CHAPTER IV

KINETICS OF PALLADIUM(II) CATALYSED OXIDATION OF MERCURY(I) BY IRON(III)-2,2'-BIPYRIDYL COMPLEX

Mercury(I) is dimeric in nature and it exists in equilibrium with metallic mercury\(^1\). The Hg(I) - Hg(I) bond is sufficiently stable to resist oxidation. The reduction potential of +0.92V in acid\(^2\) would be expected to facilitate oxidation by oxidants such as cerium(IV). However, oxidants like cobalt(III)\(^3\), cerium(IV)\(^4\) and chromium(VI)\(^5\) oxidise mercury(I) only slowly in aqueous acid. Hence different catalysts\(^6\) such as silver(I), manganese(II), ruthenium(IV), osmium(VIII) have been used to accelerate the reaction. Iron(III) on its own does not oxidise mercury(I) even in acids such as perchloric acid, sulphuric acid, nitric acid etc. It is known that 2,2'-bipyridyl is a good complexing agent\(^7\) and the complex between iron(III) and 2,2'-bipyridyl was first prepared by Blau\(^8\). To understand the oxidising action of this complex, a kinetic study of the oxidation of mercury(I) by iron(III) in presence of 2,2'-bipyridyl has been made\(^9\) and is found to be a slow reaction. We have observed that the presence of microamounts (10\(^{-6}\) mol dm\(^{-3}\)) of palladium(II) catalyse the oxidation of mercury(I) by iron(III)-2,2'-bipyridyl complex. The reaction is facile in the presence of nitric acid, but does not take place to any reasonable extent in other acid media. We have investigated the title reaction in nitric acid and methanol media to understand the plausible mechanism.
EXPERIMENTAL

Reagent grade chemicals and doubly distilled water were used throughout. The iron(III) solution used in the study was obtained by dissolving ferric ammonium sulphate (E. Merck) in 0.1 mol dm$^{-3}$ sulphuric acid and then standardising it with EDTA$^{10a}$. 2,2'-Bipyridyl (BDH) solution was prepared by dissolving the substance in methanol. Mercury(I) solution was obtained by dissolving mercury(I) nitrate (S. Merck) in 0.50 mol dm$^{-3}$ nitric acid and standardising the solution against potassium iodate solution$^{10b}$. A stock solution of palladium(II) chloride (Johnson Matthey) was prepared in 0.20 mol dm$^{-3}$ hydrochloric acid and assayed by complexometric titration with EDTA$^{11}$. Dilute solutions of palladium(II) were made from the stock solution as required. Iron(II) solution was prepared by dissolving ferrous ammonium sulphate (BDH) in 0.20 mol dm$^{-3}$ nitric acid. Mercury(II) solution was obtained by dissolving mercuric oxide (BDH) in 0.50 mol dm$^{-3}$ nitric acid. Nitric acid and sodium nitrate were used to provide the required acidity and to maintain the constant ionic strength, respectively. Methanol was purified by a literature method$^{12}$.

