Kinetic and mechanistic study of ruthenium(III) catalysed and uncatalysed oxidation of oxalic acid by acid bromate

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Received 8 February 1995; revised 30 March 1995; accepted 17 April 1995

Acid bromate-oxalic acid reaction in the presence of mercury(II)—a bromide ion scavenger, is slow and exhibits first order each in [oxidant], [oxalic acid] and [mineral acid]. The proposed mechanism assumes a slow rate determining formation of an oxalyl-bromate ester, followed by the fast decomposition to products. The same reaction in the presence of Ru(III) is accelerated and exhibits fractional order each in [substrate], [catalyst] and [acid] and first order in [bromate]. The proposed mechanism for catalysed reaction assumes a complex formation between oxalic acid and Ru(III), which subsequently undergoes decarboxylation after interacting with bromate. The mechanisms, for over all, catalysed and uncatalysed reactions are critically examined and values of rate constants of each reaction are evaluated. Activation parameters for all the reactions are also evaluated and discussed.

Catalysis by transition metal ions, plays an important role in understanding the mechanistic aspects of a particular redox reaction. Ru(III) acts as an efficient catalyst in many redox reactions, hence the use of Ru(III) chloride as a homogeneous catalyst in alkaline and acid media is of present interest. A number of oxidants like phenyl iodoacetate\(^1\), [Fe(CN)]\(^{3-}\) (ref. 2), periodate\(^3\), thallium(III)\(^4\), Ni(III)\(^5\), etc. have been employed in combination with Ru(III) to oxidise relatively inert substances. In these reactions inner-sphere and outer-sphere mechanisms have been proposed and in reactions involving hydride ion abstraction, the valency of Ru(III) remains unaltered. A scan through of the existing literature reveals lack of work on Ru(III) catalysed bromate oxidation of dicarboxylic acids. While studying Ru(III) catalysed bromate oxidations of dicarboxylic acids, certain interesting results were observed. Malonic acid, a higher homologue of oxalic acid, exhibits an induction period, the duration of which decreased with increase in concentration of reactants and temperature and the reaction exhibited a complicated kinetics with competitive and conjugative reactions. However, with oxalic acid as the substrate, the reaction is not complicated. Hence to understand the actual role of Ru(III), the title reaction is studied in detail and reported.

Materials and Methods
AnalaR grade oxalic acid (BDH), recrystallised twice from 2-propanol was used and aqueous solution of it was prepared. RuCl\(_3\) (John-Mathey) was dissolved in dilute perchloric acid and standardised by the method of Hourichi \textit{et al.}\(^6\) Sulphuric/perchloric acid (BDH, AR) was used as such. The allowance of [H\(^+\)] was made for the amount of acid present in the catalyst solution, while preparing for kinetic runs. All other chemicals used were of high purity. The stock solutions were prepared either in triply distilled water or in 1:1 aq. acetic acid and preserved in the dark. Under subdued light and nitrogen atmosphere, the reaction mixture containing requisite amounts of oxalic acid, Ru(III) (for catalysed reaction) acid and mercury(II) acetate, was thermostated for an hour at desired temperature. To this, temperature equilibrated solution of oxidant of required concentration was added. The progresses of the reaction was monitored by estimating the unreacted bromate iodometrically to a starch end point for two half lives by withdrawing the aliquots of reaction mixture at regular intervals of time. A Shimadzu multipurpose recording double beam spectrophotometer model MPS-5000 equipped with a temperature controller was used for absorption studies.

The reactions were carried out under pseudo-first order conditions using ten fold excess of [oxalic acid] over [Br(V)]. The catalysed rate constants (\(k_{\text{cat}}\)) were calculated by subtracting the va-
Table 1—Effect of varying [reactants] on the rate of uncatalysed and Ru(III)-catalysed acid bromate oxidation of oxalic acid at 303 K

<table>
<thead>
<tr>
<th>[Br(V)] (mol dm⁻³)</th>
<th>[oxalic acid] (mol dm⁻³)</th>
<th>[H₂SO₄] (mol dm⁻³)</th>
<th>[Ru(II)] (mol dm⁻³)</th>
<th>10¹² × rate constant (s⁻¹)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>k_uncat</td>
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<tr>
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<td>(3.16)</td>
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<td>(8.51)</td>
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<td>(16.59)</td>
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<td>1.0</td>
<td>1.0</td>
<td>9.56</td>
<td>(21.08)</td>
</tr>
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</table>

