CHAPTER VIII

Kinetics and Mechanistic aspects of Reduction of Ruthenium(III) Catalysed Diperiodatonickelate(IV) Complex by Paracetamol in Aqueous Alkaline Medium by Stopped Flow Technique

The general importance of diperiodatonickelate(IV) (DPN) and catalyst ruthenium(III) are given in chapter II (p.30) and chapter VI (p.176) respectively.

Paracetamol (4'-hydroxyacetanilide or acetaminophen or 4-acetamidophenol) (PAM) is a well-known drug that finds extensive applications in pharmaceutical industries. It is an antipyretic and analgesic compound,¹ which has high therapeutic value. There is hardly any work with regard to the kinetics of oxidation of this drug in the literature (except in one case²). The oxidation of paracetamol is of interest in view of the importance of understanding the mechanisms of metabolic conversion of paracetamol in biological system.

Paracetamol is primarily metabolised⁠¹ by the liver. Most of it is combined with glucuronide and sulphate, which account for about 90% of the dose excreted. About 5% of the dose is excreted unchanged and a further 5% is oxidised to a benzoquinoneimine, which is then combined with glutathione and metabolised on to cysteine and mercapturate compounds, which are safely excreted.

The uncatalysed reaction between paracetamol and DPN in an alkaline medium has been studied previously.³ A microscopic amount of ruthenium(III) is sufficient to catalyse the reaction and a variety of mechanisms are possible. In
view of lack of literature on the title reaction and multiple equilibria embracing the
different nickel(IV) periodate species, we have selected paracetamol as substrate.
The reduction of DPN by paracetamol in presence of ruthenium(III) is studied in
this chapter to understand the possible species of oxidant and ruthenium(III) and to
arrive a plausible mechanism.

EXPERIMENTAL

Materials

All chemicals used were of reagent grade. Double distilled water was used
throughout the work. Solution of paracetamol (S.D.Fine Chem) was prepared by
dissolving appropriate amount of recrystallised sample in distilled water. The
purity was checked by its IR and NMR studies. The preparation and
standardization of nickel(IV) periodate complex and other materials are described
in chapter II (p.32) and preparation of ruthenium(III) catalyst and standardization
is given in chapter VI (p.178).

Since, periodate is present in an excess in the DPN complex, the possibility
of paracetamol oxidation by periodate in presence of catalyst in aqueous alkaline
medium has been tested. It was found that the reaction is much slower than the
title reaction.

Kinetic Measurements

Kinetic runs were followed under pseudo-first order conditions with the
paracetamol concentration in excess over that of the oxidant at 25 ± 0.1 °C, unless
otherwise stated. The method and calculation of rate constants are as given in
earlier chapter III (p.72). The effect of dissolved oxygen and surface of reaction vessel on the rate of reaction were also performed as in chapter III (p.73) and found no effect.

RESULTS

Stoichiometry and Product Analysis

Different sets of reaction mixtures containing different concentrations of paracetamol and DPN with a constant amount of ruthenium(III) at constant ionic strength and alkali were kept for ca. 2 hours at 25 ± 0.1 °C in an inert atmosphere and in a closed vessel. When [DPN] was higher than [Paracetamol], the unreacted DPN was found by measuring the absorbance at 410 nm spectrophotometrically. The results indicated that two moles of DPN consumed one mole of paracetamol as in equation (1).

\[
\text{HO-}N-C-\text{CH}_3 + 2 [\text{Ni(OH)}_2(\text{H}_2\text{IO}_6)]^- + \text{NaOH} \rightarrow \text{HO-N=N-O} \\
+ 2 \text{Ni(OH)}_2 + 2 \text{H}_2\text{IO}_5^- + \text{CH}_3\text{COONa} + \text{H}_2\text{O}
\]

The stoichiometric ratio suggests that the main reaction products are quinone oxime, sodium acetate and Ni(II). Quinone oxime was identified by its IR spectra (1652 cm\(^{-1}\) due to C=O stretching, 1615 cm\(^{-1}\) due to C=N stretching of oxime, 3332 cm\(^{-1}\) due to O-H stretching) and characterized by NMR spectra (singlet at 6.8 ppm due to aromatic 2H, singlet at 7.4 ppm due to aromatic 2H, a singlet at 9.8 ppm due to H of O-H). And Ni(II) was confirmed by its dimethyl glyoxime complex and acetic acid by spot test. The reaction products do not undergo

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further oxidation under the present kinetic conditions.

