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Anodically generated manganese(III) acetate for the oxidation of α – amino acids in aqueous acetic acid: A kinetic study

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Summary. Manganese(III) acetate was prepared by the oxidation of manganese(II) acetate in aqueous acetic acid by electrolytic method. The anodically generated Mn(III) species was characterised by spectroscopic and redox potential studies. Conditions for the study of kinetics of Oxidation of α-amino acids by Mn(III) in aqueous acetic acid was investigated. Plots of log[Mn(III)] versus time for the first order process, or Mn(III) versus time for zero order process were nonlinear. The rate constants computed from $[\mathrm{Mn(III)}]^{1/2}$ versus time plots were independent of $[\mathrm{Mn(III)}]_0$ indicating that the reaction goes through competitive zero and first order path-ways in $[\mathrm{Mn(III)}]_0$. The kinetic order in [amino acid], $[H^+]$ and [Mn(II)] were found out. Effect of added anions like CH_3COO^-, F^-, Cl^- and ClO_4^- were investigated. Evidence for the transient existence of the free radical reaction intermediate is given. Dependence of reaction rate on temperature is explained and activation parameters computed from Arrhenius and Eyring plots. A mechanism consistent with the observed results is proposed and discussed.

Keywords: Amino acids – Anodically generated – Manganese(III) acetate – Kinetics – Aqueous acetic acid

Introduction

There has been a great deal of attention focussed on the oxidation of organic substrates by metal ions. Of these manganese(III) oxidations are of special significance because of their biological relevance (Boucher, 1992). Manganese(III) porphyrins have been studied as possible models for the closely related and biologically important systems. There are a number of reports on the kinetics of oxidation of various substrates by manganese(III) in perchlorate, sulphate, acetate and pyrophosphate media (Davies, 1969). Kinetics of oxidation of amino acids by various oxidising agents in general (Srivastava et al., 1978; Upadhyay and Agrawal, 1978; Gopalakrishnan and Hogy 1985; Rajanna and Saiprakash, 1979; Reddy et al., 1984; Gowda and Mahadevappa, 1983) and aquomanganic ion in particular (Beg and Kamaluddin, 1975; Kamaluddin, 1980; Ramachandran et al., 1984), have been reported. Quite recently we have studied the kinetics of oxidation of L-histidine by manganese(III) sulphate in aqueous sulphuric acid (Pinto et al., 1990), L-arginine (Chandraju et al., 1994), L-aspartic and L-glutamic acids (Sherigara et al., 1994), by manganese(III) in pyrophosphate and acetate media. In this report we have verified the current generation effeciency of electrolytic production of manganese(III) acetate in aqueous acetic acid and examined its utility as a selective oxidising agent in kinetic investigation. It is also sought to understand how the changes in the coordination environment of the oxidising species, namely Mn(III) can bring about changes in the mechanism of the related reactions.

Material and methods

The electrolysis was carried out in an undivided cell with a platinum foil electrode of generation area 4 cm^2. The cathode of generation circuit was a thin platinum spiral of effective area less than 0.2 cm^2. The electrolyte was 0.05 mol dm^{-3} solution of manganese(II) acetate (Glaxo, SQ) in aqueous acetic acid (HOAc) (90% v/v), also containing 0.5 mol dm^{-3} sodium acetate (NaOAc). NaOAc not only enhances the conductivity of the electrolyte solution but also helps by increasing the solubility of manganese(III) acetate due to the formation of complex species, $Mn(OAc)_4^-$. The optimum condition for the practical use of electrogeneration from platinum eletrodes include HOAc between 85% to 95% (v/v), current density 1 to 5 mA cm^{-2}, concentration of manganese(II) above 0.05 mol dm^{-3} and potassium acetate of 0.5 mol dm^{-3} and the current efficiency achieved was 79%. The stock solution of MAc, thus prepared was stable in aqueous HOAc (90% v/v) for about 2 to 3 days with only 5% deterioration. However freshly prepared solutions were always preferred.

