Kinetics of Ru(III)-catalysed & Uncatalysed Oxidation of Chloroacetic Acids by N-Bromosuccinimide in Aqueous Solution

P SAROJA & SUSHAMA KANDUKAR*
Department of Chemistry, Nizam College (Osmania University), Hyderabad 500 001

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The title reaction, studied in the presence of mercuric acetate and sulphuric acid is first order in \([\text{NBS}]\) both in the presence and absence of catalyst Ru(III). However, the order in [substrate] in the absence of Ru(III), is unity which changes to fractional order in its presence. Increase in \([\text{H}^+]\) retards the reaction rate. The order of reactivities of the three acetic acids is: trichloroacetic acid > dichloroacetic acid > monochloroacetic acid. Individual rate constants \((k)\), formation constants \((K_i)\) of the complexes of chloroacetic acids and the catalyst and corresponding thermodynamic parameters have been evaluated and a suitable mechanism involving the unprotonated NBS as the reactive species has been suggested.

N-Bromosuccinimide (NBS) has been extensively used as an oxidant in the study of kinetics and mechanism of oxidation of both organic and inorganic substrates. Similar work does not appear to have been carried out employing monochloroacetic acid (MCA), dichloroacetic acid (DCA) and trichloroacetic acid (TCA) as substrates and hence the title investigation.

All the chemicals used were either BDH or E. Merck (AR) samples. The solution of RuCl₃ (Johnson-Matthey) was standardised by the method given by Houriuichi and Ichiyyo¹. Purified acetic acid was used. Solution of NBS was always prepared afresh and standardised iodometrically². All the reactions were carried out in reaction flasks blackened from outside. The reaction was followed by the method described earlier³.

The results can be summarised as follows:

(i) The reaction mixture containing chloroacetic acid \((5 \times 10^{-2} \text{ mol dm}^{-3})\), H₂SO₄ \((5 \times 10^{-3} \text{ mol dm}^{-3})\), and Hg(OAc)₂ \((2 \times 10^{-2} \text{ mol dm}^{-3})\) was mixed with large excess of [NBS] and kept for 36 hr at 30°C. The unutilised NBS was estimated iodometrically till a constant value was obtained. This stoichiometric run indicated that 1 mol of NBS reacted with 1 mol of chloroacetic acid to afford 1 mol of formaldehyde (characterised as usual) in the case of MCA and DCA and 1 mol of formic acid in the case of TCA.

(ii) Under the experimental conditions \([\text{NBS}] < [\text{S}]\) (where \(S = \text{substrate}\)) and in the presence and absence of Ru(III) the plots of log \(a(a - x)\) versus time were linear passing through the origin indicating the order in [NBS] to be unity for both the catalysed and uncatalysed systems.

(iii) The rate increased with increase in \([\text{S}]\). The plot of log (rate) versus log \([\text{S}]\) in the absence of Ru(III) was linear with unit slope indicating first order dependence in \([\text{S}]\).

(iv) At fixed \([\text{Ru(III)}]\), the rate of oxidation increased considerably but order in \([\text{S}]\) changed from unity to fractional, viz. 0.6, 0.5 and 0.4 in the case of MCA, DCA and TCA respectively.

(v) The reaction rate increased with increase in \([\text{Ru(III)}]\) and order in \([\text{Ru(III)}]\) was fractional, when the gross rate \(V_g\) was considered. However, when the uncatalysed rates \(V_u\) were deducted from gross rates \(V_g\) the order in [Ru(III)] was unity as revealed by the linear plot of log \(V_c = V_g - V_u\) versus log [Ru(III)].

(vi) A four-fold change (0.02 to 0.08 mol dm⁻³) in mercuric acetate concentration had negligible effect on the rate of oxidation.

(vii) Added succinimide in the concentration range of 0.02 to 0.1 mol dm⁻³ had a negligible retarding effect.

(viii) Addition of salts, like NaClO₄ and KHSO₄ etc. did not have much effect on the rate of reaction.

(ix) The rates of reactions were retarded by increase in \([\text{H}^+]\) at constant ionic strength \((\text{NaClO}_4)\) in the presence as well as in the absence of Ru(III) catalyst. As a typical case the data for NBS-TCA system are given in Table 1.

