CHAPTER VII

Kinetic, Mechanistic and Spectral Investigation of Ruthenium(III) Catalysed Oxidation of Atenolol by Alkaline Permanganate by Stopped Flow Technique

The general importance of permanganate is given in chapter V (p.139).

The substrate, 4-(2-hydroxy-3-isopropylaminopropoxy) phenylacetamide commercially known as atenolol (ATN) a β-adrenoreceptor blocking agent is used as antihypertensive drug.¹ It is also used for anti-angina treatment to relieve symptoms, improve tolerance and as an anti-arrhythmic to regulate heartbeat and infections. It is also used in management of alcohol withdrawal, in anxiety states, migraine prophylaxis, hyperthyroidism and tremor. The derivative of oxidation product of atenolol finds its importance in biological systems such as plant growth hormones, herbicides, etc.

Ruthenium(III) acts as an efficient catalyst in many redox reactions particularly in an alkaline medium.² The catalysed mechanism can be quite complicated due to the formation of different intermediate complexes, free radicals and different oxidation states of ruthenium. The kinetics of fast reaction between ruthenate(VII), RuO₄⁻, and manganate(VI), i.e. MnO₄²⁻ have been studied³ and the reaction is presumed to proceed via an outer-sphere mechanism. The uncatalysed reaction between atenolol and permanganate in an alkaline medium has been studied previously.⁴ A microscopic amount of ruthenium(III) is
sufficient to catalyse the reaction and a variety of mechanisms are possible. Herein we describe the results of the title reaction in order to understand the active species of oxidant, reductant and catalyst in such media and to arrive at a plausible mechanism. The results of such investigation are given in this chapter.

EXPERIMENTAL

Materials

All chemicals used were of reagent grade. Solution of atenolol (M/s. S.S. Antibiotics Pvt. Ltd, Aurangabad, India) was prepared by dissolving appropriate amount of recrystallised sample in double distilled water. The solution of permanganate was prepared and standardized as given in chapter V (p.141).

The Ru(III) solution was prepared by dissolving a known weight of RuCl₃ (S.D.Fine-Chem) in HCl (0.20 mol dm⁻³). The mercury was added to the Ru(III) solution to reduce any Ru(IV) formed during the preparation of the Ru(III) stock solution which was set aside for 24 hours. The Ru(III) concentration was then assayed by EDTA titration. NaOH and NaClO₄ were used to provide the required alkalinity and the ionic strength respectively.

Kinetic Measurements

All kinetic measurements were performed under pseudo-first order conditions with excess of [Atenolol] over [MnO₄⁻] at a constant ionic strength of 0.30 mol dm⁻³. The reaction was initiated by mixing previously thermostatted solutions of MnO₄⁻ and atenolol, which also contained the necessary quantities of Ru(III), NaOH and NaClO₄ to maintain the required alkalinity and ionic strength respectively. The
temperature was maintained at 25 ± 0.1 °C. The course of reaction was followed by monitoring the decrease in the absorbance of MnO₄⁻ in a 1 cm quartz cell of Peltier Accessory (temperature control) attached Varian CARY 50 Bio UV-Vis spectrophotometer connected to a rapid kinetic accessory (HI-TECH SFA-12), at its absorption maximum of 526 nm as a function of time. The application of Beer's law to permanganate at 526 nm had been verified, giving ε = 2083 ± 50 dm³ mol⁻¹ cm⁻¹ (Literature ε = 2200 dm³ mol⁻¹ cm⁻¹). The first-order rate constants, (k_c) were evaluated by the plots of log (A_t - A_w) versus time by fitting the data to the expression A_t = A_w + (A_0 - A_w)e⁻ᵏᶜᵗ, where A_t, A_0 and A_w are absorbance's of permanganate at time t, 0 and ∞ respectively. The first order plots in almost all cases were linear to 80 % completion of the reaction and k_c were reproducible within ± 5 %. During the course of measurements, the solution changed from violet to blue and then to green. The spectrum of the green solution was identical to that of MnC₄²⁻. It is probable that the blue colour originated from the violet of permanganate and the green from the manganate, excluding the accumulation of hypomanganate. It is also evident from the Figure VII (i) (p.219) that the absorbance of permanganate decreases at 526 nm whereas the absorbance of manganate increases at 608 nm.

