

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

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The kinetics of the oxidation of glycolic acid by aquamanganese(III) ions in perchlorate solution ($I = 4 \text{ mol dm}^{-3}$) has a first order dependence both in $[\text{Mn(III)}]$ and $[\text{glycolic acid}]$, and a zero order dependence in $[\text{Mn(II)}]$ and $[\text{H}^+]$. 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 $[\text{H}^+]$ and $[\text{Mn(II)}]$ is explained by assuming that the reactivity of $\text{Mn}^{3+}(\text{aq.}) \sim \text{MnOH}^{2+}(\text{aq.})$ and that Mn(IV) is not an active oxidant. A suitable mechanism has been proposed for the oxidation, which has $\Delta H^\ddagger = 110 \pm 4 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 88 \pm 8 \text{ JK}^{-1} \text{ mol}^{-1}$. 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 Davies². A number of similarities in the kinetics of oxidation of 2-hydroxy-2-methylpropanoic acid³ and isopropanol⁴ have been observed including the formation of the identical free radical ($>\dot{\text{C}}\text{OH}$). This prompted us to undertake the title investigation because the oxidation of glycolic acid was expected to produce the radical $\dot{\text{C}}\text{H}_2\text{OH}$ similar to that produced in the oxidation of methanol⁵, 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 methanol⁵.

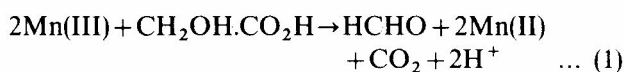
Materials and Methods

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 indicator⁶. Its electrolytic oxidation to obtain aquamanganese(III) ions is described elsewhere⁷. The manganese(III) solution was always prepared fresh and standardised by adding a known volume of manganese(III) into a known excess of Fe(II) and back titrating the unreacted Fe(II) against vanadium(V) solution using barium diphenylsulphamate as the indicator.

The stock solutions of glycolic(Fluka, puriss) and perchloric(E. Merck, G.R.) acid were standardised

against a standard alkali. Vanadium(V) solution was prepared by dissolving ammonium metavanadate (Hopkins & Williams, G.R.) in hot water and on cooling the required volume of perchloric acid was added so that overall $[\text{HClO}_4] \sim 1 \text{ mol dm}^{-3}$. 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 $[\text{Mn(III)}]$, at different acidities and molar ratios, were prepared at room temperature ($\sim 25\text{-}27^\circ$). 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-dinitrophenylhydrazine hydrochloride. The precipitated hydrazone was separated and purified. The m.p. of the hydrazone was 166° and the mixed m.p. with an authentic hydrazone prepared from formaldehyde was 167° (lit.⁸ 166°). Formaldehyde was estimated quantitatively using chromotropic acid⁹. These determinations indicated that $\Delta[\text{Mn(III)}]/\Delta[\text{HCHO}] = 1.98 \pm 0.2$. 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).



Rate measurements—The kinetics of the reaction was followed titrimetrically as described earlier⁷ 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

†For part I, see ref. 1.

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

$\{10^3 [\text{Mn(III)}]=2.0 \text{ M}, [\text{HClO}_4]=3.0 \text{ M}, [\text{Mn(II)}]=0.067 \text{ M and } I=4.0 \text{ M}\}$

$10^2 [\text{CH}_2\text{OH.CO}_2\text{H}]_0$ (M)	$10^4 k_{\text{obs}}, \text{ s}^{-1}$ at			
	17	25	30	35
0.5	0.65	2.19	4.42	8.50
1.0	1.20	4.20	8.48	17.00
1.5	1.77	6.05	12.5	25.5
2.0	2.32	8.10	16.6	—
2.5	2.90	10.00	20.7	—
5.0	5.72	19.8	—	—

adopting the titrimetric method it was ensured that the presence of glycolic acid, in concentrations as used in the kinetic studies, in the quenching solution of Fe(II) did not change the titre value of vanadium(V) solution.