KINETICS

The kinetics were followed at 25 ± 0.1°C, unless otherwise stated and at I = 0.12 mol dm$^{-3}$. The reaction was initiated by mixing reactant solutions thermally equilibrated at the desired temperature. Iron(III) solution contained 2,2'-bipyridyl and the required amounts of nitric acid and sodium nitrate and
the mercury(I) solution contained a known amount of palladium(II). The reaction was generally followed under pseudo-first order conditions, with mercury(I) and 2,2'-bipyridyl in excess, by measuring the absorbance of one of the products, iron(II)-2,2'-bipyridyl in the reaction mixture, at 510 nm in a 1 cm cell placed in the thermostatted compartment of a Hitachi 150-20 spectrophotometer. At this wavelength, all the other materials present in the solution have negligible absorption. Precaution was taken to avoid any effect of light by covering the reaction vessel with black paper. Beer’s law had been verified earlier between $1.0 \times 10^{-5}$ and $1.2 \times 10^{-4}$ mol dm$^{-3}$ of iron(II)-(bipyridyl)$_3$ complex at 510 nm under the reaction conditions. The molar absorption coefficient was found to be $\varepsilon = 10,000 \pm 100$ dm$^{-3}$ mol$^{-1}$cm$^{-1}$ (Fig. IV(i) (p.105)). The initial rates were determined by plotting the concentrations of iron(II)-2,2'-bipyridyl versus time by plane-mirror method$^{13}$. The first order rate constants, $k_{\text{obs}}$, were obtained from a plot of log[iron(III)-2,2'-bipyridyl] versus time and the plots were linear over 70% completion of the reaction. The initial rates and first order rate constants were reproducible to within $\pm 5\%$. An example run is shown in Table IV(i) (p.106) and the concerned graph is shown in Fig. IV(ii) (p.107). All the kinetic runs were carried out in 50% methanol-water (v/v) except that, when studying solvent effects, the methanol content in the reaction mixture was varied.
Verification of Beer's law for Iron(II)–2,2’-bipyridyl complex at 510 nm in aqueous nitric acid–methanol media at 25°C.
Table IV(i)

Palladium(II) catalysed oxidation of mercury(I) by iron(III)-2,2'-bipyridyl complex at 25°C.

Example run

\[ \text{[Fe(III)]} = 5.0 \times 10^{-5} \quad \text{[2,2'-bipy]} = 1.0 \times 10^{-2} ; \quad \text{[Hg(I)]} = 1.0 \times 10^{-3} ; \]

\[ \text{[HNO}_3\text{]} = 0.05 ; \quad \text{[Pd(II)]} = 8.0 \times 10^{-5} ; \]

\[ I = 0.12 / \text{mol dm}^{-3} ; \quad \text{Solvent: 50% methanol-water (v/v)} \]

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Optical density at 510 nm</th>
<th>([\text{Iron(II)-2,2'-bipy}] \times 10^6 ) (mol dm(^{-3}))</th>
<th>([\text{Iron(III)-2,2'-bipy}] \times 10^5 ) (mol dm(^{-3}))</th>
<th>5+ ( \log[\text{Iron(III)-2,2'-bipy}] )</th>
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</thead>
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<td>0.342</td>
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</table>
Fig. IV(ii)

Palladium(II) catalysed oxidation of mercury(I) by iron(III) -2,2'-bipyridyl complex at 25° C.

(Conditions as in Table IV(i) (106))
RESULTS

Stoichiometry

Different sets of concentrations of reactants, the iron(III)-2,2'-bipyridyl complex, mercury(I) and the catalyst, palladium(II), in 0.02 mol dm$^{-3}$ nitric acid at a constant ionic strength of 0.12 mol dm$^{-3}$ were kept at 25 ± 1.0°C for over 24h and afterwards analysed for iron(II)-(bipyridyl)$_3$ complex and mercury(I) respectively by measuring the absorbance at 510 nm and by titration with potassium iodate. The results showed that one mole of iron(III) was required to oxidise one mole of mercury(I).

$$\text{Fe(III)} + \text{Hg(I)} \xrightarrow{\text{Pd(II)}} \text{Fe(II)} + \text{Hg(II)} \quad (1)$$

REACTION ORDERS

The order each in oxidant, the iron(III)-bipyridyl complex, reductant, mercury(I), catalyst, palladium(II) and 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 reaction. The resulting data were employed to plot log(initial rate) versus log(concn.) graphs and the orders were obtained from such graphs.

Effect of [iron(III)]

The concentration of iron(III) was varied in the range $3.0 \times 10^{-5}$ to $3.0 \times 10^{-4}$ mol dm$^{-3}$ at fixed [Hg(I)], [HNO$_3$], [Pd(II)], [Bipy] and ionic strength (Table IV(ii) (p.110)). The linearity of the plot of log(initial rate) versus log(concn.) indicated a reaction order in [Fe(III)] as unity (Fig. IV(iii))
First order plots under these conditions were linear to over 70% completion of the reaction for different initial [Fe(III)] which confirms the unit order in [iron(III)].