*Values in parentheses are obtained in the presence of perchloric acid

1For catalysed reactions: [HOAc·H₂O] = 30-70% (v/v), [Hg(OAc)₂] = 0.01 mol dm⁻³

values of uncatalysed rate constants (k_uncat) from the rate constants of the overall reaction (k_overall). The reproducibility of k values is within ±3% and mean values are reported.

**Results and Discussion**

The production of bromine by an autocatalytic reaction (Eq. 1) and its subsequent reaction with the substrate was eliminated by the addition of mercury(II)—a bromocomplexing agent, as it forms unionised mercury(II)-bromo-complexes, without involving in the kinetic studies even with multiple concentration range of mercury(II).

\[
\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ = 3\text{Br}_2 + 3\text{H}_2\text{O}; K = 10^{13} \quad \ldots (1)
\]

Uncatalysed and Ru(III)-catalysed reactions exhibit first order in [bromate] as revealed from the plots of log[bromate] against time up to two half-lives. The rate constants are independent of initial [bromate] (Table 1). The pseudo-first order rate constants increase linearly (uncatalysed reaction) with increase in [oxalic acid] (Table 1). In the case of catalysed reaction, the order in [oxalic acid] is fractional (0.7). The non-linear increase in rate constant towards a limiting value at higher [substrate] and a definite intercept on y-axis in the Michaelis-Menten’s plot is indicative of complex formation, prior to the rate determining step. Values of rate constant increases with increase in [acid] (Table 1). It is evident from the plots of log k versus log[acid], the catalysed reaction has a fractional order dependence on [acid], whereas, the order in [acid] is unity in the case of uncatalysed reaction. A change in the concentration of added salts like Na₂SO₄, NaHSO₄, NaClO₄ has a marginal effect. Increase in polarity of the medium (by changing H₂O-HOAc content) decreases the rate suggesting a charge disparity in the transition state. Br(V)/oxalic acid reaction is found to be accelerated by the addition of Ru(III) chloride. The k_cat values increases with increase in the [Ru(III)] as shown in
Table 2—Activation parameters of oxalic acid-Br(V)-Ru(III)-reaction at 303 K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>308</th>
<th>313K</th>
</tr>
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<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td></td>
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<tr>
<td>Catalysed</td>
<td>16.66</td>
<td>25.15</td>
<td>42.64</td>
<td>62.94</td>
<td>113.03</td>
</tr>
<tr>
<td>Overall</td>
<td>19.30</td>
<td>30.08</td>
<td>51.41</td>
<td>78.74</td>
<td>140.68</td>
</tr>
<tr>
<td>Uncatalysed</td>
<td>2.64</td>
<td>4.93</td>
<td>8.77</td>
<td>15.90</td>
<td>27.65</td>
</tr>
<tr>
<td>Perchloric acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalysed</td>
<td>22.31</td>
<td>35.32</td>
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<td>82.65</td>
<td>159.76</td>
</tr>
<tr>
<td>Overall</td>
<td>24.04</td>
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<td>60.25</td>
<td>100.80</td>
<td>177.82</td>
</tr>
<tr>
<td>Uncatalysed</td>
<td>1.73</td>
<td>3.27</td>
<td>5.82</td>
<td>10.35</td>
<td>18.05</td>
</tr>
</tbody>
</table>

Table 1 and a slope of 0.60 is obtained in the double logarithmic plot.

Activation parameters evaluated for the overall, catalysed and uncatalysed reactions are incorporated in Table 2. As expected the energy of activation (ΔH* + RT) for the catalysed reaction is less than that of the uncatalysed reaction. The entropy of activation for all the reactions of oxalic acid-bronate have been found to be negative. This is due to compactness of the transition state as compared to the ground state, causing a restriction on the translational and rotational freedom, thus reducing the entropy of the system.