The observed first order rate constant, k_{obs} , with respect to Mn(III), was calculated from the linear ($r > 0.998$) plots of $\log(a-x)$ against time. The reproducibility of the k_{obs} was within $\pm 3\%$ and the mean values are reported in Table 1.

Test for free radical—Partly oxidised reaction mixtures under nitrogen atmosphere polymerised acrylonitrile indicating that free radicals were generated during the course of the reaction. Addition of acrylonitrile to a solution of aquamanganese(III) ions or of glycolic acid separately under similar conditions of acidity did not result in any polymerisation.

Results

A scrutiny of the kinetic data revealed the following:

(i) The invariance of k_{obs} with different initial $[\text{Mn(III)}]_0$ in the range 0.0012–0.0036 mol dm⁻³ confirmed the first order dependence of the reaction in $[\text{Mn(III)}]$. The average $10^4 k_{\text{obs}}$ was $3.08 \pm 0.06 \text{ s}^{-1}$ under the conditions, $[\text{H}^+]=3.0$, $[\text{CH}_2\text{OH.CO}_2\text{H}]=0.0125$, $[\text{Mn(II)}]=0.2$ and $I=4 \text{ mol dm}^{-3}$ at 22°.

(ii) Rate measurements in solutions of different $[\text{HClO}_4]_0$ in the range 1.0–3.6 mol dm⁻³, at constant concentrations of other reactants and ionic strength, indicated that k_{obs} was independent of $[\text{H}^+]$. The average $10^4 k_{\text{obs}}$ was $2.44 \pm 0.04 \text{ s}^{-1}$ under the conditions, $[\text{Mn(III)}]=0.002$, $[\text{CH}_2\text{OH.CO}_2\text{H}]=0.0125$, $[\text{Mn(II)}]=0.1$, $I=4 \text{ mol dm}^{-3}$ at 25°.

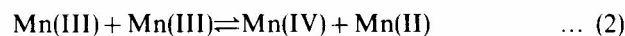
(iii) When sodium perchlorate was replaced by manganese(II) perchlorate keeping the ionic strength constant at 4 mol dm⁻³, k_{obs} was found to be independent of $[\text{Mn(II)}]$ in the range 0.058–0.14 mol dm⁻³, the average $10^4 k_{\text{obs}}$ value was $3.56 \pm 0.06 \text{ s}^{-1}$ under the conditions, $[\text{H}^+]=3.0$, $[\text{Mn(III)}]=0.002$ and $[\text{CH}_2\text{OH.CO}_2\text{H}]=0.01 \text{ mol dm}^{-3}$ at 24.4°C.

(iv) Increase in the initial $[\text{CH}_2\text{OH.CO}_2\text{H}]$ increased the k_{obs} proportionately. These experiments were carried out at four different temperatures and the results are reported in Table 1. The plot of k_{obs} versus $[\text{CH}_2\text{OH.CO}_2\text{H}]$ was linear with a zero intercept. This observation is similar to one reported in the oxidation of 2-hydroxy-2-methylpropanoic³ and isobutyric acids¹⁰.

Discussion

The pK_a of glycolic acid is 3.83 at 25° (ref. 11) and as such 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 species². The disproportionation equilibrium (2) is now well established^{12,13}. This equilibrium also explains as to why a large $[\text{Mn(II)}]$ is maintained to stabilise aquamanganese(III) ion during its preparation.

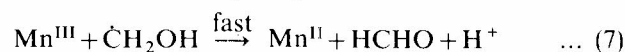
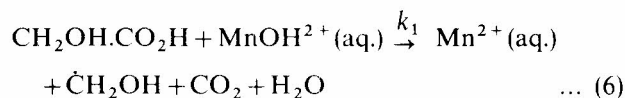
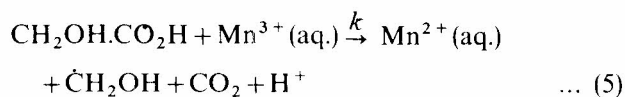
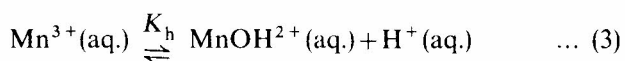


