Homogeneous catalysis of aquachlororuthenium(III) complex and evaluation of individual kinetic and thermodynamic parameters of bromate-lactic acid redox reaction at low and high acid strengths

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Aquachlororuthenium(III) complex catalysed oxidation of lactic acid (LA) by bromate at low and high acid strengths has been studied and different reaction mechanisms have been proposed, depending on the composition of the mixture. At low acid strength, the reaction exhibits 1.0 order in [bromate], 0.13 order in [LA], 0.5 order in [catalyst] and a dualistic effect in [acid]. Primary kinetic isotope effect ($k_H/k_D = 1$) has been found to be absent. However, an inverse solvent isotope effect ($k_{D2O}/k_{H2O} = 0.75$) is observed. The proposed mechanism involves oxidation of the formed Ru(III)-substrate complex by bromic acid, through complexation, to Ru(V)-substrate intermediate in the rate-determining step, which subsequently decomposes into CH$_3$CHO and CO$_2$ through C-C bond cleavage with regeneration of Ru(III) in the fast step. The same reaction at high acid strength exhibits first order each in [bromate] and [LA], 1.5 order in [catalyst], and an inverse fractional (-0.25) order in [acid]. The reaction also exhibits solvent isotope effect, while primary isotope effect is absent. The rate law is interpreted by a mechanism involving oxidation of Ru(III) to Ru(V) by Br(V) followed by the ternary complex formation between the formed Ru(V) and the preformed Ru(III)-substrate binary complex, which decomposes into products in the rate-determining step with regeneration of the catalyst. Spectroscopic data and the effects of dielectric constant and ionic strength are also in accordance with the mechanisms proposed. All the individual rate/formation constants involved in the mechanism proposed have been determined at different temperatures and their thermodynamic parameters have been evaluated and discussed.

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Hydroxy acids may be oxidised either as alcohols yielding corresponding oxoacids or may undergo decarboxylation to yield an aldehyde. In copper(II)-catalysed oxidation of lactic acid (LA) by V(V) an intermediate complex has been reported with the products of oxidation being CH$_3$CHO and CO$_2$. A mechanism involving hydride ion transfer to the oxidant with C-H bond cleavage has been envisaged in the oxidation of LA by hexamethylene tetramine bromine and benzyltriethylammonium chlorochromate. Proton transfer to the oxidant is reported in the oxidation of LA by Tl(III). However, in chromic acid oxidation of LA, Samal et al. have proposed an ionic mechanism in which both C-C and C-H bond cleavaged products have been formed.

Ruthenium(III) chloride hydrate is a non-toxic homogeneous catalyst. Its efficiency as a homogeneous catalyst can be seen from the oxidation studies of organic substrates using different oxidants. Potassium bromate as an oxidant has also been used in Ru(III)-catalysed oxidation of organic substrates like alcohols, hydroxy acids and carboxylic acids. In these oxidations, chemical nature (structure) of organic substrate is the key factor for different mechanisms (inner sphere and outer sphere) proposed, including hydride ion abstraction. On the other hand, it is interesting to note that the kinetic results of the aquachlororuthenium(III) complex catalysed oxidation of LA by bromate at low and high acid strengths are not the same, they are dependent on the strength of acid employed. The results obtained are also different from the earlier reports. This prompted us to investigate thoroughly the kinetics and mechanism of aquachlororuthenium(III) complex catalysed bromate-lactic acid redox reaction at low and high acid strengths, hitherto unreported. The present studies are aimed at understanding the mechanism of aquachlororuthenium(III) complex catalysed bromate-lactic acid redox reaction at low and high acid strengths and to evaluate the individual kinetic and thermodynamic parameters.
Materials and Methods

All the chemicals used were of highest purity available. Lactic acid (Merck) was further purified by distillation under vacuum just before use. Its solutions were prepared with doubly distilled water and standardised by cerate oxidimetry. Acetic acid (BDH), was purified by refluxing it with CrO₃ and acetic anhydride for 6 h and then distilled. Ruthenium trichloride hydrate (Johnson Matthey) was purified by evaporation with conc. HCl. Its solution was prepared in HClO₄ (0.3 mol dm⁻³) eliminating the traces of Ru(IV) by treating with mercury. The solution was allowed to stay for a day to attain equilibrium and was tested negative with iodide for Ru(IV). This solution was standardised by cerate oxidimetry. Acetic acid was prepared by dissolving KBrO₃ in doubly distilled water and the concentration was determined by iodometric method. Mercuric acetate solution was prepared in purified acetic acid. HClO₄ (Merck) and NaClO₄ (Merck) were used to provide the required acidity and to maintain the ionic strength respectively. α-Deuteriolactic acid (DLA) was prepared by the reported method, and its isotopic purity, as ascertained by its NMR spectrum was 94±5%. D₂O (purity 99.4%) was obtained from BARC, Mumbai, India. Schimadzu multipurpose recording double beam UV-visible spectrophotometer (model MPS-5000) equipped with a temperature controller was used for absorption studies.