The effect of dissolved oxygen on the rate of reaction was studied by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results was observed. In view of
Spectroscopic changes occurring in the Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate with \([\text{ATN}] = 1.5 \times 10^{-3}, [\text{MnO}_4^-] = 1.5 \times 10^{-4}, [\text{Ru(III)}] = 1.0 \times 10^{-6}, [\text{OH}^-] = 0.05, \text{ and } I = 0.30; \text{ mol dm}^{-3} \text{ at } 25^\circ \text{C}, \text{ Scanning time interval } = 120 \text{ sec.} \)
the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used during the experiments.

In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.

Regression analysis of experimental data to obtain the regression coefficient, 'r' and standard deviation, 'S' of points from the regression line was performed using a Pentium-IV personal computer.

RESULTS

Stoichiometry and Product Analysis

The reaction mixtures containing an excess permanganate concentration over atenolol, and constant [Ruthenium(III)], 0.05 mol dm⁻³ NaOH and at constant ionic strength of 0.30 mol dm⁻³ was allowed to react for 2 hours at 25 ± 0.1 °C. The remaining permanganate was then analysed spectrophotometrically. The results indicated that eight moles of MnO₄⁻ were consumed by one mole of atenolol as given by equation (1). The results are given in Table VII (i) (p.222).
For identification of products, the reaction mixture containing excess of atenolol was kept for completion of reaction. The reaction product, 4-carboxy methoxy phenyl acetic acid was extracted with ether and recrystallised from aqueous alcohol and the purity was checked by HPLC. This is identified as 4-carboxy methoxy phenyl acetic acid by its IR spectrum, which showed a band at (υ) 1690 cm$^{-1}$ due to $>$C=O stretching of acid and a broad band at 2845 cm$^{-1}$ due to O-H stretching. 4-carboxy methoxy phenyl acetic acid was further characterised by $^1$H NMR spectrum (DMSO), showed a singlet at 9.6 $\delta$ due to two carboxylic OH, a doublet ($J=9$ Hz) at 6.94 $\delta$ due to C$_3$- and C$_5$- protons, another doublet ($J=9$ Hz) at 7.20 $\delta$ due to C$_7$- and C$_9$- protons, a singlet at 3.53 $\delta$ due to methylene protons of ph-CH$_2$-and another singlet at 4.58 $\delta$ due to methylene protons of ph-O-CH$_2$-respectively and Mass spectra ESI technique (solvents : Acetonitrile + water + ammonium acetate) ($M^++17$) (ammoniated) 228 and ($M^+$) m/z 211. Ammonia was identified by using Nessler's reagent.$^6$ The product, Ni(II) which remains in aqueous layer and it was identified by its dimethyl glyoxime complex.$^7$
Table VII (i)

Stoichiometry of Ruthenium(III) Catalysed Oxidation of Atenolol by alkaline Permanganate at 25 °C.

$[\text{OH}^-] = 0.05; \quad [\text{Ru(III)}] = 1.0 \times 10^{-6};$

$I = 0.30 / \text{mol dm}^{-3}.$

<table>
<thead>
<tr>
<th>$[\text{MnO}_4^-] \times 10^4$ (mol dm$^{-3}$)</th>
<th>$[\text{ATN}] \times 10^4$ (mol dm$^{-3}$)</th>
<th>$[\text{MnO}_4^-] \times 10^4$ (mol dm$^{-3}$)</th>
</tr>
</thead>
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</table>
N-(isopropyl) amino carboxylic acid which is soluble in water was identified by spot test.\textsuperscript{8} It was observed that the 4-carboxy methoxy phenyl acetic acid and N-(isopropyl) amino carboxylic acid do not undergo further oxidation under the present kinetic conditions. A spectrofluorimetric study has been performed as in chapter III (p.77).