Chromatographically pure amino acids (AA), L-glycine, L-alanine, L-valine and L-leucine were further assayed by standard methods (Vogel, 1958). An aqueous stock solution of the substrate (0.1 mol dm^{-3}) was prepared and used as needed. Solution of NaOAc needed to maintain the ionic strength of the reaction mixture was a special quality (SQ) sample from Glaxo. Glacial HOAc employed for the work was from Glaxo (SQ), further purified by refluxing with chromic oxide for four hours and then distilled. Electronic absorption spectra of the freshly prepared MAc at different HOAc and NaOAc concentration were recorded using a Shimadzu 160 A u-v vis spectrophotometer with 1 cm quartz cell (Fig. 1).

Kinetic measurements

The kinetic studies were made in glass stoppered pyrex boiling tubes under substrate excess conditions, [AA] $\gg$ [MAc]. The reaction were initiated by the rapid addition of requisite amounts of oxidant solution (1.0×10^{-3} to 6.0×10^{-3} mol dm^{-3}) thermally equilibrated at a desired temperature, to solution containing known amount of the substrate (4.0×10^{-2} to 14.0×10^{-2} mol dm^{-3}) and NaoAc (0.1 to 0.8 mol dm^{-3}), HOAc and water so as to maintain HOAc concentration between 40% to 70% (v/v). The

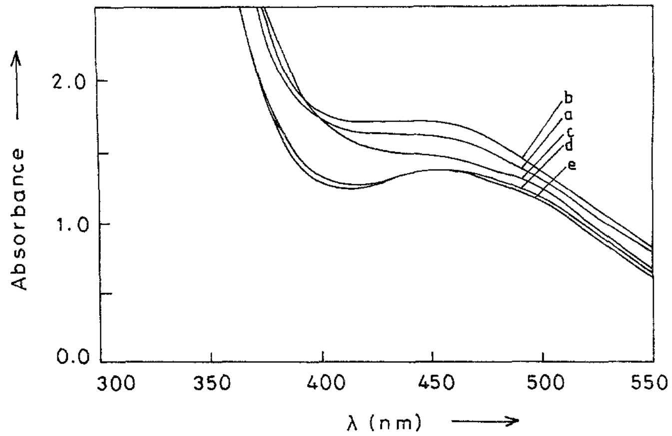


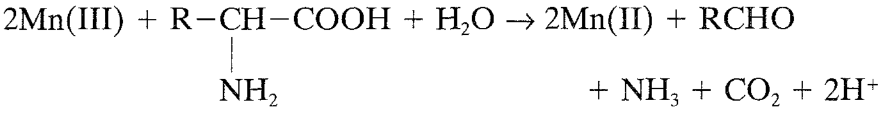
Fig. 1. Absorption spectra of 0.01 mol dm^{-3} manganese(III) acetate in aq. HOAc (v/v), 10^2[Mn(III)] (mol dm^{-3}) = 1.0. *a* 100% HOAc (v/v); *b* 100% HOAc (v/v) + 0.5 mol dm^{-3} NaOAc; *c* 60% HOAc (v/v); *d* 70% HOAc (v/v); *e* 80% HOAc (v/v)

progress of the reaction was monitored for at least two half-lives by iodometric estimation of unreacted Mn(III) at regular intervals of time. The rate constants were computed from graphical methods and the values were reproducible within ±5% error.

Results and discussion

Stoichiometry and product analysis

The stoichiometric conditions were established by taking 0.1 mol dm^{-3} of the AA and 0.01 mol dm^{-3} of manganese(III) acetate in presence of 0.6 mol dm^{-3} NaOAc by maintaining HOAc concentration 60% (v/v). The reaction mixture was kept at 50°C in a thermostat for about 3 to 4 hours and one of the products formed was identified, Vogel (1958) as aldehyde by its derivative 2,4-dinitrophenyl hydrazone isolable up to 90%. The observed stoichiometry can be represented by the equation:



$$2\mathrm{Mn(III)} + \underset{\substack{|\\ \mathrm{NH_2}}}{\mathrm{R{-}CH{-}COOH}} + \mathrm{H_2O} \rightarrow 2\mathrm{Mn(II)} + \mathrm{RCHO} + \mathrm{NH_3} + \mathrm{CO_2} + 2\mathrm{H^+} \quad (1)$$

where R = H(Gly), CH_3(Ala), $(CH_3)_2CH$(Val) and $(CH_3)_2$ $CHCH_2$ (Leu).