**Reaction Orders**

As the reduction of diperiodatnickelate(IV) by paracetamol in alkaline medium proceeds with a measurable rate in the absence of ruthenium(III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant ($k_T$) is equal to the sum of the rate constants of the catalysed ($k_c$) and uncatalysed ($k_u$) reactions, so $k_c = k_T - k_u$. Hence the reaction orders have been determined from the slopes of log($k_c$) versus log(concentration) plots by varying the concentrations of paracetamol, Ru(III) and alkali in turn while keeping the others constant.

**Effect of [Diperiodatnickelate(IV)]**

The concentration of diperiodatnickelate(IV) was varied in the range, $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ mol dm$^{-3}$ at fixed [Paracetamol], [Ru(III)], [OH$^-$] and ionic strength. The non-variation in the pseudo-first order rate constants at various concentrations of DPN indicates the order in [DPN] as unity as shown in Table VIII (i) (p.256). This was also confirmed from the linearity of plots of log (Absorbance) versus time ($r \geq 0.9994$, $S \leq 0.026$) up to 85 % completion of the reaction as shown in Figure VIII (i) (p.257).

**Effect of [Paracetamol]**

The substrate, paracetamol was varied in the range of $6.0 \times 10^{-4}$ to $6.0 \times 10^{-3}$ mol dm$^{-3}$ at 25 °C keeping all other reactants concentrations constant including ruthenium(III) catalyst. The $k_c$ values increased with increase in concentration of
paracetamol indicating an apparent less than unit order dependence on [Paracetamol] (Table VIII (i) (p.256)) from the linearity of the plot of log $k_c$ versus log [Paracetamol] ($r \geq 0.99994, S \leq 0.0232$). However, at lower concentrations of paracetamol, the reaction was first order in paracetamol and at high concentration of paracetamol, the reaction was independent of [Paracetamol]. The order in paracetamol changes from first order to zero order as the [Paracetamol] varies.

Effect of [Ruthenium(III)]

The ruthenium(III) concentration was varied from $1.0 \times 10^{-8}$ to $1.0 \times 10^{-7}$ mol dm$^{-3}$ range, at constant concentration of diperiodatonickelate(IV), paracetamol, alkali and ionic strength. The order in [Ru(III)] was found to be unity (plot of log $k_c$ versus log [Ru(III)] ($r \geq 0.99992, S \leq 0.0122$)) as shown in Table VIII (i) (p.256).

Effect of [Alkali]

The effect of [Alkali] on the rate of reaction was studied at constant concentrations of paracetamol, diperiodatonickelate(IV), ruthenium(III) and a constant ionic strength at $1.0$ mol dm$^{-3}$. The rate constants increased with increase in [alkali] and the order was found to be less than unity (log $k_c$ versus log [OH$^-$] ($r \geq 0.9995, S \leq 0.0308$)) and Table VIII (ii) (p.259). Similar, as in the case of paracetamol, the order in alkali changes from first order to zero order as the [Alkali] varies.

Effect of [Periodate]

The effect of [IO$_4^-$] was observed by varying the concentration from $5 \times 10^{-4}$ to $5 \times 10^{-4}$ mol dm$^{-3}$ at constant concentrations of diperiodatonickelate(IV), paracetamol,
Table VIII (i)

Effect of variation of [DPN], [Paracetamol] and [Ru(III)] on the Ruthenium(III) Catalysed Reduction of Diperiodatonickelate(IV) by Paracetamol in aqueous alkaline medium at 25 °C.

\[ [IO_4^-] = 2.0 \times 10^{-5}, \quad [OH^-] = 0.20; \]

\[ I = 1.0 \text{ / mol dm}^3. \]

<table>
<thead>
<tr>
<th>DPN x 10^5 (mol dm^-3)</th>
<th>PAM x 10^4 (mol dm^-3)</th>
<th>Ru(III) x 10^8 (mol dm^-3)</th>
<th>kT x 10^2 (s^-1)</th>
<th>ka x 10^3 (s^-1)</th>
<th>kc x 10^2 (s^-1)</th>
<th>Found</th>
<th>Calculated</th>
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<td>3.76</td>
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</tbody>
</table>
Figure VIII (i)

First order plots of the Ruthenium(III) Catalysed Reduction of Diperiodatonickelate(IV) by Paracetamol in aqueous alkaline medium at 25 °C.