**Reaction Orders**

As the permanganate oxidation of atenolol 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 reductant, Ru(III) and alkali in turn while keeping the others constant.

**Effect of [Permaganate]**

The potassium permanganate concentration was varied in the range of $2.0 \times 10^{-5}$ to $2.0 \times 10^{-4}$ mol dm$^{-3}$, and the linearity of plots of log ($A_t - A_w$) versus time ($r \geq 0.9998, S \leq 0.0131$) up to 80% completion of the reaction (Figure VII (ii) (p.224)) indicated a reaction order of unity in [MnO$_4$]. This was also confirmed by variation of [MnO$_4$], which did not result any change in the pseudo-first order rate constants, $k_c$ as in Table VII (ii) (p.226).
Figure VII (ii)

First order plots of Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium at 25 °C.

\[ [\text{MnO}_4^-] \times 10^4 \text{ (mol dm}^{-3}) \]:

(1) 0.2; (2) 0.4; (3) 1.0; (4) 1.5; (5) 2.0

(Conditions as given in Table VII (ii) (p.226))
Effect of [Atenolol]
The substrate concentration was varied in the range $1.0 \times 10^{-3}$ to $1.0 \times 10^{-2}$ mol dm$^{-3}$ at 25 °C while keeping all other reactant concentrations and conditions constant including ruthenium(III) catalyst. The $k_c$ values increased with increase in concentration of atenolol indicating an apparent less than unit order dependence on [Atenolol] as shown in Table VII (ii) (p.226) and Figure VII (iii) (p.227) ($r \geq 0.9992$, $S \leq 0.0124$).

Effect of [Ruthenium(III)]
The ruthenium(III) concentration was varied from $8.0 \times 10^{-7}$ to $8.0 \times 10^{-6}$ mol dm$^{-3}$ range, at constant concentration of permanganate, atenolol, alkali and ionic strength. The order in [Ru(III)] was found to be unity from the linearity of the plots of log $k_c$ versus log [Ru(III)] as shown in Table VII (iii) (p.228) and Figure VII (iv) (p.229) ($r \geq 0.9995$, $S \leq 0.0122$).

Effect of [Alkali]
The effect of alkali on the reaction has been studied at constant concentrations of atenolol, potassium permanganate, ruthenium(III) and at constant ionic strength of 0.30 mol dm$^{-3}$. The rate constants increased with increasing [Alkali] and the order was found to be less than unity as shown in Table VII (iii) (p.228) and Figure VII (iv) (p.229) ($r \geq 0.9991$, $S \leq 0.0116$).
Table VII (ii)

Effect of variation of [Permanganate] and [Atenolol] on Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium at 25 °C.

\[ [\text{Ru(III)}] = 1.0 \times 10^{-6}; \quad [\text{OH}^{-}] = 0.05; \]

\[ 1 = 0.30 / \text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>([\text{MnO}_4^-] \times 10^3) (mol dm(^{-3}))</th>
<th>([\text{ATN}] \times 10^3) (mol dm(^{-3}))</th>
<th>(k_T \times 10^2) (s(^{-1}))</th>
<th>(k_p \times 10^2) (s(^{-1}))</th>
<th>(k_c \times 10^2) (s(^{-1}))</th>
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226
Figure VII (iii)

Order in [Atenolol] on the Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium at 25 °C.