The reaction mixture initiates polymerisation of the organic monomers like acrylonitrile or methyl methacrylate. As neither manganese(III) acetate or the amino acids do this when added separately to an aqueous solution of these monomers, it can be assuemed that free radicals are involved in the reaction.

Stability of the oxidant

It was verified that 0.005 mol dm^{-3} solution of MAc was stable in HOAc – H_2O medium containing HOAc about 80% (v/v) for about 24 hours and thereafter disproportionation slowly set in, and black particles of MnO_2 were formed.

$$2\mathrm{Mn(III)} \rightleftharpoons \mathrm{Mn(II)} + \mathrm{Mn(IV)} \qquad (2)$$

The acetic acid concentrations were varied in the range 40 to 90% (v/v) and the extent of disproportionations were recorded (Table 1). The concentration of Mn(III) in solution was estimated by idometry. The changes in concentration with time was monitored for 30 hours and further. Whenever black particles of MnO_2 appeared due to the disproportionation reaction, the solution was filtered and the concentration of the clear filterate was recorded. Previous studies have established that Mn(III) species can be stabilised by (i) increase of acidity (ii) increase of Mn(II) concentration or (iii) complex formation. As HOAc being a strong donor solvent, its higher content would help to enhance the stability of Manganese(III) acetate solution (Bhat et al., 1992). At lower concentrations of HOAc, Mn(III) deteriorated at a faster rate, but its stability could be enhanced by taking higher amount of manganese(II) acetate in solution (Table 1).

The visible spectra of freshly prepared MAc solutions at different concentrations of acetic acid and acetate ion showed the presence of a complex species, $Mn(OAc)_4^-$, formed at higher acetate concentration which probably resulted from the replacement of a water ligand by an acctate ion. The occurance of the λ max at 450 nm is attributed to the existence of the above manganese(III) complex anion species (Midgley and Thomas, 1984).

The formal redox potential, E_0' of Mn(II)–Mn(III) couple is a measure of the oxidising power of the oxidant and it generally alters on anionic complexation. Different but known amount of Mn(III) were anodically gener-

Table 1. Changes in concentration of 0.005 mol dm^{-3} solution of manganese(III) acetate in varying acetic acid (% v/v), manganese(II) acetate and sodium acetate

HOAc %(v/v)	Added [Mn(II)] (mol dm^{-3})	[NaOAc] (mol dm^{-3})	% of Mn(III) found at time (hours)						
			1.0	2.0	3.0	6.0	12.0	18.0	24.0
80	–	–	100	100	100	100	100	100	100
70	–	–	100	100	100	100	100	99.8	98.1
	0.1	0.5	100	100	100	100	100	100	98.9
60	–	–	100	100	100	100	98.0	97.3	96.0
	0.05	0.5	100	100	100	100	98.5	97.7	96.8
	0.1	0.5	100	100	100	100	99.6	98.7	97.6
50	–	–	100	99.2	98.7	98.0	97.1	96.0	94.3
	0.1	0.5	100	100	100	98.9	97.8	96.5	95.3
40	–	–	100	97.6	96.3	95.4	94.7	90.1	85.0
	0.02	–	100	99.8	99.6	96.0	95.1	90.9	86.7
	0.1	–	100	100	99.8	96.8	95.7	91.5	87.5
	0.2	–	100	100	100	98.0	96.5	92.3	88.9
	0.5	–	100	100	100	99.0	97.2	93.4	90.1
	0.5	0.5	100	100	100	99.5	98.1	94.0	91.2

ated in a measured volume of the anolyte and electrode potentials E (V vs SCE) were measured each time. The measurements were made at different concentrations of HOAc, and in the presence of added anions like CH_3COO^-, Cl^-, F^- and ClO_4^- and E_0' (V vs SCE), in the changed environment was computed (1.126, 1.181, 1.140 and 1.169 V), E_0' (V vs SCE) for the pure system was 1.160 V. There is a small but significant change in the redox potential value due to the added anions.

