Kinetics & Mechanisms of Oxidations by Metal Ions: Part II†—Oxidation of Glycolic Acid by Aquamanganese(III) Ions

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Received 27 November 1981; accepted 8 March 1982

The kinetics of the oxidation of glycolic acid by aquamanganese(III) ions in perchlorate solution ([I = 4 mol dm⁻³]) has a first order dependence both in [Mn(III)] and [glycolic acid], and a zero order dependence in [Mn(II)] and [H⁺]. Two equivalents of Mn(III) are consumed for the oxidation of each molecule of glycolic acid into formaldehyde. Reaction mixtures initiate the polymerisation of acrylonitrile suggesting the generation of free radicals. The insensitivity of the rate to changes in [H⁺] and [Mn(II)] is explained by assuming that the reactivity of Mn³⁺ (aq.) ~ MnOH⁺ (aq.) and that Mn(IV) is not an active oxidant. A suitable mechanism has been proposed for the oxidation, which has ΔH° = 110 ± 4 kJ mol⁻¹ and ΔS° = 88 ± 8 J K⁻¹ mol⁻¹. Some comments on the explanation of retarding effect of Mn(II) in the oxidation of methanol [C.F. Wells & C. Barnes, J. chem Soc. (A), (1971) 430] are also made.

The oxidation of organic compounds by aquamanganese(III) ions has been reviewed by Davies. A number of similarities in the kinetics of oxidation of 2-hydroxy-2-methylpropanoic acid and isopropanol have been observed including the formation of the identical free radical (>COH). This prompted us to undertake the title investigation because the oxidation of glycolic acid was expected to produce the radical CH₂OH similar to that produced in the oxidation of methanol, and the investigation also provided an opportunity to compare the kinetics of oxidation of an α-hydroxy acid with that of a primary alcohol with a view to understanding the retarding effect of Mn(II) in the oxidation of methanol.

Materials and Methods

The manganese(II) perchlorate (G.F. Smith) solution was standardised against sodium salt of EDTA (BDH) in the presence of ammonium hydroxide using 4-(2-pyridylazo)resorcinol indicator. Its electrolytic oxidation to obtain aquamanganese(III) ions is described elsewhere. The manganese(III) solution was always prepared fresh and standardised by adding so that overall [HClO₄] ~ 1 mol dm⁻³. Sodium perchlorate (anhydrous, G.F. Smith) solution was standardised gravimetrically. All the solutions were prepared in doubly distilled water.

Stoichiometry and product study—Reaction mixtures having excess glycolic acid over known [Mn(III)], at different acidities and molar ratios, were prepared at room temperature (~25-27°C). After the completion of the reaction, indicated by the disappearance of the Mn(III) colour, a part of the reaction mixture was treated with 2,4-dinitrophenyl-hydrazine hydrochloride. The precipitated hydrazone prepared from formaldehyde was 167° (lit. 8 166°). Formaldehyde was estimated quantitatively using chromotropic acid. These determinations indicated that Δ[Mn(III)]/Δ[HCHO] = 1.98 ± 0.2. This ratio was not affected when the reactions were carried out under nitrogen atmosphere. Thus the stoichiometry for the reaction can be expressed by Eq. (1).

2Mn(III) + CH₂OH.CO₂H → HCHO + 2Mn(II) + CO₂ + 2H⁺ … (1)

Rate measurements—The kinetics of the reaction was followed titrimetrically as described earlier under pseudo-first order conditions i.e. a large excess of glycolic acid was always present in the reaction mixture. Ionic strength was kept constant at 4 mol dm⁻³ with sodium perchlorate. However, before

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†For part I, see ref. 1.
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Table I—The Dependence of the Observed Pseudo-first Order Rate Constant $k_{obs}$ on the $[\text{CH}_2\text{OH.CO}_3\text{H}]_0$ at Different Temperatures

<table>
<thead>
<tr>
<th>$[\text{CH}_2\text{OH.CO}_3\text{H}]_0$ (M)</th>
<th>17</th>
<th>25</th>
<th>30</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.65</td>
<td>2.19</td>
<td>4.42</td>
<td>8.50</td>
</tr>
<tr>
<td>1.0</td>
<td>1.20</td>
<td>4.20</td>
<td>8.48</td>
<td>17.00</td>
</tr>
<tr>
<td>1.5</td>
<td>1.77</td>
<td>6.05</td>
<td>12.5</td>
<td>25.5</td>
</tr>
<tr>
<td>2.0</td>
<td>2.32</td>
<td>8.10</td>
<td>16.6</td>
<td>--</td>
</tr>
<tr>
<td>2.5</td>
<td>2.90</td>
<td>10.00</td>
<td>20.7</td>
<td>--</td>
</tr>
<tr>
<td>5.0</td>
<td>5.72</td>
<td>19.8</td>
<td>--</td>
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</tr>
</tbody>
</table>

