CHAPTER III

KINETIC AND MECHANISTIC STUDY OF QUINOLINIUMDICHROMATE (QDC) OXIDATION OF MERCURY(I) IN AQUEOUS SULPHURIC ACID IN PRESENCE OF MICRO AMOUNTS OF PALLADIUM(II) - AUTOCATALYSIS IN CATALYSIS

Nowadays the development of newer chromium(VI) reagents\textsuperscript{1-4} for the oxidation of organic substrates continues to be a subject of interest. The reagent employed in this investigation, quinoliniumdichromate, (QDC)(C\textsubscript{9}H\textsubscript{7}NH\textsuperscript{+})\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} is a useful and versatile oxidant that deserves further evaluation. A literature survey reveals that although several organic compounds are oxidised by quinoliniumdichromate and their mechanisms have been established, there are no reports on the oxidation of inorganic substrates by quinoliniumdichromate except in one case\textsuperscript{5}.

The oxidation of mercury(I) by different oxidants has been received attention\textsuperscript{6}. However the quinoliniumdichromate-mercury(I) reaction is immeasurably slow even though the redox potentials of the two couples, Hg(II)/Hg(I): +0.92V and quinoliniumdichromate i.e. Cr(VI)/Cr(III): + 1.33V, permits a reasonable reaction in acid solution. No reports of the reaction, catalysed or uncatalysed seem to be available in the literature. However, the reaction is facile in the presence of palladium(II) as a catalyst and in aqueous sulphuric acid, but does not take place to any reasonable extent in other acid media. Furthermore, the usual redox type of catalysis seems to be precluded in this case as the quinoliniumdichromate-palladium(II) reaction does not occur to any measurable extent, even at elevated temperatures (ca 90\textdegree C) in aqueous
acid. Indeed palladium redox chemistry seems to be essentially limited to organic compounds, only a few studies of redox reactions with inorganic species being available. Since the quinolinium dichromate-mercury(I) reaction is a non-complementary case, has different mechanistic possibilities. Most studies using palladium(II) as a catalyst have employed it in the form of palladium(II) chloride and the nature of its active form in such reactions remains obscure. We have investigated the effect of chloride as well as acid on palladium(II) catalysed oxidation of mercury(I) to determine the active species of catalyst and oxidant. The palladium(II) catalysed chromium(VI) oxidation of mercury(I) has been studied earlier. But the same reaction in presence of quinoline base follows different kinetic parameters and effects. Hence to explore the mechanism, the study of title reaction is undertaken, in this chapter.

**EXPERIMENTAL**

**Materials**

Reagent grade chemicals and double distilled water were used throughout this work. Quinolinium dichromate was prepared by the reported method as follows: Quinoline (12.9 g, 0.1 mol dm$^{-3}$) was slowly added to a cooled solution of chromium trioxide (10 g 0.1 mol dm$^{-3}$) in water (0.01 dm$^3$) with stirring. After 30 minutes the solution was diluted with acetone (0.04 dm$^3$) and cooled to -20°C. The orange solid, which separated out, was filtered, washed with acetone, dried in vacuum and then recrystallised from water. It was characterised by IR spectra and its melting point (160°C). The stock solution of quinolinium dichromate (QDC) (0.47633 g) of 0.01 mol dm$^{-3}$ in 0.1 dm$^3$ was prepared in water and standardised as follows: 0.1 dm$^3$ of boiled
water, 3 g of potassium iodide and 2 g of sodium hydrogen carbonate were taken into a 0.5 dm³ stoppered conical flask. The flask is shaken well until the salts are dissolved, and then, 0.06 dm³ of concentrated hydrochloric acid (AR) and ~0.025 dm³ of quinolinium dichromate solutions were added. The liberated iodine was titrated against standard sodium thiosulphate solution using starch as an indicator. The mercury(I) solution was obtained by dissolving an appropriate quantity of mercury(I) nitrate (Fluka) in 1 mol dm⁻³ perchloric acid (70%). The solution was standardised\textsuperscript{10(a)} by taking 0.005 dm³ of Hg(I) solution in a conical flask containing 0.01 dm³ of chloroform and ~0.005 dm³ of concentrated hydrochloric acid. (after adding hydrochloric acid the solution becomes milky white). The contents were titrated against standard potassium iodate solution (after adding potassium iodate solution, white milky disappears and reddish colour appears in the organic layer). Addition of potassium iodate solution was continued, till the organic layer becomes colourless. The palladium(II) solution was obtained by dissolving palladium chloride (Johnson Matthey) in 0.20 mol dm⁻³ hydrochloric acid (AR) and assaying for palladium(II) by complexometric titration with EDTA\textsuperscript{10(b)}. For some kinetic runs, chloride has to be absent and it is removed from the palladium(II) stock solution by precipitation with silver nitrate followed by repeated centrifugation. The resulting clear solution contains less than 1.0×10⁻⁶ mol dm⁻³ chloride and silver ions. Such extremely low concentrations of Ag⁺ and Cl⁻ ions were found to have no significant effect on the reaction. The required chloride concentration was maintained by adding sodium chloride. The chromium(III) solution was prepared by dissolving chromium(III) potassium sulphate (BDH, AR), Cr₂(SO₄)₃·K₂SO₄·24H₂O in water. The mercury(II)
solution was obtained by dissolving mercuric oxide, HgO (BDH) in 0.50 mol dm$^{-3}$ sulphuric acid. The ionic strength was kept constant with sodium sulphate. Use of sodium perchlorate was precluded since precipitation occurred under the reaction conditions.

**Kinetics**

Since the reaction was too fast to be monitored by the usual method, kinetic measurements were performed on a Hitachi 150-20 spectrophotometer (Tokyo-Japan) connected to a rapid kinetic accessory (HITECH SFA-12 unit). Kinetics were followed at 25 ± 0.1°C and $I = 1.60$ mol dm$^{-3}$. The reaction was initiated by mixing the pre-equilibrated reactant solutions, which also contained the known concentrations of sulphuric acid and sodium sulphate to give the required acidity and ionic strength. The reaction was followed under second order conditions, in equivalent concentrations ($a=b$), by measuring the absorbance of the quinoliniumdichromate in the reaction mixture at 440 nm. Application of Beer's law under the reaction conditions had been verified earlier between $1.0 \times 10^{-4}$ and $2.0 \times 10^{-3}$ mol dm$^{-3}$ of quinoliniumdichromate at 440 nm with ε resulting as $395 \pm 10$ dm$^{-3}$ mol$^{-1}$ cm$^{-1}$ (Fig. III(i)(p.72)). An example run is given in Table III(i)(p.73). The second order plots were non linear due to autocatalytic effect of the one of the products, chromium(III). The concentration versus time plots were found to be sinusoidal curves, which indicates the autocatalysis (Fig. III(iv)(p.82)). Hence the choice of initial rates over 5% completion of the reaction was made. The initial rates of the reaction were obtained from the slopes of concentrations versus time curves at the initial stages (5%) of the reaction by the plane mirror method. The initial rates were reproducible within ± 5%.
Fig. III(i)

Verification of Beer's law for quinolinium dichromate at 440 nm in 0.50 mol dm$^{-3}$ sulphuric acid at 25$^\circ$C
Palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium at 25°C

\[
[\text{QDC}] = 2.0 \times 10^{-4} ; \\
[\text{H}_2\text{SO}_4] = 0.50 ; \\
[\text{Pd(II)}] = 4.0 \times 10^{-6} \text{ (mol dm}^{-3}\text{)}
\]