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

The substrate, mercury(I), concentration was varied in the range 2.5×10^{-4} to 3.0×10^{-3} mol dm^{-3} at 25°C, keeping all other reactant concentrations and conditions constant as shown in Table IV(ii) (p.110). It was found that the rate of the reaction is independent of the [Hg(I)] i.e., the order with respect to [Hg(I)] was found to be zero.

**Effect of [catalyst]**

At fixed [oxidant], [reductant], [bipy] and [acid], and I = 0.12 mol dm^{-3}, the palladium(II) concentration was varied in the range 1.0 \times 10^{-6} to 2.0 \times 10^{-5} mol dm^{-3} (Table IV(ii) (p.110)). The order in palladium(II) concentration was obtained from a plot of log(initial rate) versus log(concn.) and was found to be unity (Fig. IV(iii) (p. 111)).

**Effect of [acid]**

At constant ionic strength, I = 0.12 mol dm^{-3} and with other concentrations and conditions remaining constant, the rate was found to
Table IV(ii)

Effect of variation of [Fe(III)], [Hg(I)], [Pd(II)] and [Bipy] on the palladium(II) catalysed oxidation of mercury(I) by iron(III)-2,2'-bipyridyl complex at 25°C.

\[ [\text{HNO}_3] = 0.05 \; \text{mol dm}^{-3} \; ; \; [I] = 0.12 \; \text{mol dm}^{-3} \; ; \; \text{Solvent} : 50\% \text{ methanol-water} (v/v) \]

<table>
<thead>
<tr>
<th>[Fe(III)] × 10^5 (mol dm(^{-3}))</th>
<th>[Hg(I)] × 10^3 (mol dm(^{-3}))</th>
<th>[Pd(II)] × 10^6 (mol dm(^{-3}))</th>
<th>[bipy] × 10^2 (mol dm(^{-3}))</th>
<th>Initial rate × 10^6 (mol dm(^{-3}) s(^{-1}))</th>
<th>(k_{obs} \times 10^3) (s(^{-1}))</th>
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</thead>
<tbody>
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<td>3.0</td>
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<td>1.0</td>
<td>1.23</td>
<td>1.21</td>
</tr>
<tr>
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<td>1.0</td>
<td>1.95</td>
<td>2.02</td>
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<td>1.5</td>
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</table>
**Fig. IV(iii)**

Order in $[\text{Fe(III)}]$ and $[\text{Pd(II)}]$:

Effect of variation of $[\text{Fe(III)}]$ and $[\text{Pd(II)}]$ on the palladium(II) catalysed oxidation of mercury(I) by iron(III)-2,2'-bipyridyl complex at $25^\circ\text{C}$.

(Conditions as in Table IV(ii) (p.110))
decrease with the increase in \([H^+]\) (Table IV(iii) (p.113)). The order with respect to [acid] was found to be negative and fractional (Fig. IV(iv) (p.114)).

**Effect of [2,2'-bipyridyl]**

At constant \([\text{Fe(III)}], \ [\text{Hg(I)}], \ [\text{Pd(II)}] \) and \([H^+]\), other conditions remaining the same, the 2,2'-bipyridyl concentration was varied between \(4.0 \times 10^{-3}\) and \(1.5 \times 10^{-2}\) mol dm\(^{-3}\) at \(I = 0.12\) mol dm\(^{-3}\) (Table IV(ii) (p.110)). The order with respect to [2,2'-bipyridyl] was found to be less than unity (Fig. IV(iv) (p.114)).