Since the rate was independent of $[\text{Mn(II)}]$, it was concluded that Mn(IV) was not an active oxidant. This observation and conclusion are similar to those gathered in the oxidation of 4-ketopentanoic acid by aquamanganese(III) ions¹⁴. Similarly the possibility of the formation of a glycolic acid-Mn(II) complex was also ruled out. It is with respect to equilibrium (2) and the observed retardation of the oxidation of methanol⁵ 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^{13,15} of aquamanganese(III) ions in solutions of varying acidities established that $\text{Mn}^{3+}(\text{aq.})$ ion was considerably hydrolysed even at high acidity. Wells and Davies¹⁶ reported that K_h 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 $\Delta H_h = 20 \text{ kJ mol}^{-1}$. This value of the enthalpy has been used to calculate the K_h 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 $[\text{glycolic acid}]$, an outer-sphere mechanism (Scheme 1) is first considered.

Equilibrium (4) is consistent with the known protonation of carboxylic acids¹⁶ and 2-hydroxy-2-methylpropanoic acid^{3,17}. The protonated species are considered to be unreactive^{3,16,17}. The rate of



Scheme 1

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

$$-\frac{d[\text{Mn}^{\text{III}}]}{dt} = \frac{2(k + k_1 K_h [\text{H}^+]^{-1})[\text{Mn}^{\text{III}}]_0 [\text{CH}_2\text{OH.CO}_2\text{H}]_0}{(1 + K_h [\text{H}^+]^{-1})(1 + K_c [\text{H}^+])} \quad \dots (8)$$

Now two assumptions have been made to explain the invariance of k_{obs} with respect to $[\text{H}^+]$ and these are: (i) $k \sim k_1$; and (ii) $1 \gg K_c [\text{H}^+]$. With these assumptions Eq. (8) reduces to Eq. (9),

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

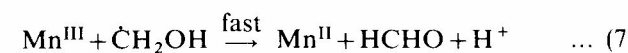
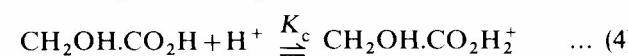
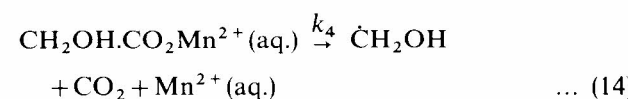
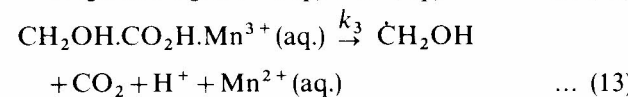
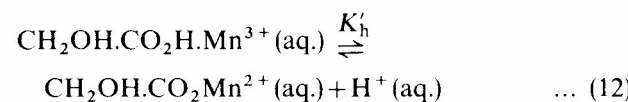
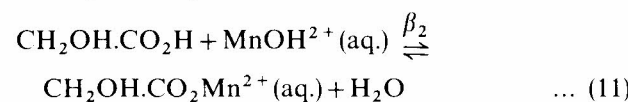
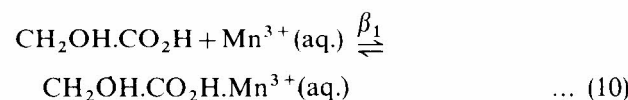
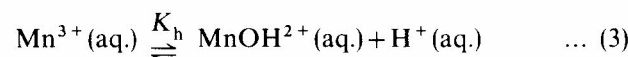
The experimental value of K_c is not as yet known. However, the same could be estimated by extrapolation of the linear relation between $\log K_c$ corresponding to acetic, *n*-propanoic and *n*-butyric acids and $\Sigma\sigma^*$, where σ^* is the Taft's constant¹⁸. The K_c value so obtained was $0.00043 \text{ dm}^3 \text{ mol}^{-1}$ which justifies the assumption (ii).

