Kinetics of Ru(III) catalysed oxidation of phenethyl alcohol and para-substituted phenethyl alcohols by Ce(IV) in aqueous nitric acid medium

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A simple, rapid and sensitive spectroscopic method for the kinetics of Ru(III) catalysed oxidation of phenethyl alcohol (PA) by Ce(IV) in aqueous nitric acid medium has been reported under varying conditions. The reaction is followed spectrophotometrically by measuring the decrease in absorbance of Ce(IV) at 350 nm. The rates show first order dependence on [Ce(IV)] and the rate constants evaluated at different [Ce(IV)] are found to be almost the same. Increase in [Ru(III)] has linear relation with the rate of oxidation and order in [Ru(III)] has been found to be fractional. Variation in ionic strength of the medium has significant effect on the rate of reaction. The rates of the reaction have been measured at different temperatures and the activation parameters for all the substrates computed. The rates decrease in the order − OCH₃ > −CH₃ > −H > −Ce(NO₃)₂ of para substituted phenethyl alcohols. Hammett’s plot of log kₒw versus σ is found to be valid. The correlation between enthalpies and free energies of activation is reasonably linear with an isokinetic temperature of 425K. The rate constant kₒ follows corresponding equation, kₒ = Qₑ x e⁻ᴱᵃ x s⁻¹. Ea increases with introduction of electron-withdrawing groups into the benzene ring. The introduction of electron-releasing groups lowers the Ea for the reaction. Similarly, logA decreases with substitution of electron-withdrawing groups and increases with substitution of electron-releasing groups. A plausible mechanism consistent with the experimental results has been proposed.

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Oxidation of alcohols has been studied by several workers. Aromatic alcohols have found wide applications in synthetic and pharmaceutical industries. Among the aromatic alcohols, phenethyl alcohols are found in a number of essential oils such as Champaca rose and alleppeopine. Richard et al. have studied antibacterial activity and found that these are being used as preservatives in ophthalmic solutions. Due to their synthetic importance several workers have made attempts to study these compounds by different oxidants, such as sodium-N-bromobenzene sulphonamide and peroxydisulphate. Oxidation of phenethyl alcohols by Ce(IV) in aqueous nitric acid medium has not been reported so far. Further, phenethyl alcohols are found to be resistant to oxidation under normal conditions though there are number of reports on the oxidation of aromatic alcohols like benzyl alcohols. Oxidations of benzyl alcohols are comparatively easier than phenethyl alcohols, because stable intermediate benzyl free radical is assumed to be formed in the oxidations of benzyl alcohols. Due to the addition of one more methylene (−CH₂−), phenethyl alcohols are found to be resistant to oxidation. Hence, it is worthwhile to study oxidation of phenethyl alcohol and its substituted derivatives in the presence of Ru(III) by Ce(IV) in aqueous HNO₃ medium.

Experimental
All chemicals were of the highest purity and were used without further purification. Doubly distilled water was used throughout. Ceric ammonium nitrate stock solution was prepared by dissolving the required amount of (NH₄)₆Ce(NO₃)₈ in 1 mol dm⁻³ of HNO₃. The solution was standardised and stored in a dark coloured bottle. Stability of the oxidant was checked at regular intervals by adding definite volume of it to a known excess of ferrous ammonium sulphate solution and backtitrating the unreacted ferrous with standard ceric nitrate solution using ferroin as an indicator. Working solutions were prepared by appropriate dilution of the stock solution with double distilled water.

Phenethyl alcohol stock solutions were prepared in water-acetonitrile mixture (60:40 v/v). Ionic strength of the medium was varied between 0.25-2.50 mol dm⁻³ using concentrated aqueous solutions of KNO₃ and HNO₃.