The reaction rates (uncatalysed and catalysed) are neither accelerated in the presence of benzoic peroxide nor retarded in the presence of acrylic monomers, ruling out the involvement of free radicals in the reaction.

In acid solutions, possible inorganic bromine species with odd oxidation number that exist in singlet ground state are Br⁻, HOBr, HBrO₂, BrO⁻, BrO⁻ and Br₂O₅. Atleast some of the free radical species, Br, BrO and BrO₂ and singlet dimers Br₂ and Br₂O₄ may be mechanistically important. For all considerations perbromate ion, BrO₄⁻, can be neglected, because it is quite unstable with respect to disproportionation. Br₂O₅ formation takes place only at very high acid strengths.

According to Edwards types of intermediate postulated in bromate oxidations are called acceptors or electrophilic particles and these are formed by the action of oxyanions with protons and subsequent dehydration as shown below:

\[
\begin{align*}
\text{BrO}_3^- + \text{H}^+ & \rightleftharpoons K_{p1} \text{HBrO}_3 \\
\text{HBrO}_3 + \text{H}^+ & \rightleftharpoons K_{p2} \text{H}_2\text{Br}^+\text{O}_3 \\
\text{H}_2\text{Br}^+\text{O}_3 & \rightleftharpoons K_{p3} \text{Br}^+\text{O}_2 + \text{H}_2\text{O}
\end{align*}
\]

Hence, the oxidation in this study may be a reaction between substrate and one of the oxidant species. The effect of solvent polarity and rate acceleration with increase in [acid] mitigate the chances of unprotonated bromate, BrO₃⁻, to be the reactive species. Amis et al. proposed Br⁺O₂⁻ as the oxidising species in acid bromate oxidation of iodide. Anbar and Guttmann and Wright and Barton on the other hand suggested that in moderately strong acid solutions H₂Br⁺O₃ is the existing form. Beck and coworkers and Sanjeeva Reddy and Sundaram have suggested that both, HBrO₃ and H₂Br⁺O₃, are the existing forms of bromate in moderately strong acid solutions.

Oxalic acid is a dibasic acid with dissociation constants \( K_{a1} = 5.9 \times 10^{-2} \) and \( K_{a2} = 6.4 \times 10^{-5} \), at 30°C in aqueous solutions. As the second dissociation constant \( K_{a2} \) is very low, oxalic acid mainly exists in aqueous solutions as \( \text{H}_2\text{C}_2\text{O}_4 \) (OX) and \( \text{HC}_2\text{O}_4^- \) (OX⁻).

**Mechanism for the uncatalysed reaction**

To account for the kinetic findings of uncatalysed reaction a mechanism for the bromate-oxalic...
acid reaction is envisaged as a slow rate determining formation of oxalic-bromate ester followed by a fast decomposition to products (Scheme 1).

Scheme 1 leads to rate law (5).

$$\text{Rate} = -\frac{d[\text{Br(V)}]}{dt} = k_x[\text{OX}][\text{HBrO}_2] + k_y[\text{OX}][\text{H}_2\text{Br}^+\text{O}_3] + k_z[\text{OX}^-][\text{H}_2\text{Br}^+\text{O}_3]$$

(5)

In an aqueous solution of 0.01 mol dm$^{-3}$ oxalic acid, 87.1% of it exists in the form of HC$_2$O$_4^-$(OX$^-$). But in the presence of molar mineral acid solutions, the dissociation of oxalic acid is suppressed to a larger extent and only 5.5% exists in the dissociated (OX$^-$) form. Therefore in 0.01 mol dm$^{-3}$ oxalic acid, the concentrations of OX and OX$^-$ are 94.43 x 10$^{-4}$ mol dm$^{-3}$ and 5.57 x 10$^{-4}$ mol dm$^{-3}$ respectively. Hence the contribution of (OX$^-$) towards rate of oxidation is only five percent and-for all practical purposes it can be overlooked.