The values of $k (= k_{\text{obs}}/2[\text{CH}_2\text{OH.CO}_2\text{H}]_0)$ are reported in Table 2 and the values of ΔH^\ddagger and ΔS^\ddagger , 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-methylpropanoic acid³ the rapid increase in the initial absorbance at high $[\text{HMP}]/[\text{Mn(III)}]$ 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.



Scheme 2

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

$$-\frac{d[\text{Mn}^{\text{III}}]}{dt} = \frac{\{2(k_3\beta_1 + k_4\beta_2 K_h [\text{H}^+]^{-1})[\text{Mn}^{\text{III}}]_0 [\text{CH}_2\text{OH.CO}_2\text{H}]_0\}}{\{1 + K_h [\text{H}^+]^{-1} + (1 + k_c [\text{H}^+])\beta_1 + \beta_2 K_h [\text{H}^+]^{-1}\}[\text{CH}_2\text{OH.CO}_2\text{H}]_0} \quad \dots (15)$$

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

$$k_{\text{obs}} = \frac{2k_3\beta_1[\text{CH}_2\text{OH.CO}_2\text{H}]_0}{(1 + \beta_1[\text{CH}_2\text{OH.CO}_2\text{H}]_0)(1 + K_c[\text{H}^+])} \quad \dots (16)$$

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

$$k_{\text{obs}} = 2k_3\beta_1[\text{CH}_2\text{OH.CO}_2\text{H}]_0 \quad \dots (17)$$

Table 2—Values of the Rate Constant $k (= k_3\beta_1)$ at Different Temperatures and Values of the Thermodynamic Parameters

$\{10^3 [\text{Mn(III)}] = 2.0 \text{ M}, [\text{HClO}_4] = 3.0 \text{ M}, \text{ and } I = 4.0 \text{ M}\}$				
Temp. (°C)	17	25	30	35
$10^4 k(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$	56	195	408	850

$$\Delta H^\ddagger = 110 \pm 4 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = 88 \pm 8 \text{ JK}^{-1} \text{ mol}^{-1}$$

Equation (17) is identical with Eq. (9) where $k_3\beta_1 = k$ and this once again shows why the kinetic data cannot distinguish between the two mechanisms.

The common features in the oxidation of isopropanol⁴ and 2-hydroxy-2-methylpropanoic acid³ are the rate limiting formation of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radical and the invariance of the rate with acidity and Mn(II) concentration when $[\text{H}^+] > 2 \text{ mol dm}^{-3}$. Similarly the oxidations of methanol⁵ and glycolic acid proceed through the rate-limiting formation of $\dot{\text{C}}\text{H}_2\text{OH}$ radical. However, the rate of oxidation of methanol⁵ 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 methanol⁵ 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 methanol⁵. 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 Mn(II) in the oxidation of methanol⁵ was explained as due to the interaction between Mn^{2+} and the free radical $\dot{\text{C}}\text{H}_2\text{OH}$ inside the solvent cage, both being produced by intramolecular electron transfer in Mn(III)-methanol complex. However, this explanation appears untenable in view of the absence of any retarding effect of Mn^{2+} in the oxidation of glycolic acid unless there are reasons to believe that Mn(III)-glycolic acid complex (Scheme 2) cannot have intramolecular electron transfer inside the solvent cage. The retardation in the case of methanol⁵ with Mn(II) is perhaps due to possible parallel oxidation by Mn(IV) whence the retardation by Mn(II) is understandable in view of the equilibrium (2). The possibility of the involvement of Mn(IV) in the

oxidations of Hg, Hg(I)^{12} and Ti(I)^{12} by aquamanganese (III) ions and that of formaldehyde by manganese(III) sulphate²² has been suggested. A similar observation has been recorded by us²³ in the oxidation of *n*-propanol and formaldehyde by aquamanganese(III) ion. That alcohols are susceptible to oxidation by Mn(IV) is already known²⁴.

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