(Conditions as in Table VII (ii) (p.226))
Table VII (iii)

Effect of variation of [Ru(III)] and [OH'] on the Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium at 25 °C.

\[ [\text{MnO}_4^-] = 1.5 \times 10^{-4}, \quad [\text{ATN}] = 1.5 \times 10^{-3}, \]

\[ I = 0.30 / \text{mol dm}^{-3}. \]

<table>
<thead>
<tr>
<th>[Ru(III)] ( \times 10^6 ) (mol dm(^{-3} ))</th>
<th>[OH'] (mol dm(^{-3} ))</th>
<th>( k_T \times 10^2 ) (s(^{-1} ))</th>
<th>( k_a \times 10^2 ) (s(^{-1} ))</th>
<th>( k_c \times 10^2 ) (s(^{-1} )) Found</th>
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228
Figure VII (iv)

Order in [Ru(III)] and [OH\textsuperscript{-}] on the Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium at 25 °C.

(Conditions as in Table VII (iii) (p.228))
Effect of Ionic Strength

The effect of ionic strength was studied by varying the NaClO₄ concentration in the reaction medium. The ionic strength was varied from 0.05 to 0.50 mol dm⁻³ at constant concentrations of permanganate, atenolol, ruthenium(III) and alkali. It was found that the rate constant decreased with increasing concentration of NaClO₄ (Table VII (iv) (p.231)). The plot of log $k_C$ versus $I^{1/2}$ was linear with a negative slope as shown in Figure VII (v) (p.232) ($r \geq 0.9997$, $S \leq 0.0112$).

Effect of Solvent Polarity

The effect of relative permittivity ($\varepsilon_T$) on the rate constant has been studied by varying the t-butanol–water content in the reaction mixture with all other conditions being maintained constant including ruthenium(III) catalyst. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids⁹ as in chapter II (p.45). No reaction of the solvent with the oxidant occurred under the experimental conditions employed. The rate constant, $k_C$ increased with decreasing relative permittivity of the medium (Table VII (iv) (p.231)). The plot of log $k_C$ versus $1/\varepsilon_T$ was linear with a positive slope as shown in Figure VII (v) (p.232) ($r \geq 0.9989$, $S \leq 0.0141$).

Effect of Initially Added Products

The initially added products, such as manganate, and 4-carboxy methoxy phenyl acetic acid, did not have any significant effect on the rate of the reaction.

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### Table VII (iv)

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

\[
\begin{align*}
[MnO_4^-] &= 1.5 \times 10^{-4}, \\
[ATN] &= 1.5 \times 10^{-3}, \\
[Ru(III)] &= 1.0 \times 10^{-6}, \\
[OH^-] &= 0.05;
\end{align*}
\]

\[
\begin{align*}
I &= 0.30 / \text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>I (mol dm$^{-3}$)</th>
<th>$k_c \times 10^2$ (s$^{-1}$)</th>
<th>$%$ of t-butanol-water</th>
<th>$\varepsilon_T$</th>
<th>$k_c \times 10^2$ (s$^{-1}$)</th>
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*t-butanol-water (V/V)
Figure VII (v)

Effect of Ionic Strength (I) and Relative Permittivity ($\varepsilon_r$) on the Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium at 25 °C.

(Conditions as in Table VII (iv) (p.231))
Test for Free Radicals

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 24 hours under nitrogen atmosphere. On dilution with methanol, white precipitate of polymer was formed, indicating the presence of intervention of free radicals in the reaction. The blank experiment of either permanganate and ruthenium(III) or atenolol and ruthenium(III) alone with acrylonitrile did not induce polymerization under the same condition as those induce with reaction mixtures. Initially added acrylonitrile decreases the rate indicating the free radical intervention, which is the case in earlier work.10

