. Silverstein, G. Clayton Bassler and Terence C. Morill,
"Spectrometric Identification of Organic compounds", 5th Edn, John

Tatchell,
"Vogel's Text Book of Practical Organic Chemistry", ELBS, 5th

15. D. R. Lide,
"CRC Handbook of Chemistry and Physics", 73rd edition, CRC
16. K. B. Wiberg,

"Oxidation in Organic Chemistry", Part A, Academic, New York, p. 69 (1965);

S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor,

17. P. Sykes,


18. B. P. Sinha and H. P. Mathur,

Z. Phys. Chem. (Leipzig), 246, 342 (1971);

S. Nadimpalli, R. Rallabandi and L. S. A. Dikshitulu,
Transition Met. Chem., 18, 510 (1993);

S. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor,

19. N.N. Halligudi, S.M. Desai and S.T. Nandibewoor,

Int. J. Chem. Kinet., 31, 789 (1999);

F.M. Moore and K.W. Hicks,

Inorg. Chem., 14, 413 (1975);

K.W. Hicks,


20. G.C. Sarma and M.K. Mahanti,


21. W. Watanabe and F.H. Westheimer,

J. Chem. Phys., 17, 61 (1949);
M. Rahman and J. Rocek,

22. S.A. Chimatadar, S.B. Koujalagi and S.T. Nandibewoor,

23. K. J. Laidler,

24. E.A. Moelwyn-Hughes,
"The Kinetics of Reaction in Solutions", Clarendon press, Oxford, (1947);
E.A. Moelwyn-Hughes,

25. K.J. Laidler and H. Eyring,
Ann. New York Acad. Sci., 39, 303 (1940);
K.J. Laidler and P.A. Landskroener,
Trans. Faraday Soc., 52, 200 (1957);
K.J. Laidler,

26. S. W. Benson,

27. A.A. Frost and R.G. Pearson,
28. S.G. Entelis and R.P. Tiger,

29. E. S. Amis,
   "Solvent Effects on Reaction Rates and Mechanism", Academic

30. L. N. Ferguson,

31. R. A. Abramovitch,
    Can. J. Chem., 36, 151 (1958);
    D. F. Martin, M. Shamma and W.C. Fernelius,