[DPN] x 10^5 (mol dm^{-3}):

(1) 1.0; (2) 2.0; (3) 4.0; (4) 6.0; (5) 10

(Conditions as given in Table VIII (i) (p.256))
ruthenium(III), alkali and constant ionic strength. It was found that the added periodate retarded the rate, and order in periodate was inverse fractional (log \( k_c \) versus log \([IO_4^-]\) \((r \geq 0.9998, S \leq 0.0423)\) as shown in Table VIII (ii) (p.259).

**Effect of Ionic Strength**

The effect of ionic strength was studied by varying the potassium nitrate concentration in the reaction medium. The ionic strength of the reaction medium was varied from 0.2 to 2.0 mol dm\(^{-3}\) at constant \([DPN], [Paracetamol], [Ruthenium(III)], [IO_4^-]\) and [Alkali]. It was found that the ionic strength has negligible effect on the rate of the reaction (Table VIII (iii) (p.261)).

**Effect of Solvent Polarity**

The relative permittivity (\(\varepsilon_r\)) effect was studied by varying the t-butyl alcohol-water content in the reaction mixture with all other conditions being constant including Ru(III) catalyst. Attempts to measure the relative permittivities of the mixture of t-butyl alcohol-water were not successful. However, they were computed from the values of pure liquids\(^5\) as in chapter II (p.45). It was also found that there was no reaction of the solvent with the oxidant under the experimental conditions. The rate constants \(k_c\), increased with the decrease in the dielectric constant of the medium as in Table VIII (iii) (p.261). The plot of log \(k_c\) versus \(1/\varepsilon_r\) was linear with positive slope \((r \geq 0.9998, S \leq 0.0112)\).
Table VIII (ii)

Effect of variation of $[\text{OH}]$ and $[\text{IO}_4^-]$ on the Ruthenium(III) Catalysed Reduction of Diperiodatonickelate(IV) by Paracetamol in aqueous alkaline medium at 25 °C.

$[\text{DPN}] = 6.0 \times 10^{-5};$  
$[\text{Paracetamol}] = 8.0 \times 10^{-4};$  
$[\text{Ru(III)}] = 6.0 \times 10^{-8};$  
$I = 1.0 / \text{mol dm}^{-3}.$

<table>
<thead>
<tr>
<th>$[\text{OH}]$ (mol dm$^{-3}$)</th>
<th>$[\text{IO}_4^-]$ x 10$^5$ (mol dm$^{-3}$)</th>
<th>$k_T$ x 10$^2$ (s$^{-1}$)</th>
<th>$k_a$ x 10$^3$ (s$^{-1}$)</th>
<th>$k_c$ x 10$^2$(s$^{-1}$)</th>
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<td>2.67</td>
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<td>3.38</td>
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<td>2.71</td>
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<td>1.23</td>
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<td>0.71</td>
<td>0.37</td>
<td>0.34</td>
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</table>
Effect of Initially Added Products

The initially added products such as Ni(II) and quinone oxime did not have any significant effect on the rate of the reaction.

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 24 hours in a nitrogen atmosphere. On dilution with methanol, no precipitate was resulted, indicating the absence of intervention of free radicals in the reaction.