Kinetic studies

The reaction mixture, containing LA, HClO₄, mercuric acetate and catalyst solutions, was thermally equilibrated for an hour at the desired temperature under subdued light and a nitrogen atmosphere. The reaction was initiated by the addition of temperature-equilibrated oxidant of requisite concentration. Rate of the reaction was followed from the determination of [bromate] to starch end-point idometrically at regular time intervals. All the reactions were carried out under pseudo-first order conditions using 10-fold excess of [LA] over [bromate]. The pseudo-first order rate constants (k, s⁻¹) with respect to Br(V) were computed from the linear plots (r²≥0.98) of log [bromate], against time. All most all kinetic runs were followed to more than 80% completion of the reaction. The catalysed rate constants were evaluated as: \( k_{\text{cat}} = k_{\text{total}} - k_{\text{uncatalysed}} \) and denoted as \( k_l \) and \( k_H \) at low and high acid strengths respectively. The rate constants (\( k_l \) and \( k_H \)) were reproducible to within ±5%.

Different sets of reaction mixtures containing an excess of [LA] over [bromate] in HClO₄, and with constant amounts of catalyst and Hg(OAc)₂, were kept for 12 h at 40°C in an inert atmosphere. The reaction mixtures were treated with known excess of 2,4-DNP.HCl solution, heated on a steam bath for 15 min and left at room temperature for 6 h when the yellow crystals of 2,4-DNP derivative of the product was obtained. The crystals were filtered, washed with water and dried. The crude derivative was chromatographed over neutral alumina (30 times by wt.) and eluted with dry benzene. The purified 2,4-DNP derivative, thus obtained, was recrystallised from ethanol, filtered (at low temperature) and dried to record the yield and m.pt. of the sample. The m.pt. of the sample was recorded as 148-149°C, which coincided well with the m.pt. (148°C) of the 2,4-DNP derivative of the authentic sample of acetaldehyde. The yield obtained was 85 ± 5%. However, at higher acid strengths, the yield was less (≈75 ± 5%), which may be due to further oxidation of the formed CH₃CHO to CH₃COOH.

The stoichiometry of the reaction was determined by equilibrating various [KBrO₃]/[LA] ratios at 40°C for 12 h. Estimation of unconsumed LA (after separating the formed CH₃CHO in the form of its 2,4-DNP derivative) revealed that 3 moles of lactic acid consumed 1 mole of bromate, according to Eq. (1).

\[
3\text{CH}_3\text{CHOHCOOH} + \text{BrO}_3^- \xrightarrow{\text{Ru}^{III}/\text{H}^+} \text{CH}_3\text{CHO} + 3\text{CO}_2 + \text{Br}^- + 3\text{H}_2\text{O} \quad (1)
\]

CO₂ was identified by bubbling a N₂ gas through the reaction mixture and passing the liberated gas through a U-shaped tube containing a saturated Ba(OH)₂ solution. Bromide ion was estimated by adding a AgNO₃ solution, resulting in the formation of a pale yellow (AgBr) precipitate.

Results and Discussion

The reduction of bromate with excess LA is autocatalytic in character. LA reacts with bromate under formation of Br₂ and HOBr, which are reduced further to Br⁻ ions. The kinetics of the reaction of LA with Br₂ is studied and found that the reactive species are Br₂ and HOBr, and that \( k_{\text{HOBr}} \gg k_{\text{Br}_2} \). Tribromide ions are kinetically inactive. Hence, bromate ions are consumed not only by the reaction with LA but also
Table 1—Effect of varying [bromate], [lactic acid], [catalyst], [acid] and solvent composition on the rate of bromate-lactic acid redox reaction at low and high acid strengths at 313 ± 0.1K

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<th>10^5 [Ru(III)] (mol dm⁻³)</th>
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<th>HOAc-H₂O % (v/v)</th>
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[^1]: [HClO₄] = 0.03 mol dm⁻³, HOAc-H₂O = 5-95% (v/v); [Hg(OAc)] = 5.0 × 10⁻³ mol dm⁻³.
Acid effect is carried out at constant ionic strength using NaClO₄.
Reported rate constants are the mean of duplicate experiments.
with Br⁻ ions. If bromide ions are masked in the solution by adding a suitable complexing agent such as mercury(II), the Br⁻ ions cannot take part in follow-up reactions and the overall reaction loses its autocatalytic character. This is exactly what is observed with the addition of mercury(II) acetate. Added mercury(II) forms non-ionised mercury(II)-bromocomplexes of high stability constants (HgBr⁺, $K_1 = 2.51 \times 10^8$ dm$^3$ mol$^{-1}$; HgBr$_2$, $K_2 = 3.8 \times 10^8$ dm$^3$ mol$^{-1}$) and the kinetic results remained the same over a wide concentration range of mercuric acetate. In order to mask the Br⁻ ions formed, an optimum concentration (0.005 mol dm$^{-3}$) of mercuric acetate is employed. Therefore, the reported rate constants and thermodynamic parameters pertain to Br(V) oxidation only.