The observed pseudo-first order rate constant, $k_{obs}$, was found to be independent of $[\text{CH}_2\text{OH.CO}_3\text{H}]$ in the range 0.02-2.0 M. The rate of reaction was found to be independent of the acidity of the reaction mixture, indicating that free radicals were generated during the course of the reaction. Addition of acrylonitrile to a solution of aquamanganese(III) ions did not result in any polymerisation. The observed pseudo-first order rate constant, $k_{obs}$, with the mean values are reported in Table I. The plot of $k_{obs}$ versus $-\text{log}(a-x)$ against time. The reproducibility of the $k_{obs}$ was within ±3%. The results are reported in Table 1. The plot of $k_{obs}$ versus $[\text{CH}_2\text{OH.CO}_3\text{H}]$ increased the $k_{obs}$ proportionately. These experiments were carried out at four different temperatures and the results are reported in Table I. The plot of $k_{obs}$ versus $[\text{CH}_2\text{OH.CO}_3\text{H}]$ was linear with a zero intercept. This observation is similar to one reported in the oxidation of 2-hydroxy-2-methylpropanoic acid and isobutyric acids.

### Discussion

The $pK_2$ of glycolic acid is 3.83 at 25°C (ref. 11) and as such the existence of $\text{CH}_2\text{OH.CO}_2^-$ in solutions $>1\text{ mol dm}^{-3}$ perchloric acid may be neglected. This means that the reactive entity is glycolic acid.

The freshly prepared aquamanganese(III) solutions obtained by electrolytic oxidation have negligible dimeric species. The disproportionation equilibrium (2) is now well established. This equilibrium also explains as to why a large $[\text{Mn(II)}]$ is maintained to stabilise aquamanganese(III) ion during its preparation.

\[
\text{Mn(III)} + \text{Mn(II)} \rightarrow \text{Mn(IV)} + \text{Mn(II)} \quad \ldots \quad (2)
\]

Since the rate was independent of $[\text{Mn(II)}]$, it was concluded that Mn(IV) was not an active oxidant. This observation and conclusion are similar to those gathered in the oxidation of 4-ketopentanoic acid by aquamanganese(III) ions. Similarly the possibility of the formation of a glycolic acid-Mn(II) complex was also ruled out. It is with respect to equilibrium (2) and the observed retardation of the oxidation of methanol by Mn(II) that we suspect that Mn(IV) could also be an active oxidant for methanol. The evidence for the involvement of Mn(IV) in methanol oxidation is provided elsewhere in the paper.

The spectral studies of aquamanganese(III) ions in solutions of varying acidities established that $\text{Mn}^{3+}($aq. $)$ ion was considerably hydrolysed even at high acidity. Wells and Davies reported that $K_b$ for reaction (3) has a value 0.93 mol dm$^{-3}$ in perchloric acid solution of ionic strength 4 mol dm$^{-3}$ (maintained with sodium perchlorate) at 25°C, and $\Delta H_b = 20\text{ kJ mol}^{-1}$. This value of the enthalpy has been used to calculate the $K_b$ at the other desired temperatures.

The data are not definitive enough as to help in differentiating between outer-sphere and inner-sphere mechanisms. Consistent with the observed first order dependence in [glycolic acid], an outer-sphere mechanism (Scheme I) is first considered.

Equilibrium (4) is consistent with the known protonation of carboxylic acids and 2-hydroxy-2-methylpropanoic acid. The protonated species are considered to be unreactive. The rate of...
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\[ \text{CH}_2\text{OH.CO}_2\text{H} + \text{Mn}^{3+} (\text{aq.}) \rightarrow \text{CH}_2\text{OH} + \text{CO}_2 + \text{H}^+ \] (3)

\[ \text{CH}_2\text{OH.CO}_2\text{H} + \text{Mn}^{4+} (\text{aq.}) \rightarrow \text{CH}_2\text{OH} + \text{CO}_2 + \text{H}^+ \] (4)

\[ \text{CH}_2\text{OH.CO}_2\text{H} + \text{MnOH}_2^+ (\text{aq.}) \rightarrow \text{CH}_2\text{OH} + \text{CO}_2 + \text{H}^+ \] (5)

\[ \text{CH}_2\text{OH.CO}_2\text{H} + \text{MnOH}_2^+ (\text{aq.}) \rightarrow \text{CH}_2\text{OH} + \text{CO}_2 + \text{H}_2\text{O} \] (6)

\[ \text{Mn}^{3+} + \text{CH}_2\text{OH} \rightarrow \text{Mn}^{4+} + \text{HCHO} + \text{H}^+ \] (7)