Effect of Temperature

The rate of reaction was measured at different temperatures under varying paracetamol concentration. The rate of reaction increased with the increase of temperature. The rate constants, k of slow step of Scheme 1 were obtained from intercepts of the plots of [Ru(III)]/k, versus 1/[Paracetamol] (r ≥ 0.9978, S ≤ 0.0162) at different temperatures. The data are subjected to least square analysis as in chapter II (p.50) and were tabulated in Table VIII (iv a) (p.262). The energy of activation corresponding to these constants was evaluated from the plot (Y*sa) log k versus 1/T as shown in Figure VIII (ii) (p.263) (r ≥ 0.9989, S ≤ 0.0241) and other activation parameters are obtained as in chapter II (p.50) and are tabulated in Table VIII (iv b) (p.262).
Table VIII (iii)

Effect of Ionic Strength (I) and Relative Permittivity ($\varepsilon_T$) on the Ruthenium(III) Catalysed Reduction of Diperiodatonickelate(IV) by Paracetamol in aqueous alkaline medium at 25 °C.

\[
\begin{align*}
[\text{DPN}] &= 6.0 \times 10^{-5}; \\
[\text{Paracetamol}] &= 8.0 \times 10^{-4}; \\
[\text{Ru(III)}] &= 6.0 \times 10^{-8}; \\
[\text{OH}^-] &= 0.20; \\
[\text{IO}_4^-] &= 2.0 \times 10^{-5}; \\
I &= 1.0 / \text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>$I$ \ (mol dm$^{-3}$)</th>
<th>$k_e \times 10^2$</th>
<th>$%$ of *t-butanol-water</th>
<th>$\varepsilon_T$</th>
<th>$k_e \times 10^2$ \ (s$^{-1}$)</th>
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</thead>
<tbody>
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* *t-butanol-water (V/V)
Table VIII (iv)

(a) Effect of temperature on the slow step of the mechanism of Ruthenium(III) Catalysed Reduction of Diperiodatonickelate(IV) by Paracetamol in aqueous alkaline medium.

\[
\begin{align*}
[\text{DPN}] &= 6.0 \times 10^{-5}; \\
[\text{Paracetamol}] &= 8.0 \times 10^{-4}; \\
[\text{Ru(III)}] &= 6.0 \times 10^{-8}; \\
[\text{OH}^-] &= 0.20; \\
[\text{IO}_4^-] &= 2.0 \times 10^{-5}; \\
I &= 1.0 / \text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(k \times 10^{-7}) (dm(^3) mol(^{-1}) s(^{-1}))</th>
<th>(\log k) (Y)</th>
<th>(1/T \times 10^3) (X)</th>
<th>(Y^*_{\text{calc}})</th>
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*Calculated

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

<table>
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<tr>
<th>Activation Parameters</th>
<th>Catalysed reaction</th>
<th>Uncatalysed reaction</th>
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<tbody>
<tr>
<td>(E_a) (kJ mol(^{-1}))</td>
<td>21.8 ± 0.9</td>
<td>46 ± 2</td>
</tr>
<tr>
<td>(\log A)</td>
<td>10.7 ± 0.4</td>
<td>6.6 ± 0.3</td>
</tr>
<tr>
<td>(\Delta H^#) (kJ mol(^{-1}))</td>
<td>19.2 ± 0.8</td>
<td>43 ± 2</td>
</tr>
<tr>
<td>(\Delta S^#) (JK(^{-1}) mol(^{-1}))</td>
<td>-48 ± 2</td>
<td>-242 ± 12</td>
</tr>
<tr>
<td>(\Delta G^#) (kJ mol(^{-1}))</td>
<td>14.8 ± 0.7</td>
<td>177 ± 6</td>
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Figure VIII (ii)

Effect of temperature on the Ruthenium(III) Catalysed Reduction of Diperiodatonickelate(IV) by Paracetamol in aqueous alkaline medium.