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Optical density of QDC at 440 nm.</th>
<th>[QDC] \times 10^4 (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0810</td>
<td>2.051</td>
</tr>
<tr>
<td>10</td>
<td>0.0790</td>
<td>2.000</td>
</tr>
<tr>
<td>20</td>
<td>0.0743</td>
<td>1.880</td>
</tr>
<tr>
<td>30</td>
<td>0.0660</td>
<td>1.671</td>
</tr>
<tr>
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<td>0.0560</td>
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</tr>
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<td>0.0440</td>
<td>1.114</td>
</tr>
<tr>
<td>60</td>
<td>0.0329</td>
<td>0.835</td>
</tr>
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<td>0.532</td>
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<tr>
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<tr>
<td>90</td>
<td>0.0056</td>
<td>0.142</td>
</tr>
<tr>
<td>100</td>
<td>0.0205</td>
<td>0.052</td>
</tr>
</tbody>
</table>

\[
[\text{Hg(I)}] = 6.0 \times 10^{-4} ; \\
1 = 1.60 / \text{mol dm}^{-3}
\]

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Optical density of QDC at 440 nm.</th>
<th>[QDC] \times 10^4 (mol dm(^{-3}))</th>
</tr>
</thead>
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<tr>
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<td>0.0800</td>
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<tr>
<td>12</td>
<td>0.0740</td>
<td>1.873</td>
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<td>1.772</td>
</tr>
<tr>
<td>24</td>
<td>0.0630</td>
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<td>0.0540</td>
<td>1.367</td>
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<tr>
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<td>0.0450</td>
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<td>66</td>
<td>0.0032</td>
<td>0.080</td>
</tr>
<tr>
<td>72</td>
<td>0.0008</td>
<td>0.020</td>
</tr>
</tbody>
</table>
RESULTS

Stoichiometry

Different sets of concentrations of reactants and catalyst, palladium(II), in 0.50 mol dm\(^{-3}\) sulphuric acid at constant ionic strength, 1.60 mol dm\(^{-3}\), were kept over 8h at 25\(^{0}\)C in a closed container. When \([\text{QDC}] > [\text{mercury(I)}]\), the remaining quinoliniumdichromate was assayed by measuring the absorbance at 440 nm, whereas under the conditions \([\text{mercury(I)}] > [\text{QDC}]\), when quinoliniumdichromate had fully reacted, the remaining mercury(I) concentration was determined by titration with potassium iodate\(^{10(a)}\). The one of the products, chromium(III) concentration was determined by measuring the absorbance at 584 nm. The results showed that one mole of quinoliniumdichromate was required to oxidise three mole of mercury(I) as in equation 1 (Table III(ii) (p.75)). The catalyst concentration was unchanged at the end of the reaction as found by estimating it spectrophotometrically as the palladium(II) azide complex\(^{11}\).

\[
Pd(II) + \text{QDC} + 3 \text{Hg(I)} \rightarrow \text{Cr(III)} + 3 \text{Hg(II)}
\]

Reaction order

The order with respect to oxidant, reductant, catalyst and acid concentrations were found from log-log plots of initial rates versus concentrations at constant ionic strength, \(I = 1.60\) mol dm\(^{-3}\).

Effect of [quinoliniumdichromate]

The concentrations of quinoliniumdichromate were varied in the range of \(5.0 \times 10^{-5} - 5.0 \times 10^{-4}\) mol dm\(^{-3}\) at fixed concentrations of mercury(I), sulphuric acid,
Table III(ii)

Stoichiometry* of palladium(II) mediated oxidation of mercury(I) by quinoliniumdichromate in aqueous sulphuric acid medium at 25°C

\[
\begin{align*}
[Pd(II)] &= 8.0 \times 10^{-6} \; ; \quad [H_2SO_4] = 0.50 \; ; \quad I = 1.60 / \text{mol dm}^{-3} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>[QDC] x10^4</th>
<th>[Hg(I)] x10^3</th>
<th>[QDC] x10^4</th>
<th>[Hg(II)] x10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taken</td>
<td>Taken</td>
<td>Found</td>
<td>Found</td>
</tr>
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<td>1.00</td>
<td>1.80</td>
<td>0.00</td>
<td>0.29</td>
</tr>
<tr>
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<td>6.00</td>
<td>1.80</td>
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<tr>
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<td>0.60</td>
<td>0.36</td>
<td>0.59</td>
</tr>
<tr>
<td>6.00</td>
<td>0.30</td>
<td>0.48</td>
<td>0.28</td>
</tr>
</tbody>
</table>

*All concentrations are in mol dm\(^{-3}\)
palladium(II) and at ionic strength $I = 1.60 \text{ mol dm}^{-3}$ (Table III(iii)(p.77)). The order in quinolinium dichromate concentrations was determined by the slope of the plot of the log(initial rate) versus log(concn.) and was found to be unity (Fig. III(ii)(p.78)).

**Effect of [mercury(I)]**

The concentration of mercury(I) was varied in the range of $5.0 \times 10^{-5}$ and $6.0 \times 10^{-4} \text{ mol dm}^{-3}$ keeping the concentrations of the oxidant, acid and catalyst constant at a fixed ionic strength (Table III(iii)(p.77). The order with respect to mercury(I) concentration was determined by the slope of the plot of the log(initial rate) versus log(concn.) and was found to be less than unity, $ca.0.42$ (Fig. III(ii)(p.78).

**Effect of [palladium(II)]**

At constant reactant concentrations ($3[\text{QDC}] = [\text{Hg(I)}] = 6.0 \times 10^{-4} \text{ mol dm}^{-3}$), constant acidity and ionic strength ($[\text{H}_2\text{SO}_4] = 0.50 \text{ mol dm}^{-3}$ and $I = 1.60 \text{ mol dm}^{-3}$), the palladium(II) concentration was varied between $1.0 \times 10^{-6}$ and $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ and the order was found to be unity (Table III(iii)(p.77); Fig. III(iii)(p.81).

**Effect of initially added products**

(i) **Effect of [chromium(III)]**

The initially added product, chromium(III) was studied in the $5.0 \times 10^{-5} - 5.0 \times 10^{-4} \text{ mol dm}^{-3}$ concentration range while keeping the reactant concentrations and all other conditions constant. It was observed that added chromium(III) enhances the reaction rate with an order of less than unity ($0.73$) (Table III(iv)(p.80); Fig. III(iii)(p.81). This result indicates the autocatalysis by the product, chromium(III), which is also evident from the concentration of quinolinium dichromate versus time plots (sinusoidal curves) (Fig. III(iv)(p.82)) and a linear plot of (Initial rate) versus
Table III(iii)

Effect of quinolinium dichromate, mercury(I) and palladium(II) concentrations on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium at 25°C

\[ [\text{H}_2\text{SO}_4] = 0.50 \text{ mol dm}^{-3} \]
\[ I = 1.60 \text{ mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>[QDC] (\times 10^4) (mol dm(^{-3}))</th>
<th>[Hg(I)] (\times 10^4) (mol dm(^{-3}))</th>
<th>[Pd(II)] (\times 10^6) (mol dm(^{-3}))</th>
<th>Initial rate (\times 10^7) (mol dm(^{-3})s(^{-1}))</th>
</tr>
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<tr>
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</tr>
<tr>
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<td>6.0</td>
<td>8.0</td>
<td>3.45</td>
</tr>
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<td>6.0</td>
<td>8.0</td>
<td>3.45</td>
</tr>
<tr>
<td>2.0</td>
<td>6.0</td>
<td>10.0</td>
<td>4.29</td>
</tr>
</tbody>
</table>
Fig. III(ii)

Order with respect to quinoliniumdichromate and mercury(I) concentrations on the palladium(II) mediated oxidation of mercury(I) by quinoliniumdichromate in aqueous sulphuric acid medium at 25°C

(Conditions as in Table III(iii)(p.77))
(rate)_{cal} for chromium(III) variations (Fig. III(iv)(inset)(p.82)). However in case of palladium(II) catalysed chromium(VI) oxidation of mercury(I) reaction\(^9\) such autocatalysis was not observed.