The effect of [bromate] on the rate of reaction was studied by varying [bromate]$_0$ in the range 4.0-20.0 $\times 10^{-4}$ mol dm$^{-3}$ (Table 1). The reaction, at low and high acid strengths, exhibits first order in [bromate] as visualised from the linear plots ($r \geq 0.98$) of log [bromate] against time to 90% completion of the reaction. Further, $k_m$ and $k_L$ were found to be independent of initial [bromate] (Table 1), however, $k_H$ decreased with increase in [bromate]$_0$ (Table 1). The same trend in $k_H$ (s$^{-1}$) was also observed at different studied temperatures (Table 2).

The rate of reaction increased linearly with increase in [LA]$_0$ (Table 1) and the plots of log $k_m$ or log $k_H$ against log[LA] were linear with unit slopes ($r \geq 0.99$). However, $k_L$ varied non-linearly with an increase in [LA] (Table 1) while the plot of log $k_L$ versus log [LA] was linear ($r = 0.996$), with a slope value of 0.13. As the order in [LA] is low (at low acid strength) plotting 1/$k_L$ versus 1/[LA] cannot be linear. Nevertheless, plot of [LA]/$k_L$ against [LA] was linear with a definite intercept on y-axis. Accordingly, involvement of LA in complexation is visualised.

The effect of [HClO$_4$] on the rates of reactions was studied while maintaining the ionic strength constant involving NaClO$_4$. It is interesting to note that the effect of [acid] is different under different experimental conditions. Uncatalysed reaction rate increases with increasing [HClO$_4$] (Table 1) and the log-log plot of $k_m$ versus [acid] was linear ($r = 0.994$) with a slope value of $1.6 \pm 0.1$. However, $k_H$ decreased with increase in [HClO$_4$] (Table 1). Further, log $k_H$ versus log [HClO$_4$] plot was linear ($r = 0.996$) with a slope...
value of $-0.25 \pm 0.05$. The same trend in $k_H$ was observed at all the studied temperatures (Table 2). On the other hand, the value of $k_L$ increases with increasing [HClO$_4$] and reaches a maximum (Table 1) at $1.0 \text{ mol dm}^{-3}$. Further increase in [acid] resulted in a decrease of reaction rate. A change in the concentration of added salt like NaClO$_4$ had no effect on the rates of catalysed and uncatalysed reactions (Table 3).

The catalytic effect of aquachlororuthenium(III) complex on the rate of reaction was studied in the 3.8-20.0x10$^{-5}$ mol dm$^{-3}$ range, while keeping all other [reactants] and conditions constant including [HClO$_4$]. The rate of reaction increases with increase in [catalyst]$_0$ (Table 1). It is interesting to note that the order with respect to [catalyst] is variable and depends on the strength of the acid used. At low (0.03 mol dm$^{-3}$) acid strength, the order with respect to [catalyst] is 0.5 $\pm$ 0.03 as is evident from the linear plot of log $k_L$ versus log [Ru(III)] ($r = 0.998$). However, at 1.0 mol dm$^{-3}$ HClO$_4$ the order in [catalyst] was found to be 1.5 $\pm$ 0.05 from the linear plot ($r = 0.997$) of log $k_H$ versus log [catalyst].

The dielectric constant ($D$) effect was studied by varying the HOAc-H$_2$O composition in the reaction mixture, all other conditions being kept constant. The inertness of the solvent towards oxidant has been tested earlier. Increasing acetic acid content of the medium increased $k_{un}$ in contrast to $k_{cat}$ ($k_L$ and $k_H$) wherein a positive effect followed by a negative effect on the rate of catalysed reaction was observed as the percentage of acetic acid in the solvent composition is increased (Table 1). The plot of log $k_{un}$ versus $1/D$ was linear with a positive slope. However, positive and negative slopes with a maximum were obtained in the log $k_{cat}$ ($k_L$ or $k_H$) against $1/D$ plots.

Both, uncatalysed and aquachlororuthenium(III) complex catalysed, bromate-lactic acid redox reactions (at low and high acid strengths) failed to induce polymerisation of acrylonitrile/acryl amide monomer, indicating non-intervention of free radicals in the reactions.