(x) The reaction rates decreased with increase in percentage of acetic acid in the solvent medium.

<table>
<thead>
<tr>
<th>([\text{H}^+](\text{mol dm}^{-3}))</th>
<th>(10^7 V) (mol dm⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>2.08 (2.40)</td>
</tr>
<tr>
<td>0.5</td>
<td>1.67 (3.00)</td>
</tr>
<tr>
<td>2.5</td>
<td>1.45 (3.45)</td>
</tr>
<tr>
<td>5.0</td>
<td>1.25 (4.00)</td>
</tr>
<tr>
<td>10.0</td>
<td>0.83 (6.00)</td>
</tr>
<tr>
<td>20.0</td>
<td>0.63 (8.00)</td>
</tr>
</tbody>
</table>

Table 1—Effect of Variation of \([\text{H}^+]\) on Rate of Oxidation of Chloroacetic Acids
Table 2—Kinetic and Thermodynamic Parameters for Uncatalysed and Catalysed Reactions

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( k \times 10^4 ) (mol(^{-1}) dm(^3) s(^{-1}))</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
<th>( \Delta G^\dagger ) (kJ mol(^{-1}))</th>
<th>( -\Delta S^\dagger ) (JK(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uncatalysed reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCA</td>
<td>1.67</td>
<td>68.9</td>
<td>96.3</td>
<td>98.7</td>
</tr>
<tr>
<td>DCA</td>
<td>2.50</td>
<td>57.5</td>
<td>95.1</td>
<td>132.5</td>
</tr>
<tr>
<td>TCA</td>
<td>6.66</td>
<td>46.0</td>
<td>92.2</td>
<td>161.1</td>
</tr>
<tr>
<td>Catalysed reaction*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCA</td>
<td>6.57</td>
<td>26.8</td>
<td>69.5</td>
<td>149.2</td>
</tr>
<tr>
<td>DCA</td>
<td>8.76</td>
<td>23.0</td>
<td>68.8</td>
<td>159.4</td>
</tr>
<tr>
<td>TCA</td>
<td>17.00</td>
<td>17.2</td>
<td>67.1</td>
<td>172.9</td>
</tr>
</tbody>
</table>

*Values of \( K_1 \) (dm\(^3\) mol\(^{-1}\)) are found to be 8.00, 9.24 and 10.3 at 303 K for MCA, DCA and TCA respectively.

example, under the conditions [NBS] = 5.0 \times 10^{-5} mol dm\(^{-3}\), [TCA] = 5.0 \times 10^{-2} mol dm\(^{-3}\), [Hg(OAc)\(_2\)] = 2.0 \times 10^{-2} mol dm\(^{-3}\), \([H^+] = 5.0 \times 10^{-3} mol dm\(^{-3}\) and temp. = 303 K, \( 10^7 \) rate decreased from 3.3 to 0.8 mol dm\(^{-3}\) s\(^{-1}\) in the absence of catalyst and from 4.16 to 1.67 mol dm\(^{-3}\) s\(^{-1}\) in the presence of \( 2.0 \times 10^{-5} mol dm\(^{-3}\) of Ru(III) when percentage (v/v) of acetic acid was increased from 10 to 80.

The reaction was carried out at three different temperatures in the range of 300 to 325 K and the thermodynamic parameters have been computed using Arrhenius equation (Table 2).

Uncatalysed reaction

The rate of reaction decreased with increase in \([H^+]\) (Table 1). This may be explained by assuming an equilibrium between unprotonated and protonated NBS (NBS + H\(^+\) = N\(^+\)BSH) and that unprotonated species is the reactive one.

The observed first order dependence in [NBS] as well as in [S] in the uncatalysed reaction is suggestive of a mechanism shown in Scheme 1 (taking MCA as a typical example).

Scheme 1 leads to the rate law (1),

\[
-\frac{d[NBS]}{dt} = k' [NBS][S] 1 + K[H^+] \quad \ldots (1)
\]

which is in complete accord with the observations.