(ii) Effect of mercury(II)

The initially added product, mercury(II), was studied in the range of \(1.0 \times 10^{-4} - 5.0 \times 10^{-4}\) mol dm\(^{-3}\) concentration while keeping the reactant concentrations and all other conditions constant. It was observed that the added mercury(II), does not change the rate appreciably (Table III(iv)(p.80)).

Effect of varying acidity

At constant reactant concentrations and other constant conditions the sulphuric acid concentration was varied between 0.20 and 1.0 mol dm\(^{-3}\) and the initial rate increases with increase in the concentration of H\(^+\) ion. The H\(^+\) ion concentrations were calculated as in ChapterII, p.38, from the added sulphuric acid concentration and the known equilibrium constant of the acid-sulphate equilibrium\(^{12}\) and the values are given in Table III(v)(p.83). The order with respect to H\(^+\) ion concentration was determined by the slope of the plot of the log(Initial rate) versus log(concn.) and the order was found to be less than unity, \(ca.0.51\) (Fig. III(v)(p.87)).

Effect of added chloride

For this purpose palladium(II) solutions, which did not contain any chloride, were used. The initial rate increased with increase in Cl\(^-\) ion concentration (Table III(vi)(p.86)). This is ascribable to the formation of palladium(II) chloride complexes. The order in Cl\(^-\) ion concentration under the experimental conditions was close to unity \(ca.0.91\) (Fig. III(v)(p.87)). Palladium(II) is known to form chloride
Table III(iv)

Effect of initially added products, chromium(III) and mercury(II) concentrations on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in an aqueous sulphuric acid medium at 25°C

\[ [QDC] = 2.0 \times 10^{-4} ; \]
\[ [Pd(II)] = 8.0 \times 10^{-6} ; \]
\[ I = 1.60 / \text{mol dm}^{-3} \]
\[ [Hg(I)] = 6.0 \times 10^{-4} ; \]
\[ [H_2SO_4] = 0.50 ; \]

\[
\begin{array}{cccc}
[Cr(III)] \times 10^4 & \text{Initial rate} \times 10^6 & [Hg(II)] \times 10^4 & \text{Initial rate} \times 10^7 \\
\text{(mol dm}^{-3} \text{)} & \text{(mol dm}^{-3} \text{ s}^{-1}) & \text{(mol dm}^{-3} \text{)} & \text{(mol dm}^{-3} \text{ s}^{-1}) \\
\hline
\text{Exptl} & \text{Cacl} & \text{Exptl} & \text{Cacl} \\
0.50 & 1.25 & 1.25 & 1.0 & 3.38 \\
1.0 & 2.31 & 2.38 & 2.0 & 3.48 \\
2.0 & 4.15 & 4.33 & 3.0 & 3.51 \\
3.0 & 5.77 & 5.95 & 4.0 & 3.41 \\
4.0 & 7.63 & 7.34 & 5.0 & 3.43 \\
5.0 & 8.95 & 8.53 & & \\
\end{array}
\]
Order with respect to palladium(II) and chromium(III) concentrations on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium at 25°C

(Conditions as in Table III(iii)(p.77) and Table III(iv)(p.80))
Effect of initially added product chromium(III) concentrations on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium at 25°C

(Conditions as in Table III(i)(p.73))

(a) [Pd(II)] = 4.0 \times 10^{-6} ; \quad (b) [Pd(II)] = 8.0 \times 10^{-6} / mol dm^{-3}

Inset: (Conditions as in Table III(iv)(p.80))

\[ \text{*(rate)}_{\text{calc}} = [\text{QDC}] [\text{Pd(II)}] [\text{Hg(I)}]^{0.42} [\text{H}^+]^{0.51} [\text{Cr(III)}]^{0.73} \]
Table III(v)

Effect of sulphuric acid concentration on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium at 25°C

\[
\begin{align*}
[\text{QDC}] &= 2.0 \times 10^{-4} ; \\
[\text{Hg(I)}] &= 6.0 \times 10^{-4} ; \\
[\text{Pd(II)}] &= 8.0 \times 10^{-6} ; \\
I &= 3.70 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>[H$_2$SO$_4$] (mol dm$^{-3}$)</th>
<th>[H$^+$] (mol dm$^{-3}$)</th>
<th>Initial rate (\times 10^7) (mol dm$^{-3}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>5.21</td>
</tr>
<tr>
<td>1.0</td>
<td>0.911</td>
<td>6.45</td>
</tr>
</tbody>
</table>
complexes of formula Pd(Cl)$_{n-2}$, $n$ having values 1 to 4, the cumulative stability constants $\beta_1$ to $\beta_4$ being $1.0 \times 10^4$, $3.1 \times 10^7$, $5.4 \times 10^9$ and $1.3 \times 10^{11}$ respectively is shown in the following equilibria.

$$
Pd^{2+} + Cl^{-} \rightleftharpoons PdCl^{+} \quad K_1 \quad (2)
$$

$$
PdCl^{+} + Cl^{-} \rightleftharpoons PdCl_2 \quad K_2 \quad (3)
$$

$$
PdCl_2^{-} + Cl^{-} \rightleftharpoons PdCl_3^{2-} \quad K_3 \quad (4)
$$

$$
PdCl_3^{2-} + Cl^{-} \rightleftharpoons PdCl_4^{3-} \quad K_4 \quad (5)
$$

The approximate concentrations of such species may be calculated from equation (6), using the concentrations of the dissolved palladium(II) and chloride taking into account of their competing equilibria.

$$
[Pd(II)]_t = [Pd(II)]_r \{1 + \beta_1[Cl^{-}] + \beta_2[Cl^{-}]^2 + \beta_3[Cl^{-}]^3 + \beta_4[Cl^{-}]^4\} \quad (6)
$$

(Subscripts 't' and 'r' stands for total and free respectively)

For example, a sample calculation of different palladium(II) species is given below. The values of $\alpha$ shows the fractions of the different chloride species of palladium(II) of the total palladium(II).