(Conditions as in Table VIII (iv a) (p.262))
DISCUSSION

The water soluble Ni(IV) periodate complex is reported \(^{3,6,7,9}\) to be 
\[\text{[Ni(HIO}_6\text{)}_2\text{(OH)}_2\text{]}^{6-}\]. Although, periodate is involved in multiple equilibria \((2-4)\)

\[
\begin{aligned}
H_3\text{IO}_6^- & \xrightleftharpoons{K_1} H_2\text{IO}_6^- + H^+ & K_1 = 5.1 \times 10^{-4} & (2) \\
H_4\text{IO}_6^- & \xrightleftharpoons{K_2} H_3\text{IO}_6^{3-} + H^+ & K_2 = 4.9 \times 10^{-9} & (3) \\
H_3\text{IO}_6^{2-} & \xrightleftharpoons{K_3} H_2\text{IO}_6^{3-} + H^+ & K_3 = 5.1 \times 10^{-12} & (4)
\end{aligned}
\]

which prevail to varying extends depending on the pH employed, under condition of high pH 13.3 of the study the form which predominates is understood to be the species, \(H_3\text{IO}_6^{2-}\) (not as \(H\text{IO}_6^{4-}\) present in the Ni(IV) complex.\(^7,10,11\) Periodic acid \((H_3\text{IO}_6)\) exists in acid medium and also as \(H_4\text{IO}_6^-\) around a pH of 7. Thus, under the conditions employed in the alkaline medium, the main species are expected to be \(H_3\text{IO}_6^{2-}\) and \(H_2\text{IO}_6^{3-}\). At higher concentrations, periodate also tends to dimerise. Hence at the pH employed in the study, the Ni(IV) periodate complex exists as DPN, \([\text{Ni(H}_3\text{IO}_6)_2\text{(OH)}_2]\)^{2-}, a conclusion also supported by earlier work.\(^7,10\)

It is interesting to identify the probable ruthenium(III) chloride species in alkaline media. Electronic spectral studies\(^12\) have confirmed that ruthenium(III) chloride exists in hydrated form as \([\text{Ru(H}_2\text{O})_6]^{3+}\). In the present study it is quite probable that the \([\text{Ru(H}_2\text{O})_5\text{OH}]^{2+}\) species might assume the general form \([\text{Ru}^{\text{III}}(\text{OH})_x]^{3-x}\). The \(x\) value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The reminder of the coordination sphere will be filled by water molecules. Hence, under the conditions

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[OH⁻] » [Ru(III)], ruthenium(III) is mostly present¹³ as the hydroxylated species, [Ru(H₂O)₆OH]²⁺.

The results of rate increase with increase in alkalinity and the rate decrease with increase in [Periodate] (Table VIII (ii) (p.259)) suggest that equilibria of different Ni(IV) periodate complexes as in equation (5) and (6) are possible.

\[
\begin{align*}
\text{[Ni(OH)₂(H₃IO₆)]}²⁺ + \text{OH}⁻ & \rightleftharpoons \text{[Ni(OH)₃(H₂IO₆)(H₂IO₆)]}³⁻ + \text{H₂O} & \quad (5) \\
\text{[Ni(OH)₂(H₃IO₆)(H₂IO₆)]}³⁻ & \rightleftharpoons \text{[Ni(OH)₂(H₂IO₆)]}⁺ + \text{H₃IO₆}²⁻ & \quad (6)
\end{align*}
\]

Such types of equilibria have been well noticed in literature.⁵ It may be expected that monoperiodatonickelate(IV) (MPN) is more important in the reaction than the diperiodatonickelate(IV) (DPN). The inverse fractional order in [IO₄⁻] might also be due to this reason. Added acrylonitrile monomer did not undergo polymerization under inert atmosphere indicating the absence of free radical formation in the mixture.

The reaction between DPN and paracetamol in alkaline medium in the presence of ruthenium(III) has a 1: 2 stoichiometry of reductant to oxidant with first order dependence on both [DPN] and [Ruthenium(III)], the apparent less than unit order in [OH⁻] and [Paracetamol] and inverse fractional order in [IO₄⁻]. The less than unit order in [Paracetamol] presumably results from a complex formation between the catalyst ruthenium(III) and substrate prior to the formation of the products. Spectral evidence for such a catalyst-substrate complex was obtained from the UV-Vis spectra of mixture of ruthenium(III) and paracetamol and
ruthenium(III). A hypsochromic shift, \( \lambda_{\text{max}} \), of ca. 10 nm from 256 to 266 nm is observed together with hyperchromicity at 256 nm. Such complex between a substrate and a catalyst has been observed in other studies.\(^{14} \) Indeed, it is to be noted that a plot of \([\text{Ru(III)}]_0 / k_4 \) versus \(1/[[\text{Paracetamol}] \) \((r \geq 0.9978, S \leq 0.0162)\) shows a straight line with non-zero intercept. \( K_4 \) is the composite equilibrium constant comprising the equilibrium to bind paracetamol to catalyst ruthenium(III) and as well as hydrolysis of paracetamol. When there is a strong donor group (-NH\(_2\)), CH\(_3\)COOH may not involve in the formation of the complex. The complex reacts with monoperiodatonickelate(IV) (MPN) species in a slow step to form an intermediate species of paracetamol with regeneration of catalyst ruthenium(III). This intermediate species further reacts with another molecule of MPN species in a fast step to yield the products. All the results indicate a mechanism as given in Scheme 1.