To ascertain the importance of the $\alpha$-CH bond cleavage in the rate-determining step, oxidation of DLA ($\alpha$-deuteriolactic acid) was studied. The results showed that the reactions (catalysed and uncatalysed) did not exhibit any primary kinetic isotope effect and $k_D/k_D = 1$ at all the studied temperatures. However, the reaction rate decreased when carried out in D$_2$O and $k_{D2O}/k_{H2O}$=0.75$\pm$0.05 at all the studied temperatures.

| Table 3—Effect of [NaClO$_4$] on the rate of reaction at 313 $\pm$ 0.1 K |
|-----------------------------|---------|---------|---------|
| NaClO$_4$ (mol dm$^{-3}$)   | $10^3 \times k_{un}$ (s$^{-1}$) | $10^3 \times k_H$ (s$^{-1}$) | $10^3 \times k_L$ (s$^{-1}$) |
| --                           | 2.71    | 26.05   | 28.80   |
| 0.25                         | 2.74    | 26.05   | 28.79   |
| 0.50                         | 2.70    | 26.08   | 28.82   |
| 0.75                         | 2.72    | 26.04   | 28.82   |
| 1.00                         | 2.71    | 26.10   | 28.80   |
| 1.50                         | 2.71    | 26.05   | 28.81   |

To evaluate the composite and individual reaction constants and their activation parameters, the reactions were studied under varying conditions in the temperature range 303-323 K. The energy of activation ($E_a$) corresponding to the reaction constants was evaluated from Arrhenius plot, from which the related thermodynamic parameters ($\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$) were calculated (Table 4).

The existence of CH$_3$CH(OH)COO$^-$ in mineral acid solutions does not arise as the dissociation of lactic acid ($K_a$=1.38x10$^{-1}$ at 25°C in aqueous solution) is completely suppressed. In the presence of HClO$_4$ (0.03-2.0 mol dm$^{-3}$), LA is expected to be either in unprotonated form(S) or in its protonated form (SH$^+$).

$$\begin{align*}
\text{CH}_3\text{CH(OH)COO}^- + \text{H}^+ & \xrightarrow{K_p} \text{CH}_3\text{CH(OH}_2)\text{COOH}^+
\end{align*}$$

Oxidation step involves removal of H$^+$ ion from the $\alpha$-hydroxy functional group and the process is the driving force to the decarboxylation step. Since the protonated form would have an adverse effect on the rate, the substrate should be participating in the reaction in its neutral form (undissociated/unprotonated) only. At higher [HClO$_4$], the decrease in rate may be due to [SH$^+$] formation as indicated in Eq. (2).

In acid solutions, the reactive species of bromate are likely to be BrO$_2^-$ and protonated bromate$^{19}$ (HOBrO$_2$ and/or OBr$^-(\text{OH})_2$/BrO$_2^+$). Hence, the oxidation may be a reaction involving one of the oxidant species.

From ion-exchange studies, it is confirmed that ruthenium trichloride hydrate forms (RuCl$_6$)$^{3-}$ species.
in hydrochloric acid and aquation of these species to form [RuCl(H₂O)]²⁺ requires only a few seconds.¹⁸

\[\text{[RuCl}_6^{2-} + \text{H}_2\text{O} \rightarrow \text{[RuCl}_5(\text{H}_2\text{O})]^{2+} + \text{Cl}^- \quad \ldots (3)\]

Therefore, it is assumed that Ru(III) in the form of [RuCl₅(H₂O)]²⁺, aquachlororuthenium(III) complex, is taking part in the reaction. The negative effect of Cl⁻ ions on the rate of reaction is also in accordance of the assumption.

Ru(III) does not oxidise lactic acid in a direct reaction, which excludes the reduction of Ru(III) to its lower oxidation states in the catalytic cycle. No evidence for the formation of Ru(I) and no induced polymerisation with acrylic monomers, eliminate the possibilities of these redox cycles in the present study.

Mechanism at high acid strength

The uncatalysed redox reaction²⁰, under these conditions, exhibits first order each in [bromate] and [LA], and 1.6 order in [acid]. The assumed mechanism includes slow formation of a lactic ester of bromic acid due to nucleophilic attack by the alcoholic/hydroxyl group at the bromine atom of HOB₉/OBr⁺(OH)₂, which dissociates rapidly through C-C bond cleavage²⁰ to form products, CH₃CHO and CO₂.

In 30-70% (v/v) HOAc-H₂O medium containing 1.0 mol dm⁻³ perchloric acid, and in presence of Ru(III) catalyst, the reaction is understood to occur in parallel paths with contributions from the uncatalysed and catalysed paths. Thus, the total rate constant (kₚ) is equal to sum of the rate constants of the catalysed (kₜ) and uncatalysed (kᵤₚ) reactions, so, kₚ = kₜ - kᵤₚ.

Hence, the reaction orders have been determined from the slopes of log kₚ versus log (conc.) plots by varying the concentrations of substrate, catalyst and acid turnum, while keeping the others constant.

The catalytic effect of Ru(III) on the rate of reaction was studied employing varied initial concentrations of the metal ion. The kₚ versus [Ru(III)] plot gave a smooth upward curve (Fig. 1) indicating that Ru(III) is an efficient catalyst for the redox reaction and its order (obtained from log kₚ versus [Ru(III)] plot) is 1.5 ± 0.05. The y-intercepts (Fig. 1) agree reasonably well with the mean rate constants (Table 4) for the uncatalysed reaction at different temperatures.

