Kinetics & Mechanism of Oxidation of Glycine with Aquomanganese(III) Ion in Perchlorate Medium

RAJAGOPALA VARADARAJAN* & MARY JOSEPH
Department of Chemistry, Indian Institute of Technology, New Delhi 110 029

Received 6 December 1979; accepted 17 January 1980

The title reaction has been investigated at constant ionic strength and at different acidities. The reaction is found to proceed through an outersphere mechanism. The reaction is first order in manganic ion and first order in glycine. The rate is proportional to $[H^+]^{-1}$ at a lower temperature (45°C) whereas at 55° and 65°C, it becomes proportional to $[H^+]^{-3}$. A mechanism consistent with rate data has been proposed.

Oxidation of glycine with cobalt(III) ion has been studied in perchlorate medium but the oxidation with manganic ion has not been studied. Beg and Kalamuddin have reported the oxidation of glycine with manganic sulphate. A rate equation involving $[Mn(III)]^2$ has been suggested for this oxidation. Several oxidation studies involving manganic ion with different substrates reveal a first order dependence of rate on manganic ion. Due to this anomaly, the title reaction has been investigated in perchlorate medium and the results are reported in this paper.

Materials and Methods

Manganic ion was prepared by the electrolytic oxidation of Mn(II) in perchlorate medium under nitrogen. The concentrations of HClO$_4$ and Mn(II) were always higher than that of Mn($^{II}$) to maintain the equilibrium (1).

$$\text{Mn(III)} + \text{Mn(II)} \rightleftharpoons \text{Mn(IV)} + \text{Mn(II)} \quad \text{(1)}$$

well towards the left. Mn(II) perchlorate was prepared from Mn(II) sulphate (AR, BDH), glycine (Riedel) was used as such. Mn(III) was determined by reaction with excess standard iron(II) perchlorate and subsequent spectrophotometric estimation of Fe(III) formed at 260 nm.

Since at low acidities, even in the presence of excess Mn(II), the hydrolytic constant $K_h$ is affected to some extent, most of the studies were limited upto 3M perchloric acid. The rate of decrease in $[\text{Mn(III)}]$ in these oxidations was followed spectrophotometrically at 270 nm in the thermostated cell employing a Pye Unicam SP 500 spectrophotometer. Only freshly prepared Mn(III) was used. The ionic strength was adjusted by the addition of either sodium perchlorate or manganese(II) perchlorate.

Results

Stoichiometry — The stoichiometry of this reaction was determined by keeping excess of Mn(III) with glycine for several hours and estimating the remaining Mn(III) spectrophotometrically. The stoichiometry was found to be 2 : 1 (oxidant : substrate). Mn(III)-glycine mixtures induced polymerization of acrylonitrile and hence it was concluded that free radicals are involved as intermediates.

The products of this oxidation have been found to be formaldehyde and ammonia. These were detected as in the case of oxidation of glycine by cobalt(III) ion. The course of the reaction may be represented by Eq. (2).

$$2\text{Mn(III)} + \text{NH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O} \rightarrow 2\text{Mn(II)} + \text{NH}_3 + \text{HCHO} + \text{CO}_2 + 2\text{H}^+ \quad \text{(2)}$$

The activation parameters were calculated by the method of linear regression.

Kinetics — There is no spectroscopic evidence for the formation of Mn(III)-glycine complexes as no changes occur in the absorption spectrum of Mn(III) on the addition of glycine. But slow changes in absorbance occur due to oxidation. With glycine in excess the disappearance of Mn(III) is first order and the pseudo-first order rate constant is independent of $[\text{Mn(II)}]$ (Table 1) as well as the presence or absence of oxygen (Table 1). It is found that at constant $[\text{Mn(III)}]$ and of different [glycine] (Table 2) the rate is directly proportional to [glycine] and hence the reaction is first order in glycine (Fig.1; curves at 45°C) (similar plots have been obtained at 55° and 65°C). The bimolecular rate constants in the acidity range 3 M to 6 M at an ionic strength of 6.3 M are sensitive to changes in acidities as well as temperatures (Table 3).

Discussion

At a fixed acidity, the rate is independent of $[\text{Mn (III)}]$ and $[\text{Mn(II)}]$, (Tables 1 and 2), indicating that Mn(IV) is not an active species in this oxidation. Further, the bimolecular rate constant decreases with increasing perchloric acid concentration. Assuming
that in the range of perchloric acid up to 3 M, the equilibrium (3)
\[ \text{Mn(H}_2\text{O)}_4^{2+} \rightleftharpoons \text{Mn(OH)}_2^{2+} + \text{H}^+ \]  
exists and that all pyrolytic equilibria are rapid with respect to other steps and a radical mechanism operates, then,

\[ \text{Mn}^{2+} + \text{Gly}^+ \rightarrow \text{Mn}^{2+} + \text{NH}_4^+ \text{CH}_2\text{COO}^- + \text{H}_2\text{O}^+ \]  
and

\[ \text{Mn(OH)}_2^{2+} + \text{Gly}^+ \rightarrow \text{Mn}^{2+} + \text{NH}_4^+ \text{CH}_2\text{COO}^- + \text{H}_2\text{O}^+ \]  

where \( k \) and \( k_a \) are the rate constants for the oxidation by Mn(III) and the hydrolysed species respectively. The rate expression is then given by Eq. (6)

\[
k_a = k + k_b K_h \quad [\text{H}^+]^{-1}
\]

where

\[
K_h = \frac{[\text{Mn(OH)}_2^{2+} \text{aq}][\text{H}^+]}{[\text{Mn}^{2+} \text{aq}]} \quad (8)
\]