\[
\begin{align*}
\text{[Ni(OH)\(_2\) (H\(_3\)IO\(_6\))\(_2\)]}^{2-} + \text{OH}^- \xrightarrow{K_4} \text{[Ni(OH)\(_2\) (H\(_3\)IO\(_6\) (H\(_2\)IO\(_6\))\(_3\)]}^{3+} + \text{H}_2\text{O} \\
\text{[Ni(OH)\(_2\) (H\(_3\)IO\(_6\) (H\(_2\)IO\(_6\))\(_3\)]}^{3+} \xrightarrow{K_5} \text{[Ni(OH)\(_2\) (H\(_2\)IO\(_6\))]}^{+} + \text{H}_3\text{IO}\(_6\)\(_2\)\(_2\) \\
\text{Complex (C)} + \text{CH}_3\text{COOH} \xrightarrow{K_6} \text{[Ni(OH)\(_2\) (H\(_2\)IO\(_6\))]}^{+} + \text{H}_2\text{IO}_5^- + \text{Ni(OH)}\(_2\) + \text{[Ru(H\(_2\)O\(_4\))OH]}^{2+}
\end{align*}
\]

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The probable structure of complex (C) is

In the presence of catalyst, the reaction is understood to occur in parallel paths with contribution from the uncatalysed and catalysed paths. Thus the total rate constant \( k_T \) is equal to the sum of the rate constants of the catalysed \( k_c \) and uncatalysed \( k_u \) reactions.

\[
\text{Rate}_{\text{cat}} = \text{Rate}_{\text{total}} - \text{Rate}_{\text{uncat}}
\]

Scheme 1 leads to the rate law equation (9),

\[
\text{Rate}_{\text{cat}} = -\frac{d[Ni(IV)]}{dt} = \frac{k K_4 K_5 K_6 [Ni(IV)] [H_3I0_6^2^-] [OH^-] [Paracetamol] [Ru(III)]}{[H_3I0_6^2^-] ([H_3I0_6^2^-] + K_4[H_3I0_6^2^-] [OH^-] + K_4 K_5 [OH^-]) (1 + K_6 [Paracetamol])}
\]
\[
\text{Rate} = \frac{k_c}{[\text{Ni(IV)}]} = \frac{k K_4 K_5 K_6 [\text{Paracetamol}] [\text{OH}^-] [\text{Ru(III)}]}{[\text{H}_3\text{I}O_6^2] + K_4 [\text{H}_3\text{I}O_6^2] [\text{OH}^-] + K_4 K_5 [\text{OH}^-] + K_6 [\text{H}_3\text{I}O_6^2] [\text{Paracetamol}] + K_4 K_6 [\text{H}_3\text{I}O_6^2] [\text{OH}^-] [\text{Paracetamol}] + K_4 K_5 K_6 [\text{OH}^-] [\text{Paracetamol}] + K_4 K_5 K_6 [\text{OH}^-] [\text{Paracetamol}]}
\]

Equation (8) can be arranged to (9), which is suitable for verification

\[
\frac{\text{Rate}_{cat}}{[\text{Ni(IV)}]} = k_c = k_{\text{r}} - k_{\text{u}}
\]

\[
k = \frac{k_4 K_5 K_6 [\text{Paracetamol}] [\text{OH}^-] [\text{Ru(III)}]}{[\text{H}_3\text{I}O_6^2] + K_4 [\text{H}_3\text{I}O_6^2] [\text{OH}^-] + K_4 K_5 [\text{OH}^-] + K_4 K_5 K_6 [\text{OH}^-] + K_4 K_5 K_6 [\text{OH}^-] [\text{Paracetamol}]}
\]