The observed order with respect to [Ru(III)] is interesting and different from the earlier reports⁶-¹⁷ (zero, unity and less than unity) of Ru(III)-catalysed redox reactions involving different oxidants and substrates. The reliability of 1.5 order in [catalyst] is

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### Table 4 – Composite and individual rate constants of aquachlororuthenium(III) complex catalysed bromate-lactic acid redox reaction at different temperatures and activation parameters at 313 K

<table>
<thead>
<tr>
<th></th>
<th>Rate/formation constants at 303</th>
<th>Rate/formation constants at 308</th>
<th>Rate/formation constants at 313</th>
<th>Rate/formation constants at 318</th>
<th>Rate/formation constants at 323 K</th>
<th>ΔH°</th>
<th>ΔS°</th>
<th>ΔG°</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Uncatalysed reaction</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>10⁴ × kᵤₚ (s⁻¹)</td>
<td>1.34</td>
<td>1.88</td>
<td>2.71</td>
<td>3.76</td>
<td>5.26</td>
<td>53.2</td>
<td>-163</td>
<td>104.2</td>
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<td></td>
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</tr>
<tr>
<td><strong>Catalysed reaction : At high acid strength</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁴ × kₜ (s⁻¹)</td>
<td>1.60</td>
<td>2.04</td>
<td>2.60</td>
<td>2.94</td>
<td>3.65</td>
<td>34.7</td>
<td>-203</td>
<td>98.3</td>
</tr>
<tr>
<td>10⁴ × Kᵣ (dm³ mol⁻¹)</td>
<td>2.30</td>
<td>1.89</td>
<td>1.50</td>
<td>1.26</td>
<td>1.06</td>
<td>-30.0</td>
<td>-261</td>
<td>51.8</td>
</tr>
<tr>
<td>10⁴ × Kₓ (dm³ mol⁻¹)</td>
<td>1.23</td>
<td>1.19</td>
<td>1.03</td>
<td>0.82</td>
<td>0.67</td>
<td>-24.7</td>
<td>-245</td>
<td>78.6</td>
</tr>
<tr>
<td>10⁴ × Kₚ (dm³ mol⁻¹)</td>
<td>0.64</td>
<td>0.57</td>
<td>0.48</td>
<td>0.42</td>
<td>0.36</td>
<td>-26.5</td>
<td>-336</td>
<td>78.6</td>
</tr>
<tr>
<td>10⁴ × kᵤₚ (s⁻¹)</td>
<td>1.60</td>
<td>1.90</td>
<td>2.52</td>
<td>3.28</td>
<td>4.14</td>
<td>41.5</td>
<td>66</td>
<td>62.1</td>
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<tr>
<td>10⁴ × kₛ (s⁻¹)</td>
<td>2.32</td>
<td>2.60</td>
<td>3.17</td>
<td>3.70</td>
<td>4.40</td>
<td>25.1</td>
<td>250</td>
<td>104.0</td>
</tr>
<tr>
<td><strong>Catalysed reaction : At low acid strength</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁴ × kₛ (s⁻¹)</td>
<td>0.82</td>
<td>1.60</td>
<td>2.88</td>
<td>4.40</td>
<td>8.10</td>
<td>86.4</td>
<td>-37</td>
<td>98.0</td>
</tr>
<tr>
<td>10⁴ × Kₛ (dm³ mol⁻¹)</td>
<td>0.68</td>
<td>1.10</td>
<td>1.60</td>
<td>2.40</td>
<td>3.70</td>
<td>64.4</td>
<td>-41</td>
<td>51.6</td>
</tr>
<tr>
<td>10⁴ × kₛ (s⁻¹)</td>
<td>1.08</td>
<td>2.00</td>
<td>3.48</td>
<td>5.40</td>
<td>9.50</td>
<td>82.6</td>
<td>-48.6</td>
<td>97.5</td>
</tr>
</tbody>
</table>

Average error in the values of ΔH°, ΔS° and ΔG° are ± 3 kJ mol⁻¹; ± 8 JK⁻¹ mol⁻¹ and ± 4 kJ mol⁻¹ respectively.

[KBrO₃] = 1.0 × 10⁻³ mol dm⁻³; [Lactic acid] = 0.01 mol dm⁻³; [Ru(III)] = 7.6 × 10⁻⁵ mol dm⁻³;

For Kᵤₚ, HOAc-H₂O = 30-70% (v/v) and [HClO₄] = 1.0 mol dm⁻³. For kₛ, HOAc-H₂O = 5-95% (v/v) and [HClO₄] = 0.03 mol dm⁻³.
verified from the repeated experiments using freshly prepared standard solutions of reactants including Ru(III) solution, which is prepared from two different commercial samples, Aldrich Chemical Company and Johnson Matthey, after purification.