Equation (1) may be written as

\[
-\frac{d[NBS]}{dt} \times \frac{1}{[NBS]} = k' = \frac{k'[S]}{1 + K[H^+]} \quad \ldots (2)
\]

Taking reciprocal of Eq. (2) we get

\[
\frac{1}{k'} = \frac{1}{k'[S]} + \frac{K[H^+]}{k'[S]} \quad \ldots (2)
\]

When \( 1/k' \) was plotted against [H\(^+\)] at different temperatures the plots were linear; \( k' \) values were calculated from the intercepts and when these values were substituted in the values of slope the different equilibrium constants \( (K) \) were evaluated (Table 1). These \( K \) values decreased with increase in temperature indicating that the protonation of NBS is exothermic in nature.

In order to find out the nature of reactive species, the solvent effect was studied with varying acetic acid content in the solvent. The reaction rate decreased with decrease in dielectric constant i.e. with the increase in acetic acid content, showing a dipole-dipole type of reaction in agreement with the Kirkwood's theory.

Catalysed reaction

First order dependence in [NBS] and fractional order in [S] and [Ru(III)], and the ability of platinum group metals to form complexes with organic substrates and highly enhanced rates substantiate formation of Ru(III) - S complex (Scheme 2) which slowly reacts with NBS in the rate-determining step to give products.

\[
NBS + H^+ \rightleftharpoons NBSH
\]

\[
NBS + H^+ \rightarrow [Ru(III) - S]_{complex}
\]

\[
[Ru(III) - S] + NBS \rightarrow k_{slow} [Ru(V) - S]
\]

\[
[Ru(V) - S] \rightarrow fast HCHO + HBr + Ru(III) + NH(CH_2CO)_2 + HCl
\]

Scheme 2

\[
\frac{1}{d[NBS]} = \frac{k[NBS][complex]}{dt} = k[NBS][complex] \quad \ldots (3)
\]

Scheme 2 leads to rate law (3)

\[
\frac{1}{d[NBS]} = \frac{k[NBS][complex]}{dt} = k[NBS][complex] \quad \ldots (3)
\]
where \( k' \) is the observed pseudo-first order rate constant, \( k \) the bimolecular rate constant for the slow step and \( K_1 \) the formation constant. Equation (3) explains all the experimental observations obtained. Taking reciprocal of Eq. (4) we get

\[
\frac{d[NBS]}{dt} = \frac{kK_1[NBS][S][\text{Ru(III)}]}{1 + K_1[S]} \\\ \\\ \\\ \\ (4)
\]

\[
-k' \times \frac{1}{[\text{NBS}]} = k' = \frac{kK_1[S][\text{Ru(III)}]}{1 + K_1[S]} \times \frac{1}{1 + K[H^+]} \\\ \\\ \\\ \\ \ (5)
\]

It is clear from Eq. (5) that the plot of \( 1/k' \) versus \( 1/[S] \) at fixed \([\text{Ru(III)}]\) should be linear; such Michaelis-Menten reciprocal plots were obtained for all the three acetic acids studied with an intercept on the \( 1/k' \) axis confirming the derived rate law. From the values of the intercept and slope and the values of \( K_1 \) obtained from the uncatysed reaction (Table 1) the bimolecular rate constants \( (k) \) and the formation constants \( (K_1) \) were evaluated at different temperatures (Table 2).

The rates of oxidation of different acetic acids for both uncatysed and catalysed reactions followed the order: TCA > DCA > MCA. It was observed that the formation constant \( (K_1) \) decreased with increase in temperature indicating that the reaction between Ru(III) and the chloroacetic acid is exothermic in nature. This is also indicated by the \( \Delta H \) values corresponding to the formation constants. From the results in Tables 1 and 2 it is clear that both \( \Delta H' \) and \( \Delta S' \) are important in controlling the rates of reaction, though the enthalpy factor seems to be predominating. This point was also verified by calculating the isokinetic temperature \( (\beta) \) which was found to be 360 K for catalysed and 400 K for uncatalysed reactions. These are well above the temperature range (303 to 323 K) employed in the work. Constancy of calculated \( \Delta G' \) for catalysed and uncatalysed systems indicates that an identical mechanism is operative for all the three acids.

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References