Kinetic measurements were carried out on a 117-UV-visible spectrophotometer (Systronics). The progress of the reaction was monitored by measuring variation of absorbance of Ce(IV) at 350 nm. The kinetic studies were carried out under pseudo-first order conditions using [PA] ≫ [Ce(IV)]. To a thermally equilibrated solution containing Ce(IV), HNO₃, Ru(III), PA solutions at the same temperature were added to form the reaction mixture. A portion of such reaction mixture (2 ml) was immediately
transferred into a cuvette for absorbance measurements. The progress of the reaction was monitored at regular time intervals by observing variation of optical density with time. Nitrogen gas was bubbled through the reaction mixture to expel dissolved oxygen. H+ ion concentration and ionic strength were maintained constant by the addition of required amounts of HNO3 and KNO3 solutions respectively. The pseudo-first order rate constants \( k_{\text{obs}} \) were computed by the graphical methods and the experimental values were reproducible within ±3%.

Stoichiometry of PA-Ce(IV) reaction was determined by allowing the Ru(III) catalysed oxidation to go to completion at room temperature by maintaining PA and Ce(IV) in 1:4 molar ratio. The observed stoichiometry was found to be

\[
\text{C}_6\text{H}_2\text{CH}_2\text{CH}_2\text{OH} + 4\text{Ce(IV)} \xrightarrow{\text{Ru(III)}} \text{C}_6\text{H}_2\text{CH}_2\text{COOH} + 4\text{Ce(III)}
\]

Oxidation product of phenethyl alcohol was detected by thin layer chromatography, using butan-1-ol-ethyl acetate - water(4:1:5 v/v/v) as the solvent and iodine as detecting agent \( (R_f = 0.86) \). The reported \( R_f \) value is consistent with the value of authentic sample as the reference one. In a typical experiment the solution of PA (0.2 mol), Ce(IV) (0.05 mol) and Ru(III) (0.007 mol) were dissolved in 50 ml water - acetonitrile mixture (60:40 v/v) and allowed to stand for ca. 24 h to ensure completion of the reaction. Then it was treated with excess (100 ml) of CHCl3 to separate the organic layer. After separation of organic layer the solvent was evaporated and the residue was purified with silica gel column (eluents:butan-1-ol-ethyl acetate - water 4:1:5 v/v/v). Evaporation of the solvent afforded the pure compound. The product was characterized as phenylacetic acid based on 1H NMR (CDCl3) data: \( \delta \) 3.65 (s, 2H, -CH2-); \( \delta \) 7.20-7.40 (m, 5H, aromatic); \( \delta \) 11.25 (b s, 1H, COOH). The product was also identified by characteristic ferric hydroxamic test. The weight of the product obtained is 0.967 g, which accounts for 78% yield.

Results and discussion

Under varying conditions of \([\text{PA}]\) and \([\text{Ce(IV)}]\), kinetics of Ru(III) catalysed oxidation of phenethyl alcohol by Ce(IV) in aqueous nitric acid medium was investigated at several concentrations of the reactants. The results are shown in Table 1.

At constant \([\text{PA}]\), [Ru(III)] and [H+], the rates of the reactions were studied under varying [Ce(IV)]. Plots of log[Ce(IV)] versus time were linear (Fig. 1A) indicating a first order dependence in [Ce(IV)] from which the pseudo-first order rate constants were computed.

At constant [Ce(IV)], [Ru(III)] and [H+], the rates increased with increase in [PA]. From the slopes of log(O.D) versus time plots, the pseudo-first order rate constants \( k_{\text{obs}} \) were evaluated at different values of [PA]. The order in [PA] was found to be fractional indicating the formation of a complex between Ru(III) and PA. This fact is further supported by the linearity of plot of 1/\( k_{\text{obs}} \) versus 1/[PA] giving intercept \( (\text{Fig. 2A}) \).

Keeping [Ce(IV)] and [PA] constant, increase in [Ru(III)] increased the rate and the order in [Ru(III)] was found to be fractional. The fractional order dependence of the rate on both [PA] and [Ru(III)] indicates that there may be complex formation between them which has been confirmed by reciprocal plots of 1/\( k_{\text{obs}} \) versus 1/[Ru(III)].