Ruthenium(III) solution, in aqueous-acetic acid and perchloric acid medium, shows \( \lambda_{\text{max}} \) at 490 nm. Neither acid bromate nor lactic acid has an absorption maximum in this region. On addition of Br(V) to a solution of Ru(III) (in the absence of LA and in presence of Hg(II)), the colour of the solution is gradually changed with a shift in \( \lambda_{\text{max}} \) to 690 nm, which corresponds to Ru(V). In another independent spectral study, a change in the \( \lambda_{\text{max}} \) and molar extinction of Ru(III) solution by the addition of LA (in the absence of Br(V)) is also observed. However, there is no change in the absorbance of Ru(III) when LA is added to Ru(III) solution in the presence of 4.0 mol dm\(^{-3}\) HClO\(_4\). Nevertheless, at lower [HClO\(_4\)], an increase in the absorbance due to the addition of LA to Ru(III) solution is recorded. This indicates an outersphere complex formation between Ru(III) and LA, which is [acid] dependent. Spectral evidence for such a catalyst-substrate complex is also obtained from the UV-visible spectra of lactic acid and a mixture of Ru(III) and lactic acid solution. A hypsochromic shift of 8 nm from 254 to 246 nm is observed together with hyperchromicity at 246 nm. Kinetic evidence for such a complex formation however, was not observed in the \( 1/k_H \) versus \( 1/[\text{LA}] \) plot. This might be due to a very low concentration ratio of Ru(III) to LA, wherein the change in lactic acid concentration may be negligible due to complexation or may be due to competitive uncatalysed reaction path or both. However, formation of the substrate-catalyst complex was proved kinetically by the non-zero intercept of \( [\text{Ru(III)}]/k_H \) versus \( 1/[\text{Ru(III)}] \) plot (Fig. 2).

In the present study, a decrease of rate with increase in [H\(^+\)] is observed, which can be understood in terms of formation of the hydrolysed species of BrO\(_2^+\) as HOBrO\(_2\) in the prior equilibrium step\(^5\). Since the conjugate acid is a stronger oxidising agent than its base, HOBrO\(_2\) is considered to be the active species of oxidant. The negligible effect of ionic strength on the reaction rate also supports the existence of HOBrO\(_2\) as the active species of oxidant.
and excludes the involvement of BrO₃⁻, BrO₂⁺ and OBr⁻(OH)₂ in the reaction. The results indicate that the active species of oxidant reacts with the active catalyst species in a fast step to give ruthenium(V) and bromine(III). The formation of Ru(V) is in accord with earlier studies. In accordance with the experimental results, the mechanism as shown in Scheme 1 is proposed. Eq. (4) can be understood as:

\[ \text{Scheme 1} \]

\[ \begin{align*}
\text{Ru(III)} + \text{Br(V)} & \xrightarrow{K_f} \text{Ru(V)} + \text{Br(III)} \\
\text{Ru(III)} + \text{CH₃CH(OH)COOH} & \xrightarrow{K_C} \left[ \begin{array}{c}
\text{OH} \\
\text{H}_2\text{C} - \text{C} - \text{COOH} - \text{Ru}^{\text{III}}
\end{array} \right] \\
\left(\text{Binary complex, } C_1\right)
\end{align*} \]

\[ \begin{align*}
\text{Ru(V)} + \left[ \begin{array}{c}
\text{OH} \\
\text{H}_2\text{C} - \text{C} - \text{COOH} - \text{Ru}^{\text{III}}
\end{array} \right] & \xrightarrow{K_x} \left[ \begin{array}{c}
\text{Ru(V)} \\
\text{OH}
\end{array} \right] + \left[ \begin{array}{c}
\text{H}_{2}\text{C} - \text{C} - \text{COOH} - \text{Ru}^{\text{III}}
\end{array} \right] \\
\left(\text{Ternary complex, } C_2\right)
\end{align*} \]

\[ \begin{align*}
\left[ \begin{array}{c}
\text{Ru(V)} \\
\text{OH}
\end{array} \right] + \left[ \begin{array}{c}
\text{H}_{2}\text{C} - \text{C} - \text{COOH} - \text{Ru}^{\text{III}}
\end{array} \right] & \xrightarrow{kd\text{ (slow)}} \text{H}₃\text{CCHO} + \text{CO}_2 + 2\text{H}^+ + 2\text{Ru}^{\text{III}} \\
\left(\text{Ternary complex, } C_2\right)
\end{align*} \]

1:3 Stoichiometry between bromate and LA in presence of catalyst is also observed.

The equilibrium existing between reactants and products of Eq. (4) is continuously disturbed and always shifts towards the products side. Hence, the reaction (Eq. 4) may be treated as an irreversible reaction for all practical purposes.