Equation (9) can be arranged to (10), which is suitable for verification

\[
\frac{[\text{Ru(III)}]}{k_c} = \frac{[\text{H}_3\text{I}O_6^2]}{k K_4 K_5 K_6 [\text{Paracetamol}] [\text{OH}^-]} + \frac{[\text{H}_3\text{I}O_6^2]}{k K_5 K_6 [\text{Paracetamol}]} + \frac{1}{k K_4 [\text{Paracetamol}]} + \frac{1}{k}
\]

According to equation (10), the plots of \([\text{Ru(III)}]/k_c\) versus 1/[Paracetamol] (\(r \geq 0.9978, S \leq 0.0162\)), \([\text{Ru(III)}]/k_c\) versus 1/[OH] (\(r \geq 0.9968, S \leq 0.0213\)), and \([\text{Ru(III)}]/k_c\) versus [H_3I06^2] (\(r \geq 0.9996, S \leq 0.0186\)) should be linear as shown in Figure VIII (iii) (p.269). From the slopes and intercepts, the values of \(K_4, K_5, K_6\) and \(k\) could be derived as 0.96 ± 0.04 dm^3 mol^-1, (3.54 ± 0.15) x 10^-4 mol dm^-3, 82.6 ± 4.1 dm^3 mol^-1 and (8.05 ± 0.3) x 10^6 dm^3 mol^-1 s^-1 respectively. The values of \(K_4\) and \(K_5\) are in agreement with literature values. Using these constants, the rate
Verification of rate law (9) in the form of (10) on the Ruthenium(III) Catalysed Reduction of Diperiodatonicelate(IV) by Paracetamol in aqueous alkaline medium at 25 °C.

(Conditions as in Table VIII (i) (p.256) and Table VIII (ii) (p.259))

\[ \frac{1}{[\text{OH}^\cdot]} \times 10^4 \text{ (dm}^3\text{ mol}^{-1}) \]

\[ \frac{[\text{Ru(III)}]/k_c \times 10^6 \text{ (mol dm}^{-3}\text{ s)} }{1/[	ext{PAM}] \times 10^3 \text{ dm}^{-3} \text{ mol}^{-1}} \]

\[ [\text{IO}_4^-] \times 10^4 \text{ (mol dm}^{-3}\)
constants were regenerated (Conditions as in Table VIII (i) (p.256) and Table VIII (ii) (p.259)).

The negligibly small effect of ionic strength on the reaction is presumably due to the fact that the reaction takes place between a neutral and charged species (Scheme 1). The effect of solvent on reaction rate is described elsewhere. This effect was studied by varying the t-butyl alcohol-water content in the reaction mixture with all other conditions being constant. Increasing the content of t-butanol in the reaction medium leads to an increase in the rate of reaction. The plot of log $k_c$ versus $1/e_T$ gives a straight line with positive slope ($r \geq 0.9998$, $S \leq 0.0112$), which is contrary to the expected slower reaction between ions of the same polarity in media of lower relative permittivity. Perhaps the effect is opposed substantially by an increased formation of active reaction species in low permittivity media, thus leading to the observed net increase in the rate.