At constant [Ce(IV)], [PA] and [Ru(III)], an increase in [H+] increased the rate of oxidation. But increase in [NO3] resulted in decrease in the rate of the oxidation. Similar effects of [H+] and [NO3] was reported in the literature as well as in our earlier studies.

These results could be explained by proposing the following equilibrium in which the neutral Ce(NO3)4(H2O)2 was assumed to be the reactive species:

\[
[\text{Ce(NO}_3\text{)}_4\text{(H}_2\text{O)}_2]^{2-} \rightleftharpoons [\text{Ce(NO}_3\text{)}_4\text{(OH)}\text{(H}_2\text{O)}_2]^+ + \text{H}^+
\]

Table 1—Pseudo first order rate constants at 298K for the Ru(III) catalysed oxidation of phenethyl alcohol and substituted phenethyl alcohols by Ce(IV) in aqueous nitric acid medium 10^{-2}[\text{Ce(IV)}] = 3.00 mol dm^{-3}; [\text{H}^+] = 0.5 mol dm^{-3} 10^{2}[k_{\text{obs}}] (s^{-1}) for \( x\text{-C}_6\text{H}_2\text{CH}_2\text{CH}_2\text{OH} \), where \( x = \text{substituent} \)

<table>
<thead>
<tr>
<th>(10^{-2}[\text{PA}]) (mol dm^{-5})</th>
<th>-1H</th>
<th>-OH</th>
<th>-4CH3</th>
<th>-4CH2</th>
<th>-4Cl</th>
<th>-4NO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4.22</td>
<td>16.9</td>
<td>11.3</td>
<td>4.35</td>
<td>3.3</td>
<td>4.35</td>
</tr>
<tr>
<td>6</td>
<td>4.79</td>
<td>17.2</td>
<td>12.9</td>
<td>8.99</td>
<td>4.34</td>
<td>4.93</td>
</tr>
<tr>
<td>8</td>
<td>4.98</td>
<td>18</td>
<td>15</td>
<td>10.5</td>
<td>4.93</td>
<td>5.21</td>
</tr>
<tr>
<td>10</td>
<td>5.85</td>
<td>9.3</td>
<td>16.2</td>
<td>12.2</td>
<td>5.76</td>
<td>5.76</td>
</tr>
<tr>
<td>12</td>
<td>6.33</td>
<td>21</td>
<td>18.8</td>
<td>16</td>
<td>5.76</td>
<td>5.76</td>
</tr>
<tr>
<td>14</td>
<td>6.9</td>
<td>31.5</td>
<td>28</td>
<td>19.9</td>
<td>5.9</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Thus, it is assumed that rate could be increased with increase in [H\(^+\)] as it will influence the existence of oxidant reactive species. Further, it is very well known from literature that Ru(III) in aqueous acid medium exists in various forms, but [Ru(H\(_2\)O)\(_6\)]\(^{3+}\) was considered to be the reactive species because a reaction of RuCl\(_3\) takes place in a few seconds from [Ru(H\(_2\)O)\(_6\)]Cl\(_2\) to form [Ru(H\(_2\)O)\(_6\)]Cl\(^{4+}\) while the conversion to [Ru(H\(_2\)O)\(_6\)]\(^{3+}\) takes place in a very long period. 