Effect of Temperature

The rate of reaction was measured at different temperatures under varying atenolol concentration. The rate of reaction increased with the increase of temperature. The rate constants, $k$ of slow step of Scheme 1 were obtained from slope of the plot of $[\text{Ru(III)}]/k_c$ versus $1/\text{[Atenolol]}$ ($r \geq 0.9996, S \leq 0.0121$) at different temperatures. The data are subjected to least square analysis as in chapter II (p.50) and were tabulated in Table VII (v a) (p.234). The energy of activation corresponding to these constants was evaluated from the plot ($Y^*_{ea}$) log $k$ versus $1/T$ (Fig. VII (vi) (p.235) ($r \geq 0.9989, S \leq 0.0135$) and other activation parameters are obtained as in chapter II (p.50) and are tabulated in Table VII (v b) (p.234).
Table VII (v)

(a) Effect of temperature on the slow step of the mechanism of Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium.

\[
[MnO_4^-] = 1.5 \times 10^{-4}; \\
[Ru(III)] = 1.0 \times 10^{-6}; \\
I = 0.30 \text{ / mol dm}^3. \\
[ATN] = 1.5 \times 10^{-3}; \\
[OH^-] = 0.05;
\]

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<tr>
<th>Temperature (K)</th>
<th>(k \times 10^4) (dm(^3)\text{.mol}^{-1}\text{.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.

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<th>Uncatalysed reaction(^4)</th>
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<tr>
<td>(E_a) (kJ mol(^{-1}))</td>
<td>13.7 ± 0.7</td>
<td>24 ± 3</td>
</tr>
<tr>
<td>(\log A)</td>
<td>7.74 ± 0.4</td>
<td>-</td>
</tr>
<tr>
<td>(\Delta H^\circ) (kJ mol(^{-1}))</td>
<td>11.2 ± 0.6</td>
<td>21 ± 3</td>
</tr>
<tr>
<td>(\Delta S^\circ) (JK(^{-1}) mol(^{-1}))</td>
<td>-25.1 ± 1.3</td>
<td>-200 ± 10</td>
</tr>
<tr>
<td>(\Delta G^\circ) (kJ mol(^{-1}))</td>
<td>18.8 ± 1.0</td>
<td>82 ± 4</td>
</tr>
</tbody>
</table>
Figure VII (vi)

Effect of temperature on the Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium.

(Conditions as in Table VII (v) (p.234))
DISCUSSION

Permanganate ion, MnO₄⁻, is a powerful oxidant in an aqueous alkaline medium. As it exhibits many oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the prevailing experimental conditions at pH > 12, the reduction product of Mn(VII), i.e. Mn(VI), is stable and further reduction of Mn(VI) might be stopped.¹¹ The Diode Array Rapid Scan Spectrophotometric (DARSS) studies have shown that at pH > 12, the product of Mn(VII) is Mn(VI) and no further reduction was observed as reported¹² by Simandi et al. However, on prolonged standing, the green Mn(VI) is reduced to Mn(IV) under our experimental conditions.

The permanganate in alkaline medium exhibits various oxidation states, such as Mn(VII), Mn(V) and Mn(VI). The colour of the solution changed from violet to blue and further to green excluding the accumulation of hypomanganate. The violet colour originated from permanganate and blue from hypomanganate is observed during the course of the reaction.

It is interesting to identify the probable species of ruthenium(III) chloride in alkaline medium. Electronic spectral studies¹³ have confirmed that ruthenium(III) chloride exists in hydrated form as [Ru(H₂O)₆]³⁺. In the present study of alkaline medium it is quite probable that the species [Ru(H₂O)₃OH]²⁺ might assume the general form [Ru⁺⁻(OH)ₓ]³⁻. The value of x would always be less than six because there are no definite reports of any hexahydroxy species of ruthenium. The remainder of the coordination sphere will be filled by water molecule. Hence
under the experimental conditions [OH'] >> [Ru\textsuperscript{III}], ruthenium(III) is mostly present\textsuperscript{14} as the hydroxylated species, [Ru(H\textsubscript{2}O)\textsubscript{6}OH]\textsuperscript{2+}.