The thermodynamic quantities for the fourth and fifth equilibrium step in Scheme 1 can be evaluated as follows. The hydroxyl ion concentration and $[\text{H}_3\text{IO}_6^{2-}]$ ion concentration (as in Table VIII (ii) (p.259)) was varied at five different temperatures. The plots of $[\text{Ru(III)}]/k_c$ versus $1/[\text{OH}^-]$ ($r \geq 0.9968$, $S \leq 0.0213$), and $[\text{Ru(III)}]/k_c$ versus $[\text{H}_3\text{IO}_6^{2-}]$ ($r \geq 0.9996$, $S \leq 0.0186$) should be linear as shown in Figure VIII (iii) (p.269). From the slopes and intercepts, the values of $K_4$, $K_5$ and $K_6$ were calculated at different temperatures and these values are given in Table VIII (v a) (p.272). A van't Hoff plot was made for the variation of $K_4$ and $K_5$ with temperature [i.e., log $K_4$ versus $1/T$ ($r \geq 0.9999$, $S \leq 0.0108$) and
log $K_5$ versus $1/T$ ($r \geq 0.9998$, $S \leq 0.0114$) as shown in Figure VIII (iv) (p.273) and the values of the enthalpy of reaction, $\Delta H$, entropy of reaction, $\Delta S$, and free energy of reaction, $\Delta G$, were calculated for both $K_4$ and $K_5$. These values are given in Table VIII (v b) (p.272). A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step are fairly slow and involves high activation energy.\(^{17}\)

The difference in the activation parameters for the catalysed ($k_c$) and uncatalysed ($k_a$) reaction (Table VIII (iv b) (p.262)) explains the catalytic effect on the reaction. The catalyst, Ru(III) forms the complex with paracetamol which shows more reducing property than paracetamol itself. Hence the catalyst, Ru(III) lowers energy of activation. The moderate values of $\Delta H^\#$ and $\Delta S^\#$ were both favorable for electron transfer processes. The high negative value of $\Delta S^\#$ indicates that the complex is more ordered than the reactants.\(^{18}\) The observed modest enthalpy of activation and higher rate constant of slow step indicate that the oxidation presumably occurs by inner-sphere mechanism. This conclusion is supported by earlier work.\(^{19}\)
Table VIII (v)

(a) Effect of temperature to calculate $K_4$, $K_5$ and $K_6$ on the Ruthenium(III) Catalysed Reduction of Diperiodatonickelate(IV) by Paracetamol in aqueous alkaline medium.

$$[\text{DPN}] = 6.0 \times 10^{-5};$$
$$[\text{Ru(III)}] = 6.0 \times 10^{-4};$$
$$[\text{IO}_4^-] = 2.0 \times 10^{-5}$$

$$[\text{Paracetamol}] = 8.0 \times 10^{-4};$$
$$[\text{OH}^-] = 0.20;$$
$$I = 1.0 / \text{mol dm}^{-3}.$$

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$K_4$ (dm$^3$ mol$^{-1}$)</th>
<th>$K_5 \times 10^2$ (mol dm$^{-3}$)</th>
<th>$K_6$ (dm$^3$mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.96</td>
<td>0.035</td>
<td>82.61</td>
</tr>
<tr>
<td>303</td>
<td>1.47</td>
<td>0.052</td>
<td>64.54</td>
</tr>
<tr>
<td>308</td>
<td>2.49</td>
<td>0.079</td>
<td>44.32</td>
</tr>
<tr>
<td>313</td>
<td>3.86</td>
<td>0.118</td>
<td>25.56</td>
</tr>
<tr>
<td>318</td>
<td>5.82</td>
<td>0.189</td>
<td>10.23</td>
</tr>
</tbody>
</table>

(b) Thermodynamic quantities for the first and second equilibrium steps of Scheme 1 ($K_4$ and $K_5$ values).

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>$K_4$ Values</th>
<th>$K_5$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>$71.6 \pm 3.2$</td>
<td>$65.6 \pm 3.2$</td>
</tr>
<tr>
<td>$\Delta S$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>$239 \pm 10$</td>
<td>$153 \pm 7$</td>
</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
<td>$-10.6 \pm 0.3$</td>
<td>$18.2 \pm 0.8$</td>
</tr>
</tbody>
</table>
Effect of temperature on the Ruthenium(III) Catalysed Reduction of Diperiodatonicelate(IV) by Paracetamol in aqueous alkaline medium.

(Conditions as in Table VIII (v a) (p.272))
IMPORTANCE OF CHAPTER VIII

Among various species of nickel(IV) in alkaline medium, monoperiodatonicelate is considered as active species for the title reaction. Rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to slow step of reaction were computed. In alkaline medium, a micro amount of ruthenium(III) is sufficient to catalyse the title reaction with measurable rate. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.
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