The fractional order dependence of rate in both [PA] and [Ru(III)] indicates that there may be a complex formation between them. A large variation was observed in the rate of oxidation of PA by Ce(IV) with the change of substituents at para position. The rates were higher for PA with electron-donating substituents in the benzene ring and lower for electron-withdrawing substituents. Therefore, the reactions were studied at different temperatures for substituted PA. However, for the purpose of comparison, the rates of all the substituted phenyl alcohols were optimised corresponding to parent PA at 298K through the relationship

\[
\log A = \log k_{obs} + E_a/2.303 RT \\
E_a = 2.303RT (\log A - \log k_{obs})
\]

The energies of activation was computed by the Arrhenius plots (Fig. 2B). The calculated pseudo-first order rate constants at 298 K are shown in Table 2. The rate constant for the 4-OCH\(_3\) substituted PA is the highest 16.9\(\times\)10\(^{-4}\) s\(^{-1}\) and lowest is 3.30\(\times\)10\(^{-4}\) s\(^{-1}\) for 4-NO\(_2\) substituted PA at [Ce(IV)] = 3.00\(\times\)10\(^{-3}\) mol dm\(^{-3}\), [substrate] = 4.0\(\times\)10\(^{-2}\) mol dm\(^{-3}\), [H\(^+\)] = 5.0\(\times\)10\(^{-1}\) mol dm\(^{-3}\). Generally electron-donating groups like -OCH\(_3\), -CH\(_3\) increase the rate of the oxidation and -Cl, -NO\(_2\) groups decrease the rate of oxidation.

Based on experimental facts such as the stoichiometry, induced polymerization, rate data, orders of the species and activation parameters, the most probable mechanism proposed is as shown in Scheme 1.
R-CH$_2$OH + Ru(III) $\xrightarrow{k_{\text{fast}}}^{\text{fast}}$ [Ru(III)-Complex]  \hspace{1cm} (5)

[Ru(III)-Complex] + Ce(IV) $\xrightarrow{k_{\text{slow}}}^{\text{slow}}$ [Ru(IV)-Complex] + Ce(III)  \hspace{1cm} (6)

[RU(IV)-Complex] $\xrightarrow{\text{fast}}$ R-CH-OH + Ru(III) + H$^+$  \hspace{1cm} (7)

R-CH-OH + Ce(IV) $\xrightarrow{\text{fast}}$ R-C=O + Ce(IV)  \hspace{1cm} (8)

R-C==O + Ce(IV) $\xrightarrow{\text{fast}}$ R-C=O + Ce(III) + H$^+$  \hspace{1cm} (9)

R-\=C=O + Ce(IV) $\xrightarrow{\text{fast}}$ R-C=O + Ce(III) + H$^+$  \hspace{1cm} (10)

R-C-OH + Ce(IV) + H$_2$O $\xrightarrow{\text{fast}}$ R-C$^\text{OH}$ + Ce(III) + H$^+$  \hspace{1cm} (11)

Scheme 1

Assuming that Eq. (6) in Scheme 1 to be the rate determining step, the rate law could be written as follows

$$-d[\text{Ce(IV)}]/dt = kK[\text{Ce(IV)}][\text{PA}][\text{Ru(III)}]/[1 + K[\text{PA}]+K[\text{Ru(III)}]]$$

or

$$-2.303d \log [\text{Ce(IV)}]/dt = \frac{kK[\text{PA}][\text{Ru(III)}]}{[1 + K[\text{PA}]+K[\text{Ru(III)}]]}$$

where $k$ is the bimolecular rate constant for the slow step (6) and $K$ is the formation constant for Ru(III)-complex in the fast step (5). Eq. (13) accounts for the first order dependence of the rate on [Ce(IV)] and fractional orders with respect to both [PA] and [Ru(III)]. Taking the reciprocal of Eq. (14) we get.

$$\frac{1}{k_{\text{obs}}} = \frac{1}{[\text{PA}]} \left( \frac{1}{kK[\text{Ru(III)}]} + \frac{1}{k} + \frac{1}{k[\text{Ru(III)}]} \right)$$

At constant [Ru(III)], the plot of $1/k_{\text{obs}}$ versus $1/[\text{PA}]$ was found to be linear and from the slope and intercept of which the values of formation constant $K$ and bimolecular rate constant $k$ were calculated to be $16.1 \text{mol}^{-1}\text{dm}^3$ and $7.24 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ respectively.