Here.

$$
[Pd(II)]_t = 8.0 \times 10^{-6} \quad \text{and} \quad [Cl^{-}] = 0.5 \times 10^{-5} \text{mol dm}^{-3}
$$

Therefore,

$$
[Pd(II)]_t = 8.0 \times 10^{-6} \nonumber \\
= [Pd(II)]_r \{1 + (1.0 \times 10^{-4} \times 0.5 \times 10^{-5}) + (3.1 \times 10^{7} \times (0.5 \times 10^{-5})^2) \nonumber \\
+ (5.4 \times 10^{9} \times (0.5 \times 10^{-5})^3) + (1.3 \times 10^{11} \times (0.5 \times 10^{-5})^4)\} \nonumber \\
= [Pd(II)]_r \{1 + 0.05 + 7.75 \times 10^{-4} + 6.75 \times 10^{-7} + 8.125 \times 10^{-11}\}
$$
\[
[Pd(II)]_f = 8.0 \times 10^{-6}/1.0507756 = 7.6134 \times 10^{-6} \quad \alpha_0 = 7.6134 \times 10^{-6}/8.0 \times 10^{-6} = 0.95168
\]

Similarly,
\[
[PdCl^+] = 7.6134 \times 10^{-6} \times 0.05 = 3.8067 \times 10^{-7} \quad \alpha_1 = 0.047584
\]
\[
[PdCl_2] = 7.6134 \times 10^{-6} \times 7.75 \times 10^{-4} = 5.9004 \times 10^{-9} \quad \alpha_2 = 7.7375 \times 10^{-4}
\]
\[
[PdCl_3] = 7.6134 \times 10^{-6} \times 6.75 \times 10^{-7} = 5.13706 \times 10^{-12} \quad \alpha_3 = 6.426 \times 10^{-7}
\]
\[
[PdCl_4^-] = 7.6134 \times 10^{-6} \times 8.125 \times 10^{-11} = 6.1859 \times 10^{-16} \quad \alpha_4 = 7.7325 \times 10^{-11}
\]

Variation in the concentrations of such species with increase in the Cl\(^-\) ion concentration is given in Table III(vi)(p.86) along with the initial rates of the respective catalysed reactions, and it is found that there is a approximately parallelism only between rates and [PdCl\(^+\)] (Fig. III(vi)(p.88)). Rates of reaction with 30 different sets of concentrations of quinoliniumdichromate, mercury(I), palladium(II) and H\(^+\) ion at constant ionic strength were found to obey the rate law (7) as shown in Fig. III(vii)(p.89).

\[
\text{Rate } \propto [QDC] [Pd(II)] [Hg(I)]^{0.42} [H^+]^{0.51} \quad (7)
\]

**Effect of dielectric constant and ionic strength**

When the acetic acid content (v/v) in the reaction medium was increased, keeping the reactant concentrations and other conditions constant, the reaction rate increases. Since the dielectric constants of aqueous acetic acid are not available in the
Table III(vi)

Variation of different Pd(II) species* with chloride concentrations on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium at 25°C

\[
\begin{align*}
[QDC] &= 2.0 \times 10^{-4} ; \\
[Hg(I)] &= 6.0 \times 10^{-4} ; \\
[Pd(II)] &= 8.0 \times 10^{-6} ; \\
[H_2SO_4] &= 0.50 ; \\
I &= 1.60 / \text{mol dm}^3
\end{align*}
\]

<table>
<thead>
<tr>
<th>[Cl(^{-})] \times 10^5 (mol dm(^{-3}))</th>
<th>(\alpha_0)</th>
<th>(10^2 \alpha_1)</th>
<th>(10^4 \alpha_2)</th>
<th>(10^6 \alpha_3)</th>
<th>(10^4 \alpha_4)</th>
<th>Initial rate \times 10^7 (mol dm(^{-3}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.00</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.09</td>
</tr>
<tr>
<td>0.5</td>
<td>0.95</td>
<td>4.80</td>
<td>0.077</td>
<td>0.064</td>
<td>0.0008</td>
<td>0.52</td>
</tr>
<tr>
<td>1.0</td>
<td>0.91</td>
<td>9.10</td>
<td>0.280</td>
<td>0.049</td>
<td>0.0126</td>
<td>1.17</td>
</tr>
<tr>
<td>1.5</td>
<td>0.86</td>
<td>13.0</td>
<td>0.600</td>
<td>0.158</td>
<td>0.0569</td>
<td>2.36</td>
</tr>
<tr>
<td>2.5</td>
<td>0.79</td>
<td>19.7</td>
<td>1.530</td>
<td>0.665</td>
<td>0.4003</td>
<td>3.82</td>
</tr>
<tr>
<td>4.0</td>
<td>0.69</td>
<td>26.5</td>
<td>3.420</td>
<td>2.380</td>
<td>2.3000</td>
<td>5.75</td>
</tr>
<tr>
<td>5.0</td>
<td>0.63</td>
<td>31.7</td>
<td>4.910</td>
<td>4.280</td>
<td>5.148</td>
<td>6.50</td>
</tr>
<tr>
<td>6.0</td>
<td>0.58</td>
<td>35.0</td>
<td>6.520</td>
<td>6.810</td>
<td>9.837</td>
<td>7.98</td>
</tr>
<tr>
<td>8.0</td>
<td>0.50</td>
<td>40.0</td>
<td>9.910</td>
<td>13.80</td>
<td>26.61</td>
<td>9.83</td>
</tr>
<tr>
<td>10.0</td>
<td>0.43</td>
<td>43.0</td>
<td>13.40</td>
<td>23.30</td>
<td>56.15</td>
<td>11.2</td>
</tr>
<tr>
<td>15.0</td>
<td>0.31</td>
<td>46.7</td>
<td>21.70</td>
<td>56.7</td>
<td>204.7</td>
<td>12.5</td>
</tr>
</tbody>
</table>

*\(\alpha_0, \alpha_1, \alpha_2, \alpha_3\) and \(\alpha_4\) are the fractions of total Pd(II) of the species Pd\(^{2+}\), PdCl\(^+\), PdCl\(_2\)\(^{-}\), PdCl\(_3\)\(^{-}\) and PdCl\(_4\)\(^{-2}\) respectively. The stability constants of the different Pd(II) complexes are from reference 15.
Fig. III(v)

Order with respect to acid and chloride concentrations on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium at 25°C

(Conditions as in Table III(v) (p.83) and Table III(vi) (p.86))
Fig. III(vi)

Effect of chloride concentrations on different palladium(II) species and also on the rates of reaction on the palladium(II) mediated oxidation of mercury(I) by quinoliniumdichromate in aqueous sulphuric acid medium at 25°C

(Conditions as in Table III(vi)(p.86))
Fig. III(vii)

Plot of the initial rate of the QDC-Hg(I) reaction versus the product of reactant concentrations at 25°C and $I = 1.60 \text{ mol dm}^{-3}$
literature, similar to that of Chapter II, p.45, they were computed from the values for pure liquids\textsuperscript{15} and are given in Table III(vii)(p.91). No reaction of the solvent with the oxidant occurred under the experimental conditions employed. A plot of log(Initial rate) versus 1/D is linear with positive slope as in Fig. III(viii)(p.92). Variation of ionic strength between 1.6 and 4.0 mol dm\textsuperscript{-3}, using sodium sulphate, caused a decrease in the rate of reaction and the results are given in Table III(vii)(p.91). A plot of log(Initial rate) versus $I^{1/2}$ is linear with negative slope (Fig. III(viii)(p.92)).

**Effect of added ions**

In this case, the palladium(II) used contain chloride concentrations less than $1.0 \times 10^{-6}$ mol dm\textsuperscript{-3} as stated in the experimental section. When the reactant concentrations and other conditions were kept constant, ions such as Cu$^{2+}$, Na$^{+}$ and NO$_3^-$ did not have any significant effect on the rate of the reaction, whereas added Mn$^{2+}$ decreases the rate.