Therefore,

$$\text{Rate} = k_x[\text{OX}][\text{HBrO}_2] + k_y[\text{OX}][\text{H}_2\text{Br}^+\text{O}_3] + k_z[\text{OX}^-][\text{H}_2\text{Br}^+\text{O}_3]$$

(6)

(7)

The rate contribution of $k_y[\text{OX}][\text{H}_2\text{Br}^+\text{O}_3]$ is not much as this reaction involves an ion-dipole, wherein the ion, H$_2$Br$^+\text{O}_3$, is having more tendency to be solvated than HBrO$_3$. Hence its contribution towards the oxidation will be less. Therefore the value of $k_y < k_x$. If it is in appreciable proportion, the reaction should exhibit an order greater than one in [acid], which is not realized. With the aforesaid reasons, the interaction between oxalic acid and H$_2$Br$^+\text{O}_3$ and its contribution towards the observed rate is negligible. Moreover, theoretically it can be shown that the value of $K_{p_1}$ $K_{p_2}$ is five times less than that of $K_{p_1}$ as the values of these protonation constants are $K_{p_1}$ = 0.5 mol dm$^{-3}$, $K_{p_2}$ = 0.2 mol$^2$dm$^{-6}$ (ref. 19). The plot of log $k_{unc}$ versus $D^{-1/2}D^+$ is fairly linear, with a correlation coefficient of 0.9986 than that of log $k_{unc}$ versus 1/$D$ plot whose correlation coefficient is 0.960 only. Therefore it is presumed that ion-dipole interaction is contributing more to the reaction rate than ion-dipole. Based on the above reasons, the uncatalysed rate constant (rate/ [bromate]) is given by:

$$k_{unc} = k_xK_{p_1}[\text{OX}[\text{H}^+]]$$

(8)

The plots of $k_{unc}$ versus [oxalic acid] at fixed [H$^+$] and the plot of $k_{unc}$ versus [H$^+$] at fixed [OX] are passing through origin supporting the assumption (mechanism). $k_x$ value evaluated from the slopes of the above plots is $(1.7 \pm 0.05) \times 10^{-2}$. Because of the overall simplification, the error in $k_x$ value is around ± 5%.

**Mechanism for catalysed reaction**

The fractional order dependence on [substrate] and a definite intercept in Michaelis-Menten’s plot reveals that substrate is involved in the complex formation, may be either with bromate or catalyst. From the evidence accrued from uncatalysed oxalic acid-bromate reaction, such as first order dependence on [oxalic acid] and [bromate] and the plot of $1/k$ versus $1/[\text{OX}]$ passing through origin enable us to discard complexation between oxalic acid and bromate. In mineral acid solutions Ru(III) chloride exists in the form of [RuCl$_6$H$_2$O]$_2^{2-}$ (ref. 20-24) with an absorption maximum($\lambda_{max}$) of 490 nm. A change in the $\lambda_{max}$ and molar extinction coefficient of Ru(III) by the addition of oxalic acid (in the absence of bromate) suggests a complex formation between Ru(III) and oxalic acid, which would be an outer-sphere complex. Hence a reversible formation of Ru(III) complex with one mole of oxalic acid precedes the rate determining step (Eq. 9) which subsequently gets oxidised to CO$_2$ and H$_2$O by bromate (Eq. 10).

$$\text{OX} + \text{Ru(III)} \xrightarrow{K} [\text{Ru(III)}-\text{OX}]$$

(9)

$$[\text{Ru(III)}-\text{OX}]+\text{HBrO}_3 \xrightarrow{K} \text{[Intermediate]} \xrightarrow{k_d} \text{slow}$$

(10)

The slow oxidation process (Eq. 10) may involve transfer of electrons to Br(V) from the com-
plex of Ru(III) followed by a much faster breakdown of the Ru(V)-complex; for this, it never attains a spectroscopically detectable concentration.

As the overall reaction comprises of catalysed and uncatalysed reactions, proceeding simultaneously, the overall kinetic data is an agglomeration of these two reactions, which are contributing to the rate independently. Hence the overall reaction rate is equal to sum of the rates of catalysed and uncatalysed reactions.

\[
\frac{-d[\text{Br}(V)]}{dt} = k_d [\text{Intermediate}] + k_s K_{pl} [H^+] [OX][BrO_3^-] \quad \ldots (11)
\]

\[
[\text{Intermediate}] = K_f [\text{HBrO}_3][\text{Ru(III)}] - \text{OX} = K_f K_{pl} K_c [H^+] [\text{Ru(III)}][OX][BrO_3^-] \quad \ldots (12)
\]