**Effect of initially added products**

The addition of varying amounts of reaction products such as iron(II) in the form of ferrous ammonium sulphate and mercury(II) as mercuric oxide was studied in the \(1.0 \times 10^{-5}\) to \(1.0 \times 10^{-4}\) mol dm\(^{-3}\) concentration range, keeping the ionic strength, reactant concentrations and other conditions constant. No significant effect on the reaction was observed in either case.

**Effect of ionic strength and dielectric constant**

To study the effect of ionic strength on the reaction, the concentration of sodium nitrate was varied in the range \(0.1\) to \(0.5\) mol dm\(^{-3}\). At constant acidity and other constant conditions, as the ionic strength increased in the reaction mixture, the rate increased (Table IV(iv) (p.116)). A plot of \(\log(\text{initial rate})\) versus \(I^{1/2}\) was linear with positive slope (Fig. IV(v) (p.117)). The effect of dielectric constant on the reaction was studied by keeping the concentrations of
**Table IV(iii)**

Effect of variation of [HNO₃] on the palladium(II) catalysed oxidation of mercury(I) by iron(III)- 2,2′-bipyridyl complex at 25°C.

\[
\begin{align*}
[\text{Fe(III)}] & = 5.0 \times 10^{-5}; \\
[\text{Hg(I)}] & = 1.0 \times 10^{-3}; \\
I & = 0.12 / \text{mol dm}^3; \\
\text{Solvent} & : 50\% \text{ methanol-water (v/v)}
\end{align*}
\]

\[
\begin{array}{|c|c|}
\hline
[\text{HNO}_3] \text{ (mol dm}^3) & \text{Initial rate} \times 10^8 \text{ (mol dm}^3 \text{ s}^{-1}) \\
\hline
0.01 & 6.92 \\
0.02 & 4.63 \\
0.05 & 1.95 \\
0.08 & 0.84 \\
0.11 & 0.48 \\
\hline
\end{array}
\]
Fig. IV(iv)

Order in [2,2'-bipy] and [HNO₃]:

Effect of variation of [2,2'-bipy] and [HNO₃] on the palladium(II) catalysed mercury(I) oxidation by iron(III)-2,2'-bipyridyl complex at 25°C.

(Conditions as in Table IV (ii) (p110.) and Table IV (iii) (p113.)
reactants, acid, catalyst, ionic strength and other conditions constant and varying only the methanol content in the reaction mixture. As the methanol content increased in the reaction mixture, the rate increased (Table IV(iv) (p.116)). The values of dielectric constants of aqueous methanol were taken from the literature$^{14}$. 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 shown in Fig. IV(v) (p. 117).

**Effect of temperature**

The rate of reaction was measured at four different temperatures at constant reactant conditions and ionic strength. The rate was found to increase with increase in temperature. The data are subjected to a least square analysis as in Chapter II (p.50) and are tabulated in Table IV(v) (p.118). The energy of activation was evaluated from log \( k (\gamma_{cal}^{**}) \) versus 1/T (Fig. IV(vi) (p.119)) and other activation parameters are obtained as in Chapter II (p.54) and are listed in Table IV(v) (p.118).

**DISCUSSION**

The results of the study of iron(III)-bipyridyl complex oxidation of mercury(I) in 50% aqueous methanol under the given conditions indicate a 1:1 stoichiometry and also show unit order each in [Pd(II)] and [Fe(III)] and less than unit order in [2,2'-bipyridyl]. It is interesting to note that without the catalyst, the reaction exhibits a unit order dependence in Hg(I)$^9$, whereas, in the presence of palladium(II) catalyst, the reaction is zero order in [Hg(I)]. The
Table IV(iv)

Effect of dielectric constant (D) and ionic strength (I) on the palladium(II) catalysed oxidation of mercury(I) by iron(III)-2,2'-bipyridyl complex at 25°C.