**Rate law and kinetic and thermodynamic parameters**

The rate equation in consonance with the proposed mechanism (Scheme 1) is as follows:

\[-d[\text{Br(V)}]/dt = k_d\left[C_2\right] = k_d k_f K_e K_c [\text{LA}] \times [\text{Ru(III)}]^2 [\text{Br(V)}] \quad \text{(14)}\]

As the substrate is present in uncomplexed (protonated and unprotonated) and complexed forms, the
total [substrate] is given by:

\[ [S]_T = [S] + [SH^+] + [C_1] + [C_2] \quad \ldots (15) \]

\[ [S] = \frac{1 + K_p[H^+] + K_{[Ru(III)]}^+}{1 + K_p[H^+] + K_{[Ru(III)]}^+ + K_rK_s[Ru(III)]^2[Br(V)]} \quad \ldots (16) \]

The rate constant, \( k_H \), in terms of \([S]_T\) is given by

\[ k_H = \frac{d[Br(V)]}{dt} \frac{1}{[Br(V)]} = \frac{k_d K_rK_s[S]_T[Ru(III)]^2}{1 + K_p[H^+] + K_{[Ru(III)]}^+ + K_rK_s[Ru(III)]^2[Br(V)]} \quad \ldots (17) \]

Taking reciprocal and rearranging Eq. (17)

\[ \frac{1}{k_H} = \frac{1 + K_p[H^+] + K_{[Ru(III)]}^+ + K_rK_s[Ru(III)]^2[Br(V)]}{k_d K_rK_s[S]_T[Ru(III)]^2} \quad \ldots (18) \]

According to Eq. (18), at fixed [substrate], [catalyst] and [acid], plot of \( 1/k_H \) against [bromate] should be a straight line with a definite intercept. The same is obtained (Fig. 3; \( r \geq 0.98 \)) and \( k_d \) (decomposition constant of the ternary complex, \( C_2 \)) values are evaluated (Table 4) from the intercepts of the plots (Fig. 3) at different temperatures by studying the [bromate] effect at each temperature (Table 2).

As the term \([Ru(III)]^2 [Br(V)]\) is in the order of \( 10^{13} \), it can be neglected in comparison with other terms in the denominator of Eq. (17). Therefore,

\[ k_H = \frac{k_d K_rK_s[S]_T[Ru(III)]^2}{1 + K_p[H^+] + K_r[Br(V)]} \quad \ldots (19) \]

Taking reciprocal and rearranging Eq. (19)

\[ 1 = \frac{k_p[H^+]}{k_d K_rK_s[S]_T[Ru(III)]^2} + \frac{1}{k_d K_rK_s[S]_T[Ru(III)]^2} \quad \ldots (20) \]

According to Eq. (20), linear plot of \( 1/k_H \) against \([H^+]\), at fixed [substrate] and [catalyst] with a definite intercept on y-axis is obtained. (Fig. 4, \( r \geq 0.98 \)). The ratio of slope to the intercept is given by

\[ a = \text{slope/intercept} = K_p/1 + K_{[Ru(III)]} \quad \ldots (21) \]

Eq. (20) can be rewritten as:

\[ \frac{[Ru(III)]}{k_H} = \frac{1 + K_p[H^+]}{k_d K_rK_s[S]_T[Ru(III)]^2} + \frac{1}{k_d K_rK_s[S]_T} \quad \ldots (22) \]
If Eq. (22) holds, at constant [substrate], [Ru(III)] / $k_H$ against 1/[Ru(III)] should be linear with a definite intercept on y-axis. Such a plot is also obtained (Fig. 2; $r \geq 0.97$). $K_s$ values have been evaluated at each temperature from the effect of [catalyst] studied at different temperatures (Table 2) and $k_d$ (evaluated) and $K_f$ values ($K_f$ values are in the neighborhood of the earlier work\textsuperscript{16a}).

The ratio of intercept/slope (Fig. 2) = $K_f / k_p$ [H$^+$] = b. From the values of ‘a’ and ‘b’ $K_p$ and $K_c$ are given as:

$$K_p = \frac{a+ab[\text{Ru(III)}]}{a-ab[H^+][\text{Ru(III)}]}$$

and

$$K_c = \frac{b+ab[H^+] - 1}{1-ab[H^+][\text{Ru(III)}]}$$

From the effects of [acid] and [catalyst] at different temperatures, $K_p$ and $K_c$ values at each temperature are evaluated along with their activation parameters (Table 4). Further, it is also observed that the plot of 1/$k_H$ versus 1/[S]$_T$ (Eq. 20) is found to be linear passing through the origin.

Using these $K_c$, $K_p$, $K_c$, $K_x$ and $k_d$ values, the rate constants ($k_{d1}$) were calculated over different experimental conditions using Eq. (19) and compared with experimentally found data. There is a reasonable agreement between the calculated and experimental rate constants, which further supports the proposed mechanism (Scheme 1).

**Mechanism at low acid strength**

Under the experimental conditions, 5-95% (v/v) HOAc-H$_2$O and 0.03 mol dm$^{-3}$ perchloric acid, uncatysalysed reaction rate is almost negligible ($k_{un} \sim 10^7$, s$^{-1}$). Therefore, the obtained rate constants ($k_{d1}$, s$^{-1}$) and thermodynamic parameters pertain to catalysed reaction only.

At low acid strength, the reaction also shows 1:3 stoichiometry between bromate and LA in presence of Ru(III) catalyst and the orders were found to be unity in [bromate], 0.13 in [LA], 0.5 in [Ru(III)] and positive effect followed by a negative effect with [HClO$_4$] as well with HOAc percentage composition.