**Effect of temperature**

The rate of reaction was measured at different temperatures under the conditions of $3[QDC] = [Hg(I)] = 6.0 \times 10^{-4}$ mol dm\textsuperscript{-3}, constant acidity, $[H_2SO_4] = 0.50$ mol dm\textsuperscript{-3} and ionic strength, $I = 1.60$ mol dm\textsuperscript{-3}. The rate constants ($k_i$) of the slow step of the Scheme I were obtained from the intercepts of $[QDC][Pd(II)] / \text{(Initial rate)}$ versus $1/[Hg(I)]$ plots (Fig. III(xii)(p.103)) at four different temperatures by employing the values of $K_5$. The activation parameters for the rate determining step were obtained, by the least-square method as in Chapter II, p.48, from a plot of log $k_i(y_{\text{cal}})$ versus $1/T$ (Table III(viii a)(p.94); Fig. III(ix)(p.95)). The values of $k_i$, which lead to the activation parameters are given in Table III(viii b)(p.94).
Table III(vii)

Effect of variation of dielectric constant (D) and ionic strength (I) on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in an aqueous sulphuric acid medium at 25°C.

\[
\begin{align*}
[\text{QDC}] &= 2.0 \times 10^{-4} ; \\
[\text{Hg(I)}] &= 6.0 \times 10^{-4} ; \\
[\text{Pd(II)}] &= 8.0 \times 10^{-6} ; \\
[\text{H}_2\text{SO}_4] &= 0.50 ; \\
I &= 1.60 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>% of acetic acid - water (v/v)</th>
<th>D x 10^3</th>
<th>1/D</th>
<th>Initial rate ( \times 10^7 ) (mol dm(^{-3}) s(^{-1}))</th>
<th>I</th>
<th>(\sqrt{I})</th>
<th>Initial rate ( \times 10^7 ) (mol dm(^{-3}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>78.5</td>
<td>12.74</td>
<td>2.40</td>
<td>1.6</td>
<td>1.265</td>
<td>3.45</td>
</tr>
<tr>
<td>5</td>
<td>74.9</td>
<td>13.35</td>
<td>2.65</td>
<td>2.0</td>
<td>1.414</td>
<td>2.83</td>
</tr>
<tr>
<td>10</td>
<td>71.3</td>
<td>14.03</td>
<td>3.10</td>
<td>2.5</td>
<td>1.581</td>
<td>2.30</td>
</tr>
<tr>
<td>15</td>
<td>67.65</td>
<td>14.78</td>
<td>3.65</td>
<td>3.0</td>
<td>1.732</td>
<td>2.03</td>
</tr>
<tr>
<td>20</td>
<td>64.10</td>
<td>15.60</td>
<td>4.84</td>
<td>3.5</td>
<td>1.870</td>
<td>1.70</td>
</tr>
<tr>
<td>25</td>
<td>60.41</td>
<td>16.55</td>
<td>6.44</td>
<td>4.0</td>
<td>2.000</td>
<td>1.50</td>
</tr>
</tbody>
</table>

91
Effect of variation of dielectric constant (D) and ionic strength (I) on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in an aqueous sulphuric acid medium at 25°C

(Conditions as in Table III(vii)(p.91))
Thermodynamic quantities of first step of Scheme I are evaluated from the slope of the plot of \([QDC][Pd(II)]/(Initial\ rate)\) versus \(1/[H^+]\) at different temperatures (Fig. III(xii)(p.103)). The values of \(K_5\) at 298, 303, 308 and 313 K are 4.24, 4.65, 4.91 and 5.28 dm\(^3\) mol\(^{-1}\) respectively. The van't Hoff plot was drawn for the variation of \(K_5\) with temperature (log \(K_5\) versus \(1/T\); \(r \geq 0.996, \sigma \leq 0.023\)) (Fig. III(x)(p.97)). The values of thermodynamic quantities are listed in Table III(ix)(p.96). A comparison of these values with those values obtained for the slow step shows that the reaction before the rate determining step is fairly rapid.

**DISCUSSION**

The oxidation of mercury(I) by quinoliniumdichromate is not observed in the absence of palladium(II) and, in the presence of latter, occurs with measurable speed only in aqueous sulphuric acid. Furthermore, since quinoliniumdichromate does not oxidise palladium(II), even at the higher temperature (ca.90°C) of the aqueous sulphuric acid, it is unlikely that any higher oxidation state such as palladium(III) or palladium(IV) are involved in the reaction. In the presence of perchloric acid and nitric acid, the palladium(II) catalyst is inefficient, possibly due to active species of palladium as palladium chloride complexes, which are not possible in such media. Hence the study was undertaken in sulphuric acid and chloride medium. The reaction between mercury(I) and quinoliniumdichromate in aqueous sulphuric acid in the presence of palladium(II) has a stoichiometry of 1:3 with an apparent less than unit order in mercury(I) and \(H^+\) ion and first order dependence on quinoliniumdichromate, palladium(II) and \(Cl^-\) ion. It was observed that, one of the products, chromium(III) increases the reaction rate, whereas another product mercury(II) does not affect the
Table III(viii)

(a) Effect of variation of temperature with respect to slow step of Scheme 1 on the palladium(II) mediated oxidation of mercury(I) by quinoliniumdichromate in aqueous sulphuric acid medium

\[ [\text{QDC}] = 2.0 \times 10^{-4} \text{; } [\text{Hg(I)}] = 6.0 \times 10^{-4} \text{; } [\text{Pd(II)}] = 8.0 \times 10^{-6} \text{; } [\text{H}_2\text{SO}_4] = 0.50 \text{; } I = 1.60 \text{ / mol dm}^{-3} \]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(1/T \times 10^{3}) (K(^{-1})x)</th>
<th>(k_1 \times 10^2) (dm(^3) mol(^{-1})s(^{-1}))</th>
<th>log(k_1)</th>
<th>log(k_1) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>3.3560</td>
<td>3.88</td>
<td>-1.4112</td>
<td>-1.4202</td>
</tr>
<tr>
<td>303</td>
<td>3.3000</td>
<td>5.02</td>
<td>-1.2993</td>
<td>-1.2864</td>
</tr>
<tr>
<td>308</td>
<td>3.2470</td>
<td>6.94</td>
<td>-1.1586</td>
<td>-1.1569</td>
</tr>
<tr>
<td>313</td>
<td>3.1950</td>
<td>9.42</td>
<td>-1.0259</td>
<td>-1.0316</td>
</tr>
</tbody>
</table>

* Calculated

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

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a)</td>
<td>(23 \pm 1 \text{ kJ mol}^{-1})</td>
</tr>
<tr>
<td>(\Delta H^#)</td>
<td>(21 \pm 1 \text{ kJ mol}^{-1})</td>
</tr>
<tr>
<td>(\Delta S^#)</td>
<td>(-126 \pm 10 \text{ JK}^{-1} \text{ mol}^{-1})</td>
</tr>
<tr>
<td>(\Delta G^#)</td>
<td>(58 \pm 5 \text{ kJ mol}^{-1})</td>
</tr>
<tr>
<td>log(A)</td>
<td>(6.7 \pm 0.5).</td>
</tr>
</tbody>
</table>
Effect of variation of temperature on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium

(Conditions as in Table III(viii)(p.94))
Table III(ix)

(a) Effect of variation of temperature on the equilibrium constant with respect to slow step of Scheme 1 on the palladium(II) mediated oxidation of mercury(I) by quinoliniumdichromate in aqueous sulphuric acid medium

\[
\begin{align*}
[\text{QDC}] &= 2.0 \times 10^{-4} ; \\
[\text{Hg(I)}] &= 6.0 \times 10^{-4} ; \\
[\text{Pd(II)}] &= 8.0 \times 10^{-6} ; \\
[\text{H}_2\text{SO}_4] &= 0.50 ; \\
I &= 1.60 / \text{mol dm}^{-3}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(1/T \times 10^3)</th>
<th>(K_5)</th>
<th>(\log K_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>3.3560</td>
<td>4.24</td>
<td>0.6274</td>
</tr>
<tr>
<td>303</td>
<td>3.3000</td>
<td>4.65</td>
<td>0.6675</td>
</tr>
<tr>
<td>308</td>
<td>3.2470</td>
<td>4.91</td>
<td>0.6911</td>
</tr>
<tr>
<td>313</td>
<td>3.1950</td>
<td>5.28</td>
<td>0.7226</td>
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</tbody>
</table>