\[
\begin{align*}
[\text{Fe(III)}] &= 5.0 \times 10^{-5} ; \\
[2,2'-\text{bipy}] &= 1.0 \times 10^{-2} ; \\
[Hg(I)] &= 1.0 \times 10^{-3} ; \\
[Pd(II)] &= 8.0 \times 10^{-6} ; \\
[HNO_3] &= 0.05 ; \\
I &= 0.12 / \text{mol dm}^{-3} \\
\text{Solvent} &= 50 \% \text{ methanol-water (v/v)}
\end{align*}
\]

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<tr>
<th>% of methanol-water (v/v)</th>
<th>D</th>
<th>Initial rate $\times 10^8$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>I</th>
<th>Initial rate $\times 10^8$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
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**Fig. IV(v)**

Effect of variation of dielectric constant (D) and ionic strength (I) on the palladium(II) catalysed oxidation of mercury(I) by iron(III) -2,2'-bipyridyl complex at 25°C.

(Conditions as in Table IV (iv) (p.116))
Table IV(v)

Effect of temperature on the palladium(II) catalysed oxidation of mercury(I) by iron(III)-2,2'-bipyridyl complex.

\[
\begin{align*}
[\text{Fe(III)}] &= 5.0 \times 10^5; \\
[\text{Hg(I)}] &= 1.0 \times 10^{-3};
\end{align*}
\]

\[
\begin{align*}
[2,2'-\text{bipy}] &= 1.0 \times 10^{-2}; \\
[\text{Pd(II)}] &= 8.0 \times 10^{-6};
\end{align*}
\]

\[
[\text{HNO}_3] = 0.05; \quad I = 0.12 / \text{mol dm}^{-3}
\]

Solvent: 50% methanol-water (v/v)

(a)

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<th>\text{T* (K)}</th>
<th>\text{k \times 10^4 (s^{-1})}</th>
<th>\text{1/T \times 10^3 (x)}</th>
<th>\text{logk (y)}</th>
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<td>-3.063</td>
<td>-3.064</td>
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</table>

* Temperature, ** Calculated

(b) Activation parameters

\[
\begin{align*}
\text{E}_a &= 85 \pm 4 \text{ kJ mol}^{-1} \\
\Delta H^\# &= 83 \pm 3 \text{ kJ mol}^{-1} \\
\log A &= 5.5 \pm 0.02 \\
\Delta S^\# &= -9 \pm 1 \text{ JK}^{-1} \text{ mol}^{-1} \\
\Delta G^\# &= 97 \pm 3 \text{ kJ mol}^{-1}
\end{align*}
\]
**Fig. IV(vi)**

Effect of temperature on the palladium(II) catalysed oxidation of mercury(I) by iron(III)-2,2'-bipyridyl complex.

(Conditions as in Table IV(v) (p.118) )

\[
\frac{1}{T} \times 10^3
\]

\[
-\log k \left( y_{ca} \right)
\]

1/T x 10^3

3.20 3.24 3.28 3.32 3.36 3.40

3.0 3.1 3.2 3.3 3.4 3.5 3.6 3.7

O O O O O O
reaction is facile in HNO₃ media and not in other acids. However, in other reactions, palladium(II) acts as an efficient catalyst in the presence of H₂SO₄ and not in other acids. In the present study, the uncomplexed palladium(II) might be the active species.

The results of Milburn and Vosburgh show that iron(III) at concentrations less than 1.0 × 10⁻³ mol dm⁻³ does not dimerize. This result is also supported by other workers. In the present study, the iron(III) concentrations employed were of the order of 10⁻⁴ mol dm⁻³ and [H⁺] was in the range 0.01 - 0.1 mol dm⁻³. Hence it is reasonable to assume that there is no appreciable dimerisation under the experimental conditions, and the formation of any appreciable concentrations of hydroxylated iron(III) is unlikely in view of the low hydrolysis constant. The hydrolysis is also suppressed by the presence of large quantities of the ligand 2,2'-bipyridyl. It has been reported that 2,2'-bipyridyl exists in the singly protonated form (pKₐ = 4.35). Since the kinetic studies have been carried out in the pH range of 1-2, it is reasonable to suppose that bipyridyl is in the form of BipyH⁺.