Validity of Hammett equation for the Ru(III) catalysed oxidation of phenethyl alcohols by Ce(IV) has been tested [Fig 1(c)] and was found to be valid for these oxidation reactions. The $\rho$ value for the reaction constant was found to be $-2.083$. A negative value of $\rho$ suggests the development of an electron-deficient reaction centre in the activated complex. An isokinetic temperature was found to be 425 K from Fig 2(c) which was higher than experimental temperature range supporting that the reactions were enthalpy-controlled. As it may be seen from the data the values of $E_a$ increase with the electron-withdrawing groups, while electron-releasing groups lowered the $E_a$ values (Table 2). The observed $\Delta S^\ddagger$ values were relatively large and negative. Such large values were not uncommon in literature. It may be interpreted that the fraction of collisions that have appropriate molecular orientations become more stringent and may lead to slow rate even though the activation energy is relatively low and the concentrations are enough to ensure many collisions. The rate constant $k$ may be shown by the equation, $k=Qe^{-\Delta G^\ddagger/RT}e^{\Delta S^\ddagger/\text{RT}}$, the calculated rate constant $k$ was $\approx 3.9 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ where $Q$ can be treated as constant, which relates to number of molecular collisions per second (frequency factor).

Further, constancy in the calculated values of $\Delta G^\ddagger$ for these oxidation reactions indicates that the same type of the reaction mechanism could be operative for the oxidation reactions. The complex formation between PA and Ru(III) takes place and finally the
Table 2—Activation parameters and optimized log A value at 298K for the Ru(III) catalysed oxidation of phenethyl alcohols by Ce(IV) in aqueous HNO₃ medium

<table>
<thead>
<tr>
<th>Parameters</th>
<th>-H</th>
<th>4-OCH₃</th>
<th>4-CH₃</th>
<th>4-Cl</th>
<th>4-NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{obs}$ (s⁻¹)</td>
<td>4.22</td>
<td>16.9</td>
<td>11.3</td>
<td>4.35</td>
<td>3.3</td>
</tr>
<tr>
<td>$E_(r)$ (kJ mol⁻¹)</td>
<td>57.4</td>
<td>45.9</td>
<td>57.6</td>
<td>61.2</td>
<td>67</td>
</tr>
<tr>
<td>log A</td>
<td>6.5</td>
<td>7.1</td>
<td>6.9</td>
<td>6.5</td>
<td>6.4</td>
</tr>
<tr>
<td>$ΔH^o$ (kJ mol⁻¹)</td>
<td>54.9</td>
<td>53.4</td>
<td>49.1</td>
<td>58.7</td>
<td>64.5</td>
</tr>
<tr>
<td>$ΔS^o$ (JK⁻¹ mol⁻¹)</td>
<td>-130</td>
<td>-157</td>
<td>-141</td>
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<td>-120</td>
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<tr>
<td>$ΔG^o$ (kJ mol⁻¹)</td>
<td>93.7</td>
<td>90.3</td>
<td>91.3</td>
<td>99.5</td>
<td>100</td>
</tr>
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</table>

Optimized values corresponding to $E_(r)$ values of x-C₆H₄CH₂CH₂OH

<table>
<thead>
<tr>
<th>Parameters</th>
<th>-H</th>
<th>4-OCH₃</th>
<th>4-CH₃</th>
<th>4-Cl</th>
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<tr>
<td>$E_(r)$ (kJ mol⁻¹)</td>
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<td>$ΔH^o$ (kJ mol⁻¹)</td>
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<td>58.9</td>
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<tr>
<td>$ΔS^o$ (JK⁻¹ mol⁻¹)</td>
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<td>-157</td>
<td>-142</td>
<td>-142</td>
<td>-121</td>
</tr>
</tbody>
</table>

complex decomposes into products as per detailed proposed mechanism of oxidation is shown in Scheme 1.

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References