(b) Thermodynamic quantities with respect to slow step of Scheme 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H)</td>
<td>(11.0 \pm 0.5 \text{ kJ mol}^{-1})</td>
</tr>
<tr>
<td>(\Delta S)</td>
<td>(49.0 \pm 2.0 \text{ JK}^{-1} \text{ mol}^{-1})</td>
</tr>
<tr>
<td>(\Delta G)</td>
<td>(-4.0 \pm 0.2 \text{ kJ mol}^{-1})</td>
</tr>
</tbody>
</table>
van't Hoff plot for the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in aqueous sulphuric acid medium at 25°C
rate of the reaction. However in the palladium(II) catalysed chromium(VI) oxidation of mercury(I) is apparent less than unit order in mercury(I) and Cl⁻ ion; first order dependence on Cr(VI), palladium(II) and H⁺ ion concentrations were obtained. In this study, the initially added products have no effect on the rate of the reaction. The different behaviour in the palladium(II) catalysed oxidation of mercury(I) by chromium(VI) and quinolinium dichromate might be due to the presence of quinolinium moiety. There are reports that the reactivities of substituted pyridine, quinoline and isoquinoline complexes of chromium(VI) resembles one another. Such complexes show no dimerisation or polymerisation in solutions. In aqueous solution, quinolinium dichromate and chromium(VI) behave in different manner. Quinoline acts as an electron donor. Due to this considerable quantities of quinolinium dichromate is reduced to chromium(III). Thus chromium(III) formed immediately forms a weak complex with quinolinium dichromate, which is responsible for autocatalysis.

It is well known that in aqueous sulphuric acid solution, quinolinium dichromate exists mainly in the form of acid chromate ion, HCrO₄⁻. The results suggest that, mercury(I) reacts with palladium(II) to give a complex, which then reacts with HCrO₄⁻ in a rate determining step to give the mercury(II) product, the intermediates chromium(V) and palladium(I) being generated. The intermediate chromium(V) reacts in further fast steps to give the products and palladium(II) being regenerated. The results are accommodated in Scheme 1.
\[
\begin{align*}
QDC + H^+ & \rightleftharpoons HCrO_4^- + Q \text{(quinoline)} & K_5 \\
Hg(1) + Pd(II) & \rightleftharpoons \text{Complex (C)} & K_6 \\
C_1 + HCrO_4^- & \overset{\text{slow}}{\rightarrow} 2 \text{Hg(II)} + Cr(V) + Pd(I) & k_1 \\
Cr(V) + Pd(I) & \overset{\text{fast}}{\rightarrow} Cr(IV) + Pd(II) \\
\text{Hg(1) + Cr(IV)} & \overset{\text{fast}}{\rightarrow} \text{Hg(II) + Cr(III)}
\end{align*}
\]

Scheme 1

The evidence for complex formation was obtained from Uv-visible spectrum of both palladium(II) and mercury(I)-palladium(II) mixtures, in which a hypsochromic shift of palladium(II) from 320 to 300 nm and hyperchromicity at 300 nm, occurred (Fig. III(xi)(p.100)). This was also evident from the Michaelis-Menten plot (Fig. III(xii)(p.103)) and such complex formation between substrate and catalyst has also been observed in other studies.\textsuperscript{19} Since oxidation of mercury(I) by quinoliniumdichromate is a non-complementary reaction, it may occur by the intervention of reactive chromium(V) and chromium(IV) species. The intervention of chromium(V) is evident from the induction experiment with iodide.\textsuperscript{18} The induced oxidation of iodide yields two equivalent of iodine for each equivalent of the inductor oxidised. In any induced oxidation the inductor 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. The intervention of chromium(IV) is evident from the progressive rate decrease in the presence of...
Fig. III(xi)

Uv-visible spectra showing the formation of complex between palladium(II) and mercury(I) on the palladium(II) mediated oxidation of mercury(I) by quinolinium dichromate in an aqueous sulphuric acid medium at 25°C

\[ [\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3} \text{ in all spectras} \]

(I) Spectra of \([\text{Hg(I)}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3} \)

(II) Spectra of \([\text{Pd(II)}] = 2.0 \times 10^{-4} \text{ mol dm}^{-3} \)

(III) Spectra of mixture of \([\text{Hg(I)}] = 2.0 \times 10^{-4} \text{ and } [\text{Pd(II)}] = 0.5 \times 10^{-4} \text{ / mol dm}^{-3} \)

(IV) Spectra of mixture of \([\text{Hg(I)}] = 2.0 \times 10^{-4} \text{ and } [\text{Pd(II)}] = 1.0 \times 10^{-4} \text{ / mol dm}^{-3} \)

(V) Spectra of mixture of \([\text{Hg(I)}] = 2.0 \times 10^{-4} \text{ and } [\text{Pd(II)}] = 2.0 \times 10^{-4} \text{ / mol dm}^{-3} \)

(VI) Spectra of mixture of \([\text{Hg(I)}] = 2.0 \times 10^{-4} \text{ and } [\text{Pd(II)}] = 3.0 \times 10^{-4} \text{ / mol dm}^{-3} \)

(VII) Spectra of mixture of \([\text{Hg(I)}] = 2.0 \times 10^{-4} \text{ and } [\text{Pd(II)}] = 4.0 \times 10^{-4} \text{ / mol dm}^{-3} \)
increasing amounts of added manganese(II), the decrease reaching a limit of about 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\(^{20}\).

From Scheme 1, including the observed orders in mercury(I), quinolinium dichromate and palladium(II), the rate law may be derived as follows:

\[
\text{Rate} = - \frac{d[QDC]}{dt} = k_1 [C_1] [QDC] \quad (8)
\]

\[
\text{Rate} = k_1 K_5 K_6 [QDC] [Hg(I)] [Pd(II)] [H^+] \quad (9)
\]

\[
[QDC]_t = [QDC]_f + [HCrO_4^-]
\]

\[
= [QDC]_f + K_5 [QDC]_f [H^+]
\]

\[
= [QDC]_f (1 + K_5 [H^+])
\]

Therefore,

\[
[QDC]_f = \frac{[QDC]_t}{(1 + K_5 [H^+]}) \quad (10)
\]

In the same way,

\[
[Hg(I)]_t = [Hg(I)]_f + [C_1]
\]

\[
= [Hg(I)]_f + K_6 [Hg(I)]_f [Pd(II)]
\]

\[
= [Hg(I)]_f (1 + K_6 [Pd(II)])
\]

\[
[Hg(I)]_f = \frac{[Hg(I)]_t}{(1 + K_6 [Pd(II)]}) \quad (11)
\]

Similarly,

\[
[Pd(II)]_t = [Pd(II)]_f / (1 + K_6 [Hg(I)]}) \quad (12)
\]

and

\[
[H^+]_t = \frac{[H^+]}{(1 + K_5 [QDC])} \quad (13)
\]

Substituting for [QDC], [Hg(I)], [Pd(II)] and [H\(^+\)] from equations (10) (11), (12) and (13) respectively in equation (9) leads to equation (14)

\[
\frac{k_1 K_5 K_6 [QDC] [Hg_2^{2+}] [Pd(II)] [H^+]}{((1 + K_5 [H^+])(1 + K_6 [Pd(II)])(1 + K_6 [Hg(I)])(1 + K_5 [QDC]))}
\]

\[\text{Rate} = \quad (14)\]
In view of low concentrations of palladium(II) used and unit order in its concentration, the term \((1 + K_6[Pd(II)])\) approximates to unity. Similarly, in view of low concentration of quinolinium dichromate used and unit order in its concentration, the term \((1 + K_5[QDC])\) approximates to unity.