Mercury(II) is known to form metal chelates with 1,10-phenanthroline and 2,2'-bipyridyl. In all the kinetic runs, 2,2'-bipyridyl was taken in large excess in comparison with iron(III) and the decrease in the concentration of the ligand removed by complex formation with mercury(II) and iron(III) is therefore negligible, thereby preventing the complications due to auto inhibition. The authors propose a 1:2 complex when iron(III) is mixed with 2,2'-bipyridyl and the complex is a better oxidising species than the uncomplexed
iron(III). Hence the iron(III)-mercury(I) reaction is possible only in the presence of 2,2'-bipyridyl ligand. The greater oxidising ability of iron(III) in the presence of 2,2'-bipyridyl is presumably due to its stabilizing the lower valence state of iron(II) through back-bonding with consequent increase in the redox potential of Fe(III)/Fe(II) couple. The increase in the reaction rate by bipyridyl may also be due to the possibility that electron transfer is facilitated by the π-electron system present in the ligand. All the kinetic results may be accommodated in the Scheme 1.

\[
\begin{align*}
\text{Fe(III)}_{aq} + 2(\text{BipyH}^+) \rightleftharpoons K \Rightarrow [\text{Fe(Bipy)}_2]^{3+} + 2H^+ \quad (2) \\
\text{(complex)} \\
\text{Complex} + \text{Pd(II)} \rightarrow \quad \text{Pd(III)} + \text{Fe(II)(bipy)}_3 \quad (3) \\
\text{Pd(III)} + \text{Hg(I)} \rightarrow \quad \text{Hg(II)} + \text{Pd(II)} \quad (4) \\
\text{Scheme 1}
\end{align*}
\]

Fe(III) reacts with the protonated form of bipyridyl in a prior equilibrium step to form a complex which reacts with the catalyst, Pd(II), in a rate determining step to form the intermediate species of Pd(II) as Pd(III) with the formation of Fe(II). The Pd(III) formed then reacts with Hg(I) in a fast step to yield the product, Hg(II), to regenerate the catalyst, Pd(II). The intervention of Pd(III) intermediate formation is also found in earlier literature. In the case of the oxidation of Hg(I) by either Tl(III) or Mn(III), the formation of elemental mercury through a step such as (5) followed by the rate-determining oxidation of Hg° has been proposed.
But such a mechanism is not tenable in the present study in view of the lack of effect of Hg(II) on the rate of reaction, apart from the inhibitory effect due to the removal of bipyridyl by way of complex formation. The mechanism proposed here is similar to the one proposed by McCurdy et al., in the case of oxidation of Hg(I) by Ce(IV), and in that case also they did not observe any inhibitory effect of Hg(II) on the rate. From Scheme 1, the rate law (9) is derived as follows:

From the second step of Scheme 1, we have

\[
\text{Rate} = k [\text{Pd(II)}][C]
\]  (6)

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

\[
[C] = \frac{K[\text{Fe(III)}][\text{BipyH}^+]^2}{[\text{H}^+]^2}
\]

Therefore,

\[
\text{Rate} = \frac{kK[\text{Pd(II)}][\text{Fe(III)}][\text{BipyH}^+]^2}{[\text{H}^+]^2}
\]  (7)

The total concentration of Fe(III), \([\text{Fe(III)}]_T\) is given by

\[
[\text{Fe(III)}]_T = [\text{Fe(III)}]_f + C
\]

where 'T' and 'f' stand for the total iron(III) and free iron(III) ion respectively.

\[
\therefore [\text{Fe(III)}]_T = [\text{Fe(III)}]_f + \frac{K[\text{Fe(III)}][\text{BipyH}^+]^2}{[\text{H}^+]^2}
\]
\[
[\text{Fe(III)}]_r = \frac{[\text{Fe(III)}][\text{Pd(II)}]}{[\text{H}^+]^2 + K[\text{BipyH}^+]^2}
\]