[Mn(III)] and [AA] dependence

For the MAc oxidation of AA the plots of log [Mn(III)] versus time or [Mn(III)] versus time were nonlinear. Half order dependence with manganese(III) was indicated by the linearity or $[Mn(III)]^{1/2}$ versus time plot even beyond 75% of the reaction with a correlation coefficient of 0.998 (Fig. 2). The integral rate equation for the half order reaction is $k = \frac{2}{t}[a^{1/2} - (a - x)^{1/2}]$ where a is the initial concentration $[Mn(III)]_0$ in the reaction mixture, (a − x) is the concentration [Mn(III)] at time interval t. Therefore a plot of $[Mn(III)]^{1/2}$ versus time gives a straight line with slope equals 1/2 k. The value of the pseudo-half order rate constant remained constant with increase in initial concentration of the oxidant, $[Mn(III)]_0$. At constant $[Mn(III)]_o$, % of HOAc, [Mn(II)] and [NaOAc] the rate increased with increase in [AA]. The

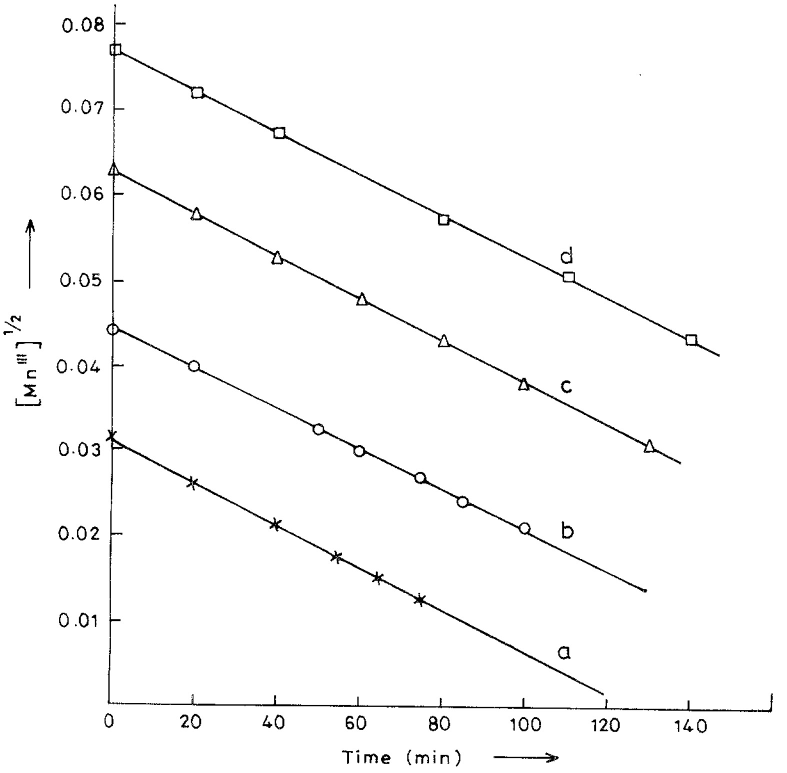


Fig. 2. Plots of $[Mn(III)]^{1/2}$ versus time. 10^2[AA](mol dm^3) = 8.0, 10^2[Mn(II)] (mol dm^{-3}) = 4.0 10[NaOAc] (mol dm^{-3}) = 6.0, % of HOAc (v/v) = 60.0, Temp = 323 K, 10^3[Mn(III)](mol dm^{-3}) = 1.0(*a*), 2.0(*b*), 4.0(*c*), 6.0(*d*)