The reaction between permanganate and atenolol in alkaline medium in presence of ruthenium(III) has a stoichiometry of 1:8 with a first order dependence on the [\textsubscript{MnO\textsubscript{4}}\textsuperscript{-}] and [Ruthenium(III)] and less than unit order dependence on both the [alkali] and [atenolol]. No effect of added products was observed. The apparent order of less than unity, in [OH'] may be an indication of the formation of permanganate species as alkali permanganate, MnO\textsubscript{4}OH\textsuperscript{2}, from permanganate ion in a prior-equilibrium step.\textsuperscript{15,16} The formation of MnO\textsubscript{4}OH\textsuperscript{2} species in alkaline medium was further supported by the Michaelis-Menten plot ([Ru(III)]/k\textsubscript{c} versus 1/[ATN]) which is linear with a positive intercept. Based on the experimental results, a mechanism can be proposed for which all the observed orders with respect to each constituent such as oxidant, catalyst, reductant and OH\textsuperscript{-} may be well accommodated. Here the hydroxylated species of ruthenium(III) reacts with ATN to give a complex (C), which on reacting with one mole of alkali permanganate species in a slow step to form a free radical derived from atenolol, and product MnO\textsubscript{4}\textsuperscript{2} with regeneration of catalyst, ruthenium(III). Such a complex formation between substrate and catalyst has also been observed in earlier work,\textsuperscript{17,18} which is also supported by the observed fractional order in [Atenolol]. The free radical derived from atenolol combines with one mole of permanganate species in a fast step to form a diol. This diol on reacting with
further six more moles of permanganate species in further fast steps gives the products as given in Scheme 1.

\[
\text{MnO}_4^- + \text{OH}^- \xrightleftharpoons[K_1]{\text{K}_2}[\text{Complex}(C)]^{2-} \rightarrow [\text{Mn(OH)}_2]^{2-}
\]

\[
\text{Complex}(C) + [\text{Ru(H}_2\text{O)}_5\text{OH}]^{2+} \rightarrow \text{products}
\]

\[
\text{products} \rightarrow \text{MnO}_4^{2-} + [\text{Ru(H}_2\text{O)}_5\text{OH}]^{2+} + \text{H}_2\text{O}
\]
Probable structure of the complex (C) is given by
Spectral evidence for such a catalyst-substrate complex was obtained from the UV-Vis spectra of atenolol and mixture of ruthenium(III) and atenolol. A hypsochromic shift, $\lambda_{\text{max}}$, of ca. 5 nm from 343 to 338 nm is observed together with hyperchromicity at 338 nm.

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 following rate law (8)

$$\text{Rate}_{\text{cat}} = k \left[ C \right] \left[ \text{MnO}_4 \text{OH} \right]^2$$

$$= k K_1 K_2 \left[ \text{ATN} \right]_t \left[ \text{MnO}_4 \right]_t \left[ \text{OH}^- \right]_t \left[ \text{Ru(III)} \right]_t$$

(2)

The total concentration of atenolol, $[\text{ATN}]_t$, is given by (Subscripts $t$ and $f$ stand for total and free)

$$[\text{ATN}]_t = [\text{ATN}]_f + [C]$$

$$= [\text{ATN}]_f + K_2 \left[ \text{ATN} \right]_f \left[ \text{Ru(III)} \right]_f$$

$$= [\text{ATN}]_f (1 + K_2 \left[ \text{Ru(III)} \right])$$

Therefore,

$$[\text{ATN}]_f = \frac{[\text{ATN}]_t}{1 + K_2 \left[ \text{Ru(III)} \right]}$$

(3)

Similarly,

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_t}{1 + K_1 \left[ \text{MnO}_4 \right]^2}$$

(4)
Substituting the equations (3), (4), (5) and (6) in equation (2), we get

\[
\text{Rate} = -\frac{d \left[ \text{MnO}_4^- \right]}{dt} = \frac{k K_1 K_2 \left[ \text{ATN} \right] \left[ \text{Ru(III)} \right] h \left[ \text{OH}^- \right]_h}{(1 + K_2 [\text{ATN}]) (1 + K_2 [\text{Ru(III)}]) (1 + K_1 [\text{MnO}_4^-]) (1 + K_1 [\text{OH}^-])}
\]