These results suggest complex formation between lactic acid and catalyst. Evidence is provided by the fractional order found in [LA]. The spectral evidence for such complex formation between Ru(III) and LA was obtained from the UV-visible spectra of the catalyst and a mixture of catalyst and LA in 0.03 mol dm$^{-3}$ perchloric acid solution. A bathochromic shift of 9 nm, from 490 to 499 nm, with an increase in molar extinction coefficient of Ru(III) solution in the presence of LA was obtained.

Formation of the complex was also proved kinetically by the non-zero intercept of the linear plot of [LA]/[LA]$_T$ versus [LA]. Hence, a reversible Ru(III) complex formation with one mole of LA precedes the rate determining step, which subsequently gets oxidised to products by bromic acid through complexation (Scheme 2).

Increase in rate with increase in [HClO$_4$], indicated that HOBro$_2$ is the active species of Br(V). Under these experimental conditions, OBr$^+(\text{OH})_2/\text{(BrO}_4^2-\text{)}$ and SH$^+$ may not be in considerable concentrations. Dielectric constant and ionic strength effects are also in accordance with the proposition.

The slow oxidation process may involve transfer of electrons to Br(V) from Ru(III)-LA in the complex, C$_3$, followed by a much faster breakdown of Ru(V)-substrate complex C$_4$ into products, CH$_3$CHO and CO$_2$, through C-C bond cleavage. The (Ru(V)-substrate complex) never attains a spectrophotometrically detectable concentration. The breakdown of the complex C$_3$ can be visualised as shown in Scheme 3.

Substrates forming five-membered rings are oxidised much more easily than if the rings are six membered. Therefore, the catalytic effect of Ru(III) is due to the formation of five membered ring complexes at very low acid strength.

HBrO$_2$ being a potential oxidant, oxidises two more molecules of LA ultimately forming Br$^-$ ion, which is also detected by using a AgNO$_3$ solution.

**Rate law and kinetic and thermodynamic parameters**

The proposed mechanism (Scheme 2) leads to the rate law (Eq. 29).
which explains fractional order dependence in LA, catalyst and acid concentrations.

Taking reciprocal and rearranging Eq. (29), after substituting the value of \( K_I \) (0.52 dm\(^{-3}\) mol\(^{-1}\), ref. 19) and [H\(^+\)] (0.03 mol dm\(^{-3}\))

\[
\frac{[\text{LA}]}{k_L} = \frac{33.85}{k_{dy} K_C K_y [\text{Ru(III)}]} + \frac{[\text{LA}]}{k_{dy}} \quad \ldots (30)
\]

From Eq. (30), at fixed [Ru(III)], a linear plot of [LA]/\(k_L\) against [LA] with a definite intercept on [LA]/\(k_L\) axis was obtained. From the intercept, \( k_{dy} \) (decomposition constant of the intermediate complex, C\(_3\)) has been evaluated. \( k_{dy} \) value can also be evaluated by the linear plot of [LA]/\(k_L\) against 1/[Ru(III)]. The close agreement of \( k_{dy} \) value obtained from two different effects supports the mechanism envisaged (Scheme 2). \( K_y \), the formation constant of the intermediate complex C\(_3\), is evaluated from \( k_{dy} \) and \( K_C \) (already discussed) and from the slope of [LA]/\(k_L\) against [LA] plot.

By studying the [substrate] effect at different temperatures (Table 5), \( k_{dy} \) and \( K_y \) values are evaluated at each temperature and recorded in Table 4. Using these
k_{dy}, K_C and K_y values, the rate constants (k_L, s^{-1}) under different experimental conditions have been calculated using Eq. (29) and compared with the experimental data. There is a good agreement between them, which further supports the envisaged mechanism (Scheme 2).

At higher acid strength, the decrease in rate with increase in [acid] is not only due to the shift in mechanism from Scheme 2 to Scheme 1 but also due to protonation of the substrate, which has an adverse effect on the rate of reaction.

The decrease in rate at higher percentage of acetic acid in solvent composition (Table 1) may be due to instability of the catalyst-substrate complex in low polar media or may be due to increase in acidity or both.

The activation energy (E_a) for the overall reaction / individual steps was evaluated from the least square slopes of log rate constant (composite/individual) against 1/T, from which the related thermodynamic parameters (∆H^#, ∆S^# and ∆G^#) have been calculated (Table 4). The activation enthalpy of K_C is negative, suggesting the formation of an outer-sphere complex between Ru(III) and LA [ruthenium(III) has a tendency to form such outer-sphere complexes with weak ligands] while temperature has an adverse effect on its stability. The negative entropy of activation is due to compactness of the formed intermediate complexes compared to the reactants.

In conclusion, mechanism of the aquachloro-ruthenium(III) complex catalysed bromate oxidation of lactic acid is variable and is dependent on the strength of acid used. No single mechanism operates at low and high acid strengths.

References