The fact that the plot of the overall bimolecular rate constant against \([\text{H}^+]^{-1}\) passes through the origin suggests that the hydrolysed species are more reactive than the aquomanganic ion in these oxidations. Further at 55° and 65°, the above plot is not linear but when overall bimolecular rate constant is plotted against \([\text{H}^+]^{-1}\), the plot becomes linear (Fig. 2). This indicates that at higher temperatures either the hydroxo species further undergoes hydrolysis as in Eq. (9).

\[
\text{Mn(OH)}_2^{2+} \text{aq} \rightleftharpoons \text{Mn(OH)}_2^{2+} \text{aq} + \text{H}^+ \quad (9)
\]

or a loose outersphere complex \([\text{Mn(OH)}_2^{2+} - \text{Gly}^+]^{-}\) loses a proton. A linear plot is obtained for \( k_a \) against \( 1/T \) K. A comparison of overall \( \Delta S \) (−40 e.s.u.) and \( E_a \) (12 kcal/mol) (Table 3) for this oxidation with those of some other oxidation react-

**Table 1** — Effect of Added Mn(II) and Mn(III) on Pseudo-first Order Rate Constants

<table>
<thead>
<tr>
<th>[Mn(II)] M</th>
<th>( k_a \times 10^4 ) (min(^{-1}))</th>
<th>[Mn(III)] M</th>
<th>( k_a \times 10^4 ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>4.60</td>
<td>0.5</td>
<td>8.2*</td>
</tr>
<tr>
<td>0.1</td>
<td>4.67</td>
<td>1.0</td>
<td>7.8*</td>
</tr>
<tr>
<td>0.2</td>
<td>4.75</td>
<td>1.5</td>
<td>7.1*</td>
</tr>
</tbody>
</table>

*Values in air

†Value under N\(_2\) atmosphere

**Table 2** — Values of Observed Rate Constants at Different [Glycine], \( k_a \times 10^4 \) min\(^{-1}\) at [HClO\(_4\)]

<table>
<thead>
<tr>
<th>10(^6) [Glycine] M</th>
<th>( k_a \times 10^4 ) (min(^{-1})) at [HClO(_4)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.78</td>
</tr>
<tr>
<td>4.0</td>
<td>3.16</td>
</tr>
<tr>
<td>6.0</td>
<td>4.47</td>
</tr>
<tr>
<td>8.0</td>
<td>5.62</td>
</tr>
<tr>
<td>10.0</td>
<td>6.84</td>
</tr>
<tr>
<td>12.0</td>
<td>7.94</td>
</tr>
</tbody>
</table>

**Fig. 1** — Plots of \( k_a \) versus [glycine] at 45°C; \( I = 6.3 \text{M} \)

\[
\frac{d[Mn^{3+} \text{aq}]}{dt} = 2[\text{Gly}][k[Mn^{3+} \text{aq}] + k_a[Mn(\text{OH})^{4+} \text{aq}]]
\]

Introducing the appropriate terms for the hydrolysed species and integrating,

\[
k_a = k + k_b K_h [\text{H}^+]^{-1}
\]

where

\[
K_h = \frac{[\text{Mn(OH)}_2^{2+} \text{aq}][\text{H}^+]}{[\text{Mn}^{2+} \text{aq}]} \quad (8)
\]
Fig. 2 — Plots of $k_2$ versus $[H^+]^{-1}$ at 45°C and $k_1$ versus $[H^+]^{-2}$ at 55°C and 65°C relations suggests that the transition state extra stability is achieved by the formation of a loose coordinate bond between the hydroxo species and the positive carbon centre of the carboxylic carbon of the amino acid as in the case of the Mn(III) oxidation of formic acid.

Table 4 — Values of Energy, Enthalpy, Entropy and Free Energy of Activation in the Acidity Range 3 M to 6 M

<table>
<thead>
<tr>
<th>$[\text{HClO}_4]$</th>
<th>$E_a$ (kcal/mol)</th>
<th>$\Delta H_{\text{is}}^{\dagger}$ (kcal/mol)</th>
<th>$\Delta S_{\text{is}}^{\dagger}$ (e.u.)</th>
<th>$\Delta G_{\text{is}}^{\dagger}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>11.96±4.59</td>
<td>11.33±4.59</td>
<td>-41.55±14.01</td>
<td>24.54±6.4</td>
</tr>
<tr>
<td>5</td>
<td>12.04±1.65</td>
<td>11.40±1.65</td>
<td>-40.58±5.03</td>
<td>24.31±2.3</td>
</tr>
<tr>
<td>4</td>
<td>12.29±0.39</td>
<td>11.66±0.39</td>
<td>-38.91±11.94</td>
<td>24.04±3.82</td>
</tr>
<tr>
<td>3</td>
<td>15.14±1.63</td>
<td>14.51±1.63</td>
<td>-29.48±4.97</td>
<td>23.88±2.27</td>
</tr>
</tbody>
</table>

Acknowledgement

One of the authors (M.J.) thanks the CSIR, New Delhi for a junior research fellowship.

References