Scheme 1

disappearance of oxidant, in terms of reactions (3)-(7), would be expressed by Eq. (8),

\[ \frac{d[\text{Mn}^{3+}]}{dt} = \frac{2(k_3 + k_4 K_{\text{H}^+}^{-1})[\text{CH}_2\text{OH.CO}_2\text{H}]_0[\text{Mn}^{3+}]}{(1 + K_b[\text{H}^+]) (1 + K_c[\text{H}^+]}} \] (8)

Now two assumptions have been made to explain the invariance of \( k_{\text{obs}} \) with respect to [H +] and these are: (i) \( k_3 = k_4 \); and (ii) \( K_c[\text{H}^+] \leq 1 \). With these assumptions Eq. (8) reduces to Eq. (9),

\[ k_{\text{obs}} = 2k[\text{CH}_2\text{OH.CO}_2\text{H}]_0 \] (9)

The experimental value of \( K_c \) is not as yet known. However, the same could be estimated by extrapolation of the linear relation between log \( K_c \) corresponding to acetic, n-propanoic and n-butyric acids and \( \sigma^* \), where \( \sigma^* \) is the Taft’s constant. The \( K_c \) value so obtained was 0.00043 dm³ mol⁻¹ which justifies the assumption (ii).

The values of \( k = k_{\text{obs}}/[\text{CH}_2\text{OH.CO}_2\text{H}]_0 \) are reported in Table 2 and the values of \( \Delta H^*_f \) and \( \Delta S^*_f \), calculated from the slope and intercept of the linear plot between log \( k \) and \( T^{-1} \) are also reported there. The positive entropy indicates that there is a probability of the formation of a transition state and in this process water molecules from the hydration sphere are set free.

Despite the above outer-sphere mechanism, which explains the kinetics, the probability of an inner-sphere mechanism cannot be ruled out specially when it is known that in the oxidation of 2-hydroxy-2-methyl-propanoic acid the rapid increase in the initial absorbance at high [HMP]/[Mn(III)] due to the formation of an intermediate Mn(III)-substrate (quinol¹⁹ and pinacol²⁰) is complete in less than 0.2 sec.

Based on this the inner-sphere mechanism of the reaction may be expressed by Scheme 2.

\[ \text{Mn}^{3+} (\text{aq.}) \rightarrow \text{Mn}^{4+} (\text{aq.}) + \text{H}^+ (\text{aq.}) \] (3)

\[ \text{CH}_2\text{OH.CO}_2\text{H} + \text{Mn}^{4+} (\text{aq.}) \rightarrow \text{CH}_2\text{OH} + \text{CO}_2 + \text{H}^+ \] (4)

\[ \text{CH}_2\text{OH.CO}_2\text{H} + \text{MnOH}_2^+ (\text{aq.}) \rightarrow \text{CH}_2\text{OH} + \text{CO}_2 + \text{H}^+ \] (5)

\[ \text{CH}_2\text{OH.CO}_2\text{H} + \text{MnOH}_2^+ (\text{aq.}) \rightarrow \text{CH}_2\text{OH} + \text{CO}_2 + \text{H}_2\text{O} \] (6)

\[ \text{Mn}^{3+} + \text{CH}_2\text{OH} \rightarrow \text{Mn}^{4+} + \text{HCHO} + \text{H}^+ \] (7)

Scheme 2

Based on the Scheme 2 the rate of disappearance of [Mn(III)] would be expressed by Eq. (15),

\[ \frac{d[\text{Mn}^{3+}]}{dt} = \frac{2(k_3 + k_4 K_{\text{H}^+}^{-1})[\text{Mn}^{3+}][\text{CH}_2\text{OH.CO}_2\text{H}]_0}{(1 + K_b[\text{H}^+]) (1 + K_c[\text{H}^+]}) \] (15)

Again, from the relations (3), (4), (7) and (10)-(12), it can be shown that \( \beta_2 K_b = \beta_1 K_h \) and if it is assumed that (a) \( k_3 \sim k_4 \) and (b) \( K_h \sim K_b \), Eq. (15) is reduced to Eq. (16),

\[ k_{\text{obs}} = \frac{2k_3[\text{CH}_2\text{OH.CO}_2\text{H}]_0}{(1 + K_c[\text{H}^+] + K_b[\text{H}^+])} \] (16)