The terms \((1 + K_1 [\text{MnO}_4^-])\) and \((1 + K_2 [\text{Ru(III)}])\) in the denominator of equation (7) approximate to unity in view of low concentrations of \(\text{MnO}_4^-\) and ruthenium(III) used. (omitting the subscripts 't' and 'f'). In terms of rate constants,

\[
\frac{\text{Rate}}{[\text{MnO}_4^-]} = \frac{k_c}{k_c} = k_f - k_a = \frac{k K_1 K_2 \left[ \text{ATN} \right] \left[ \text{Ru(III)} \right] [\text{OH}^-]}{1 + K_1 [\text{OH}^-] + K_2 [\text{ATN}] + K_1 K_2 [\text{OH}^-] [\text{ATN}]}
\]

The above equation (8) can be rearranged to the following form, which is used for the verification of the rate law.

\[
\frac{[\text{Ru(III)}]}{k_c} = \frac{1}{k K_1 K_2 [\text{ATN}] [\text{OH}^-]} + \frac{1}{k K_2 [\text{ATN}]} + \frac{1}{k K_1 [\text{OH}^-]} + \frac{1}{k}
\]

According to equation (9), the plots of \([\text{Ru(III)})/k_c\) versus \(1/[\text{ATN}]\) \((r \geq 0.9996, S \leq 0.0121)\) and \([\text{Ru(III)})/k_c\) versus \(1/[\text{OH}^-]\) \((r \geq 0.9999, S \leq 0.0113)\) are linear with an intercept supporting the Ru(III)-atenolol complex, and which is verified as shown in Figure VII (vii) (p.242). From the slope and intercept of such
Figure VII (vii)

Verification of rate law (8) in the form of (9) on the Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium at 25 °C.

(Conditions as in Table VII (ii) (p.226) and Table VII (iii) (p.228))

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

\[ 1/[[\text{ATN}] \times 10^{-3} \text{ (dm}^3\text{mol}^{-1}) \]

\[ [\text{Ru(III)}]/k_c \times 10^5 \text{ (mol dm}^{-3}\text{s}) \]
The values of $K_1$, $K_2$ and $k$ are calculated as $15.0 \pm 0.75 \text{ dm}^3\text{mol}^{-1}$, $(4.20 \pm 0.21) \times 10^2 \text{ dm}^3\text{mol}^{-1}$ and $(2.10 \pm 0.1) \times 10^5 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$. The value of $K_i$ is in agreement with earlier value.\textsuperscript{19} Using these $K_1$, $K_2$ and $k$ values, the rate constants under different experimental conditions were calculated by equation (8) and compared with experimental data. There is a good agreement between them as given in Table VII (ii) (p.226) and Table VII (iii) (p.228).

The effect of ionic strength on the rate can be understood essentially on the basis of ionic species as in Scheme 1. The effect of solvent on the reaction rate has been described in detail in the literature.\textsuperscript{20} Increasing the content of t-butanol in the reaction medium leads to an increase in the rate of reaction, which seems to be contrary to the expected interaction between neutral and anionic species in media of lower relative permittivity. However, an increase in the rate of reaction with decreasing dielectric constant may be due to stabilization of the complex (C) at low relative permittivity, which is less solvated than $\text{MnO}_4^-$ at higher relative permittivity because of its larger size. Spectrofluorimetric studies reveal that the fluorescence intensity is quenched, which may be due to the electron transfer reaction.\textsuperscript{21}