Equation (14) leads the following rate law (15),

\[
\text{Rate} = \frac{-d[QDC]}{dt} = \frac{k_1K_5K_6[QDC][Hg(I)][Pd(II)][H^+]}{1 + K_5[H^+] + K_6[Hg(I)] + K_5K_6[Hg(I)][H^+]} \tag{15}
\]

Rate law (15) accommodates all the experimental results except autocatalytic effect of chromium(III). The rate law (15) may be rearranged to equation (16), which is suitable for verification.

\[
\frac{[QDC][Pd(II)]}{\text{Rate}} = \frac{1}{k_1K_5[H^+]} + \frac{1}{k_1K_6[Hg(I)]} + \frac{1}{k_1K_5K_6[Hg(I)][H^+]} + \frac{1}{k_1} \tag{16}
\]

According to equation (16), the plot of the LHS versus \(1/[H^+]\) and LHS versus \(1/[Hg(I)]\) should be linear, and are found to be so (Fig. III(xii)(p.103)). The slopes and the intercepts of such plots leads to the values of \(k_1, K_5\) and \(K_6\) as \((3.88 \pm 0.15) \times 10^2\) \(\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}\), \(4.24 \pm 0.21 \text{ dm}^3\text{ mol}^{-1}\) and \((8.23 \pm 0.38) \times 10^3\) \(\text{dm}^3\text{ mol}^{-1}\) respectively. The modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction. The active species involved in the mechanism can be understood as follows: In aqueous sulphuric acid media, quinolinium dichromate is known to exist mainly as \(HCrO_4^-\). Mercury(I) has been shown to exist as the complex \([Hg_2(SO_4)HSO_4]^-\). Oxidation of mercury(I) is greatly facilitated in sulphuric acid solution and the reason may be that mercury(I) sulphate complexes are actively
Verification of rate law (15) in the form of (16)

(Conditions as in Table III(iii)(p.77) and Table III(v)(p.83))
involved. The variation of rate with chloride ion was shown, in the Result Section, to parallel the trend of variation of concentration of the PdCl\(^+\) species with chloride (Table III(vi)(p.86); Fig. III(vi)(p.88). Hence PdCl\(^+\) is considered as the most active palladium(II) species. The mechanism of Scheme 1 will therefore involve the species as shown in Scheme 2

\[
\begin{align*}
QDC + H^+ & \rightleftharpoons HCrO_4^- + Q(\text{quinoline}) & K_5 \\
Hg_2^{2+} + SO_4^{2-} + HSO_4^- & \rightleftharpoons [Hg_2(SO_4)HSO_4]^- & K_7 \\
Pd^{2+} + Cl^- & \rightleftharpoons PdCl^+ & K_1 \\
[Hg_2(SO_4)HSO_4]^- + PdCl^+ & \rightleftharpoons \text{Complex (C}_2\text{)} & K_6 \\
C_2 + HCrO_4^- & \xrightarrow{\text{slow}} 2\text{HgSO}_4 + PdCl + Cr(V) & k_1 \\
PdCl + Cr(V) & \xrightarrow{\text{fast}} PdCl^+ + Cr(IV) & \\
Hg^+ + Cr(IV) & \xrightarrow{\text{fast}} Hg^{2+} + Cr(III) & \\
\end{align*}
\]

Scheme 2

The probable structure of the complex (C\(_2\)) is as follows.

\[
\begin{array}{c}
\text{Hg} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{Pd} \\
\text{OH}
\end{array}
\begin{array}{c}
\text{S} \\
\text{O}
\end{array}
\begin{array}{c}
\text{S} \\
\text{O}
\end{array}
\begin{array}{c}
\text{S} \\
\text{O}
\end{array}
\]

Therefore, in terms of active species, rate law (16) takes the form (17)

\[
\text{Rate} = \frac{k_1 K_5 K_6 [HCrO_4^-] [Hg_2(SO_4)HSO_4]^- [PdCl^+] [H^+]}{1 + K_5 [H^+] + K_6 [Hg_2(SO_4)HSO_4]^- + K_5 K_6 [Hg_2(SO_4)HSO_4]^- [H^+]} 
\]

(17)
From the second equilibrium step of Scheme 2

\[ [\text{Hg}_2(\text{SO}_4)\text{HSO}_4^-] = K_7 [\text{Hg}(I)] [\text{SO}_4^{2-}] [\text{HSO}_4^-] \]  \hspace{1cm} (18)

But, total \([\text{Hg}(I)]\) is given by

\[ [\text{Hg}(I)]_t = [\text{Hg}(I)]_r + [\text{Hg}_2(\text{SO}_4)\text{HSO}_4^-] \]

\[ [\text{Hg}(I)]_t = [\text{Hg}(I)]_r + K_7 [\text{Hg}(I)]_r [\text{SO}_4^{2-}] [\text{HSO}_4^-] \]

\[ [\text{Hg}(I)]_t = [\text{Hg}(I)]_r (1+K_7 [\text{SO}_4^{2-}] [\text{HSO}_4^-]). \]

\[ \therefore \quad [\text{Hg}(I)]_r = \frac{[\text{Hg}(I)]_t}{1+K_7 [\text{SO}_4^{2-}] [\text{HSO}_4^-]} \]  \hspace{1cm} (19)

Substituting equation (19) in (18), equation (20) is obtained

\[ [\text{Hg}_2(\text{SO}_4)\text{HSO}_4^-] = \frac{K_7 [\text{Hg}(I)]_t [\text{SO}_4^{2-}] [\text{HSO}_4^-]}{1+K_7 [\text{SO}_4^{2-}] [\text{HSO}_4^-]} \]  \hspace{1cm} (20)

From the third step of Scheme 2

\[ [\text{PdCl}^+] = K_1 [\text{Pd}^{2+}] [\text{Cl}^-] \]  \hspace{1cm} (21)

Substituting equation (6) in (21),

\[ [\text{PdCl}^+] = \frac{K_1 [\text{Pd}^{2+}]_t [\text{Cl}^-]}{1+ \beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2 + \beta_3 [\text{Cl}^-]^3 + \beta_4 [\text{Cl}^-]^4} \]  \hspace{1cm} (22)

Substituting equation (20) and (22) in equation (17) and omitting subscripts, we obtain equation (23)

\[
\text{Rate} = \left\{ \begin{array}{c}
  k_1 K_1 K_2 K_6 K_7 [\text{Hg}(I)] [\text{QDC}] [\text{Pd}(II)] [\text{Cl}^-] [\text{SO}_4^{2-}] [\text{HSO}_4^-] [\text{H}^+] \\
  (1+K_7 [\text{SO}_4^{2-}] [\text{HSO}_4^-]) (1+\beta_1 [\text{Cl}^-] + \beta_2 [\text{Cl}^-]^2 + \beta_3 [\text{Cl}^-]^3 + \beta_4 [\text{Cl}^-]^4)
\end{array} \right\} \times \left\{ \begin{array}{c}
  1 + K_5 [\text{H}^+] + \frac{k_6 K_7 [\text{Hg}(I)] [\text{SO}_4^{2-}] [\text{HSO}_4^-]}{1+K_7 [\text{SO}_4^{2-}] [\text{HSO}_4^-]} + \frac{k_8 K_7 [\text{Hg}(I)] [\text{SO}_4^{2-}] [\text{HSO}_4^-] [\text{H}^+]}{1+K_7 [\text{SO}_4^{2-}] [\text{HSO}_4^-]}
\end{array} \right\}^{-1}
\]  \hspace{1cm} (23)
The reaction is accelerated in the media of low polarity, which can be quantitatively explained by the involvement of oppositely charged ions (Scheme 1). However, the decrease in the rate with increase in the ionic strength is not easy to interpret. This might be due to the presence of various ionic interactions. The negative value of the entropy of activation indicates that the complex is more ordered than the reactants. The observed modest entropy of activation and higher rate constant of the slow step indicate that the oxidation presumably occurs by an inner-sphere mechanism. This conclusion is supported by the results of earlier work\textsuperscript{22}.