Overall rate = \[
\frac{-d[\text{Br}(V)]}{dt} = k_d K_c K_f K_{pl} [H^+] [\text{Ru(III)}][OX][BrO_3^-] + k_s K_{pl} [H^+] [OX][BrO_3^-] \quad \ldots (13)
\]

At higher concentration of the catalyst, the rate of uncatalysed reaction will be very low in comparison with the catalysed reaction, hence negligible. So the rate expression can be written as:

\[
(\text{Rate})_{\text{cat}} = \frac{-d[\text{Br}(V)]}{dt} = k_d K_c K_f K_{pl} [H^+] [\text{Ru(III)}][OX][BrO_3^-] \quad \ldots (14)
\]

But, bromate is present in complexed and uncomplexed forms therefore the total [bromate] is given as:

\[
[\text{Br}(V)] = [\text{BrO}_3^-] + [\text{HBrO}_3] + [\text{H}_2\text{Br}^+\text{O}_3] + [\text{Intermediate}]
\]

\[
[\text{BrO}_3^-] = \frac{[\text{Br}(V)]}{[1 + K_{pl} [H^+] + K_{pl} K_p[H^+]^2 + K_f K_c K_{pl} [H^+] [OX] [\text{Ru(III)}]]} \quad \ldots (15)
\]

Substituting this value in Eq. (14) and rearranging we have

\[
k_{\text{cat}} = \frac{-d[\text{Br}(V)]}{dt} / [\text{Br}(V)] = k_d K_c K_f K_{pl} [H^+] [\text{Ru(III)}][OX] \quad \ldots (16)
\]

\[
\frac{1}{k_{\text{cat}}} = \frac{3.2}{k_d K_c K_f [OX][\text{Ru(III)}]} \quad \ldots (17)
\]

At fixed [Ru(III)] = 9.56 \times 10^{-5} mol dm^{-3} if [OX] is varied, the plot of \( k_{\text{cat}} \) against [OX] should be linear and the same is realized from the plot. The value of \( k_d \) calculated from the intercept \( 1/k_{\text{cat}} \) on y-axis, is 2.50 ± 0.01 \times 10^{-3}. Similarly at fixed [OX] = 0.01 mol dm^{-3}, if Ru(III) is varied, the plot \( 1/k_{\text{cat}} \) versus \( 1/\text{Ru(III)} \) should be linear such a realisation supports the proposed mechanism. In this case also the intercept on y-axis is equal to \( 1/k_d \) and the value of \( k_d \) calculated is 2.49 ± 0.01 \times 10^{-3}. From the slopes of above mentioned two plots and the knowledge of \( k_d \), the product of \( K_c K_f \) can be evaluated. The values of \( K_c K_f \) calculated are 6.97 \times 10^5 and 7.01 \times 10^5 from the above mentioned plots. The close agreement of \( k_d \) and \( K_c K_f \) values obtained from different effects supports the mechanism envisaged.

At low concentrations of the catalyst, the contribution of uncatalysed reaction is also in appreciable proportion. Hence,

\[
k_{\text{overall}} = k_{\text{cat}} + k_{\text{uncat}} \quad \ldots (18)
\]

The subsequent stage of reaction of Br(III) given in Scheme 1 and Eq. (10) to transform into bromide ion proceeds by any one of the pathways. One such pathway involving step wise two electron transfer is

\[
\text{COOH}_2 + \text{HBrO}_2 \xrightarrow{\text{fast catalyst}} \text{H}_2\text{O} + \text{HOBr} + 2\text{CO}_2 \quad \ldots (19)
\]

\[
\text{COOH}_2 + \text{HOBr} \xrightarrow{\text{fast catalyst}} \text{H}_2\text{O} + \text{H}^+ + \text{Br}^- + \text{CO}_2 \quad \ldots (20)
\]

The hypobromous acid oxidation of oxalic acid in the absence of catalyst follows third order, being first order each in [H^+], [OX] and [HOBr]. The rates of these reactions (19 and 20) are much faster than Ru(III) catalysed acid-bromate oxidation.
References
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