The difference in the activation parameters for the catalysed ($k_c$) and uncatalysed ($k_u$) reaction as in Table VII (ii) (p.226) and Table VII (iii) (p.228) explains the catalytic effect on the reaction. The catalyst, Ru(III) forms the complex with atenolol which shows more reducing property than atenolol itself. Hence the catalyst, Ru(III) lowers energy of activation. The negative value of $\Delta S^\#$
indicates that the complex (C) is more ordered than the reactants.\textsuperscript{22} The observed modest enthalpy of activation and higher rate constant of slow step (than $k_c$) indicate that the oxidation presumably occurs by inner-sphere mechanism. This conclusion is supported by earlier work.\textsuperscript{23,24}

The thermodynamic quantities for the first equilibrium step in Scheme 1 can be evaluated as follows. The hydroxyl ion concentration (Table VII (iii) (p.228)) was varied at different temperatures. The plots of $[\text{Ru(III)}]/k_c$ versus $1/[\text{OH}^-]$ ($r \geq 0.9999$, $S \leq 0.0113$) should be linear as shown in Figure VII (vii) (p.242). From the slopes and intercepts, the values of $K_1$ are calculated at different temperatures and these values are given in Table VII (vi a) (p.245). A van't Hoff plot was made for the variation of $K_1$ with temperature [i.e., log $K_1$ versus $1/T$ ($r \geq 0.9998$, $S \leq 0.0128$)] as shown in Figure VII (viii) (p.246) and the values of the enthalpy of reaction $\Delta H$, entropy of reaction $\Delta S$ and free energy of reaction $\Delta G$, were calculated. These values are also given in the Table VII (vi b) (p.245). 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.\textsuperscript{25}
Table VII (vi)

(a) Effect of temperature to calculate $K_1$ and $K_2$ for Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium.

\[
\begin{align*}
[MnO_4^-] &= 1.5 \times 10^{-4}; \\
[ATN] &= 1.5 \times 10^{-3}; \\
[Ru(III)] &= 1.0 \times 10^{-6}; \\
[OH^-] &= 0.05; \\
I &= 0.30 / \text{mol dm}^3.
\end{align*}
\]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_1$ (dm$^3$ mol$^{-1}$)</th>
<th>$K_2 \times 10^2$ (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>15.0</td>
<td>4.20</td>
</tr>
<tr>
<td>303</td>
<td>18.2</td>
<td>3.91</td>
</tr>
<tr>
<td>308</td>
<td>21.5</td>
<td>3.63</td>
</tr>
<tr>
<td>313</td>
<td>25.1</td>
<td>3.36</td>
</tr>
<tr>
<td>318</td>
<td>29.4</td>
<td>3.08</td>
</tr>
</tbody>
</table>

(b) Thermodynamic quantities for the first equilibrium of Scheme 1 ($K_1$ values).

<table>
<thead>
<tr>
<th>Thermodynamic quantities</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kJ mol$^{-1}$)</td>
<td>25.9 ± 1.4</td>
</tr>
<tr>
<td>$\Delta S$ (JK$^{-1}$ mol$^{-1}$)</td>
<td>110 ± 6</td>
</tr>
<tr>
<td>$\Delta G$ (kJ mol$^{-1}$)</td>
<td>-7.8 ± 0.4</td>
</tr>
</tbody>
</table>
Figure VII (viii)

Effect of temperature on the Oxidation of Ruthenium(III) Catalysed Oxidation of Atenolol by Permanganate in aqueous alkaline medium.

(Conditions as in Table VII (vi a) (p.245))
IMPORTANCE OF CHAPTER VII

It is interesting that the oxidant species [MnO₄⁻] requires a pH > 12, below which the system becomes disturbed and the reaction will proceed further to give a reduced product of the oxidant as Mn(IV), which slowly develops yellow turbidity. Hence, it becomes apparent that in carrying out this reaction the role of pH in a reaction medium is crucial. It is also noteworthy that under the conditions studied the reaction occurs in two successive one-electron reductions (Scheme 1) rather than two-electron in a single step. Ruthenium(III) is known to be an efficient catalyst especially 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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