Substituting the value for \([\text{Fe(III)}]_r\) from equation (8) in equation (7) and omitting the subscripts, we have,

\[
\text{Rate} = \frac{-d[\text{Fe(III)}]}{dt} = \frac{kK[\text{Fe(III)}][\text{BipyH}^+]^2[\text{Pd(II)}]}{[\text{H}^+]^2 + K[\text{BipyH}^+]^2}
\] (9)

The above rate law (9) explains all the observed orders including the zero order dependence of \([\text{Hg(I)}]\). The rate law (9) may be rearranged to equation (10) which is suitable for verification.

\[
\frac{[\text{Fe(III)}][\text{Pd(II)}]}{\text{Rate}} = \frac{[\text{H}^+]^2}{kK[\text{BipyH}^+]^2} + \frac{1}{k} \quad ([\text{BipyH}^+] = [\text{Bipy}])
\] (10)

According to equation (10), it is evident that L.H.S. versus \([\text{H}^+]^2\) and L.H.S. versus \(1/[\text{BipyH}^+]^2\) are expected to be linear and this was found to be so as shown in Fig. IV(vii) (p.124). From the slopes and intercepts of such plots, the values of constants \(K\) and \(k\) were evaluated as \(119 \pm 5\) and \(61 \pm 2\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\) respectively. Using the values of \(K\) and \(k\), the initial rates under different experimental conditions were calculated and are in good agreement with the experimental values (Table IV(ii) (p.110)).
Fig. IV(vii)

Verification of rate law (9) on the palladium(II) catalysed mercury(I) oxidation by iron(III)-2,2'-bipyridyl complex at 25° C.

(Conditions as in Table IV(ii) (p.110))
The effect of ionic strength on the rate of reaction qualitatively explains the reactions between similar charges as evidenced in Scheme 1. The effect of solvent on the rate of reaction has been described in detail in the literature. Increasing the content of methanol in the reaction medium leads to increase in the rate of reaction, which is contrary to the expected slower reaction between like ions in the media of low relative permittivity. Perhaps the effect is encountered substantially by the formation of less stable active species in less dielectric constant media to a greater extent.

The sizable negative entropy of activation is in agreement with the formation of activated complex involved in the reaction and the complex is more ordered than the reactants. The difference in the activation parameters for the catalysed and uncatalysed reactions explains the catalytic effect on the reaction. The catalyst, Pd(II) alters the path of the reaction by lowering the energy barrier, that is, it provides an alternative pathway which lowers activation parameters for the reaction.

FINDINGS

The results indicate a 1:1 stoichiometry and exhibits unit order each in [Pd(II)] and [Fe(III)] and less than unit order in [2,2'-bipyridyl]. It is interesting to note that without the catalyst the reaction exhibits a unit order dependence in [Hg(I)], whereas, in the presence of palladium(II) catalyst, the reaction is zero order in [Hg(I)]. The reaction is facile in HNO₃ media and not in other acids. However, in other reactions, palladium(II) acts as an efficient catalyst in...
the presence of H$_2$SO$_4$ and not in other acids. In the present study, the uncomplexed palladium(II) might be the active species. A suitable reaction mechanism is proposed and the reaction constants of the different steps involved have been evaluated.

IMPORTANCE OF CHAPTER IV

The direct reaction between mercury(I) and iron(III) is immeasurably slow. However, in the presence of 2,2'-bipyridyl, the reaction occurs slowly due to the better oxidising capacity of the complex than the uncomplexed iron(III). Palladium(II) is known to catalyse this reaction with a measurable velocity at 10$^{-6}$ mol dm$^{-3}$, especially in nitric acid medium.
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PART - II

UNCATALYSED REACTIONS