Now in the absence of an order < 1 in glycolic acid and as stated earlier that \( \beta_2 \gg K_c[\text{H}^+] \), Eq. (16) is further simplified to Eq. (17) obviously because \( \beta_2 \gg \beta_1[\text{CH}_2\text{OH.CO}_2\text{H}]_0 \),

\[ k_{\text{obs}} = 2k_3[\text{CH}_2\text{OH.CO}_2\text{H}]_0 \] (17)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>17</th>
<th>25</th>
<th>30</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^3 ) [Mn(III)] ( \cdot ) M</td>
<td>2.0 ( \cdot ) M</td>
<td>3.0 ( \cdot ) M</td>
<td>4.0 ( \cdot ) M</td>
<td></td>
</tr>
<tr>
<td>( 10^5 ) ( k ) ( \cdot ) dm ( ^3 ) ( \cdot ) mol ( ^{-1} ) ( \cdot ) s ( ^{-1} )</td>
<td>56</td>
<td>195</td>
<td>408</td>
<td>850</td>
</tr>
<tr>
<td>( \Delta H^*_f )</td>
<td>110 ± 4 kJ mol ( ^{-1} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta S^*_f )</td>
<td>88 ± 8 J K ( ^{-1} ) mol ( ^{-1} )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Equation (17) is identical with Eq. (9) where \( k_3 f_1 = k \) and this once again shows why the kinetic data cannot distinguish between the two mechanisms.

The common features in the oxidation of isopropanol\(^6\) and 2-hydroxy-2-methylpropanoic acid\(^3\) are the rate limiting formation of \((\text{CH}_3)_2\text{COH}\) radical and the invariance of the rate with acidity and \(\text{Mn(II)}\) concentration when \([\text{H}^+]>2\text{ mol dm}^{-3}\). Similarly the oxidations of methanol\(^5\) and glycolic acid proceed through the rate-limiting formation of \(\text{CH}_2\text{OH}\) radical. However, the rate of oxidation of methanol\(^5\) is dependent on \([\text{H}^+]\) and \([\text{Mn(II)}]\) whereas the rate of oxidation of glycolic acid is independent of these concentrations. It might be noted that in the oxidation of methanol\(^5\) as in the present oxidation, it was not possible to distinguish kinetically between the participation of \(\text{Mn}^{3+} (\text{aq.})\) and \(\text{MnOH}^2+ (\text{aq.})\) ions. A comparison of activation parameters is not possible for these have not been reported in the oxidation of methanol\(^5\). The positive entropy, a sum total for the reactions (10) and (13), could be due to the formation of a complex in which water molecules from the hydration spheres are set free and a reduction in the effective charge on manganese from 3+ to 2+ takes place which would also result in the liberation of water molecules.

The retarding effect of \(\text{Mn(II)}\) in the oxidation of methanol\(^5\) was explained as due to the interaction between \(\text{Mn}^{2+}\) and the free radical \(\text{CH}_2\text{OH}\) inside the solvent cage, both being produced by intramolecular electron transfer in \(\text{Mn(III)}\)-methanol complex. However, this explanation appears untenable in view of the absence of any retarding effect of \(\text{Mn}^{2+}\) in the oxidation of glycolic acid unless there are reasons to believe that \(\text{Mn(III)}\)-glycolic acid complex (Scheme 2) cannot have intramolecular electron transfer inside the solvent cage. The retardation in the case of methanol\(^5\) with \(\text{Mn(II)}\) is perhaps due to possible parallel oxidation by \(\text{Mn(IV)}\) whence the retardation by \(\text{Mn(II)}\) is understandable in view of the equilibrium (2). The possibility of the involvement of \(\text{Mn(IV)}\) in the oxidations of \(\text{Hg}, \text{Hg(I)}^{12}\) and \(\text{Tl(I)}^2\) by aquamanganese (III) ions and that of formaldehyde by manganese(III) sulphate\(^22\) has been suggested. A similar observation has been recorded by us\(^{23}\) in the oxidation of \(n\)-propanol and formaldehyde by aquamanganese(III) ion. That alcohols are susceptible to oxidation by \(\text{Mn(IV)}\) is already known\(^24\).

Acknowledgement

The authors are grateful to the CSIR and UGC, New Delhi for the award of JRF to R.R.N. and M.M. respectively. Thanks are also due to Prof. R.C. Kapoor for the laboratory facilities.

References