**Autocatalysis**

Autocatalysis by one of the products, chromium(III), is interesting. The apparent order of significantly less than unity (0.73) in [Cr(III)], when [Cr(III)] is initially present, may be attributed to the weak complex formation between the product chromium(III) and oxidant, since chromium(III) is well known as a good complexing agent\textsuperscript{23}. This is followed by the interaction of the weak complex with the reductant as in Scheme 3. The steps shown in Scheme 3 will form part of Scheme 1.

\[
\text{QDC + Cr(III) } \xrightleftharpoons{K_8} \text{ weak Complex (C}_3\text{)} \\
\text{C}_3 + \text{Hg(I)} \xrightarrow{\text{slow} \ k_2} \text{ Products}
\]

**Scheme 3**

Evidence for weak complex (C\textsubscript{3}) was obtained by comparing UV-visible spectra of chromium(III) with the mixture of quinoliniumdichromate and chromium(III). There is a hypsochromic shift of chromium(III) from 584 nm to 580 nm, nearly 4 nm in the spectra of chromium(III) and the mixture of quinoliniumdichromate and
chromium(III). However, weak complex formation between chromium(III) and palladium(II) is disregarded due to our experimental rate law and lack of spectral evidence. Indeed such weak complex formation between quinolinium dichromate and chromium (III) has been observed in the literature.

Thus, when chromium(III) is initially present, a composite Scheme involving all steps of Scheme 1 and 3 operates and the rate law is given as the sum of the catalysed and autocatalysed rates.

\[
\text{Rate}_{\text{(gross)}} = \text{Rate}_{\text{(Cat)}} + \text{Rate}_{\text{(autocat)}} \tag{24}
\]

\[
\text{Rate}_{\text{(autocat)}} = \text{Rate}_{\text{(gross)}} - \text{Rate}_{\text{(cat)}}
\]

Thus, the rate law for the autocatalytic path can be obtained as follows:

\[
\text{Rate}_{\text{(autocat)}} = k_2 [C_3] [Hg(I)] \tag{25}
\]

\[
[C_3] = K_8 [QDC]_f [Cr(III)]_f
\]

\[
\text{Rate}_{\text{(autocat)}} = k_2 K_8 [QDC]_f [Cr(III)]_f [Hg(I)] \tag{26}
\]

But,

\[
[QDC]_f = [QDC]_r + [C_3].
\]

\[
= [QDC]_r + K_8 [QDC]_f [Cr(III)]_f
\]

\[
\therefore [QDC]_r = [QDC]_f / (1 + K_8 [Cr(III)]_f) \tag{27}
\]

Similarly,

\[
[Cr(III)]_r = [Cr(III)]_r / (1 + K_8 [QDC]_r) \tag{28}
\]

Substituting equations (27) and (28) in equation (26) we have,

\[
\text{Rate}_{\text{(autocat)}} = \frac{k_2 K_8 [QDC]_r [Cr(III)]_r [Hg(I)]}{\{(1 + K_8 [QDC]_f) (1 + K_8 [Cr(III)]_f)\}} \tag{29}
\]

\[
= \frac{k_2 K_8 [QDC] [Hg(I)] [Cr(III)]}{1 + K_8 [Cr(III)] + K_8 [QDC] + K_8^2 [QDC][Cr(III)]} \tag{30}
\]
Equation (30) can be rewritten as

\[
\frac{[\text{QDC}][\text{Hg(I)}]}{\text{Rate}_{\text{autocat}}} = \frac{1 + K_8 [\text{Cr(III)}] + K_g [\text{QDC}] + K^{2}_8 [\text{QDC}][\text{Cr(III)}]}{k_2 K_8 [\text{Cr(III)}]}
\]

\[
= \frac{1}{k_2 K_8 [\text{Cr(III)}]} + \frac{1}{k_2} + \frac{[\text{QDC}]}{k_2 [\text{Cr(III)}]} + \frac{K_8 [\text{QDC}]}{k_2}
\]

Thus equation (31) can be rearranged to the form of equation (32) which is suitable for verification.

\[
\frac{[\text{QDC}][\text{Hg(I)}]}{\text{Rate}_{\text{autocat}}} = \frac{1}{k_2 [\text{Cr(III)}]} \left\{ \frac{1}{K_8} + \frac{[\text{QDC}]}{k_2} \right\} + \frac{1}{k_2} + \left\{ 1 + K_8 [\text{QDC}] \right\}
\]

At constant concentrations of oxidant and reductant, a plot of LHS versus \(1/[\text{Cr(III)}]\) of equation (32) should be linear and this was found to be so (Fig. III(xiii) (p.109)). Indeed it is to be noted that the plot shows an intercept which is in agreement with the complex formation, as in Scheme 3. The \(k_2\) and \(K_8\) values found from the intercepts and slope of such a plot were \((2.44 \pm 0.12) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\) and \((1.10 \pm 0.04) \times 10^3 \text{ dm}^3 \text{ mol}^{-1}\) respectively. Using these values the experimental rates for the added [Cr(III)] at constant concentrations of quinoliniumdichromate and mercury(I) can be regenerated (Table III(iv)(p.80)).

**FINDINGS**

The kinetics of oxidation of mercury(I) with quinoliniumdichromate (QDC) in the presence of micro amounts of palladium(II) catalyst in aqueous sulphuric acid medium has been studied under varying conditions. The active species of oxidant,
Fig. III(xiii)

Verification of rate law (30) in the form of (32)

(Conditions as in Table III(iv)(p.80))
reductant and catalyst in the reaction medium were understood to be HCrO$_4^-$, [Hg$_2$ (SO$_4$)$_2$HSO$_4$]$^-$ and PdCl$^+$ respectively. The autocatalysis by one of the products, chromium(III), was observed. A composite Scheme and the rate law were proposed. Some reaction constants involved in the mechanism have been evaluated.

**IMPORTANCE OF CHAPTER III**

The reaction between mercury(I) and QDC is very slow in sulphuric acid. Palladium(II) is known to catalyse the reaction with a measurable velocity at $10^{-6}$ mol dm$^{-3}$, especially in a sulphuric acid medium; which is not the case in perchloric acid and nitric acid media. The active species involved in the mechanism play an important role in the reaction. It is interesting to note that the autocatalysis has taken place in the catalysed reaction, making a composite reaction scheme and rate law. The overall mechanistic sequence described here is consistent with product, mechanistic, and kinetic studies.
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