plot of k versus [AA] is linear passing through the origin showing that order in [AA] is one. It may be recalled that the order with respect to $[Mn(III)]_o$ varied between one and two in the oxidation of α-amino acids by manganese(III) in aqueous H_2SO_4 or $HCLO_4$ (Beg and Kamaluddin, 1975; Kamaluddin, 1980; Ramachandran et al., 1984). The reactive species envisaged in those studies were the ionic forms of the trivalent manganese, Mn^{3+} aq. or $Mn(OH)^{2+}$ aq. as evident from u.v. vis absorption spectra and the formal redox potential value of 1.52V. The present study showed that MAc in aqueous HOAc reacted differently, as the reactive apecies envisaged in this reaction is the complexed form of Mn(III) as, $Mn(OAc)_3$ or $Mn(OAc)_4^-$ confirmed by the absorption spectra and the measured formal redox potential value of 1.16V.

Dependence of rate on [H⁺]

Kinetic measurements were performed by varying added perchloric acid concentrations. The effective hydrogen ion concentrations were evaluated from the measured pH values. The rate of reaction decreased with increase in $[H^+]$.

Dependence of rate on added salts

Mn(II) is the reduced product of the oxidant and its effect on the rate of reaction was investigated. As the initial concentration of Mn(II) was increased, the rate was progressively decreased. The data is summarised in Table 2.

The effect of anions like F^-, Cl^- and ClO_4^- on the rate of the reaction was also investigated. A slight change in the reaction rate was observed. These anions either increase or decrease the formal redox potential values and accordingly show corresponding increase of decrease in reaction rates (Table 3). For example, ions like Cl^- and ClO_4^- increase the redox potential values and also the reaction rate, ions like F^- decrease the redox potential values and also the reaction rate. This may be attributed to the displacement of the coordinated acetate ligand leading to the establishment of a new Mn(III)-Mn(II) couple with F^-, Cl^- and ClO_4^- as ligands and such redox couples have higher or lower redox potential values and thereby decrease or increase the rate.

Dependence of the rate on temperature

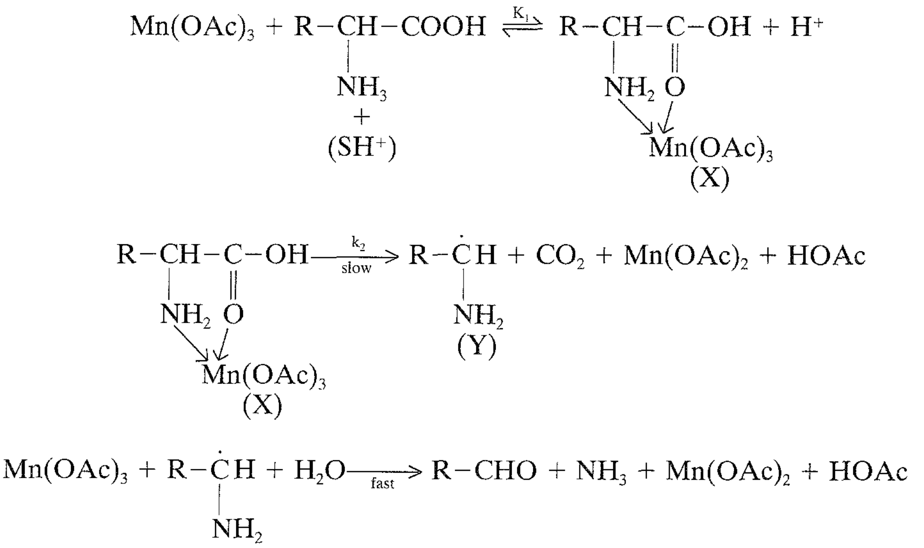
The reaction were carried out at 318K, 323K, 328K, 333K and 338K at constant [NaOAc] and [Mn(II)]. Arrhenius and Eyring plots of log k versus 1/T and log (k/T) versus 1/T, gave good straight lines. From the slopes and intercepts, the values of the activation parameters were calculated and summarised in Table 7. The variation in the reaction rate with various % of HOAc was investigated and it was found that the rate decreased with increase in %

Table 2. Pseudo-half order rate constants (k_{obs}) for the oxidation of amino acids by manganese(III) acetate of 323 K with 60% HOAc (v/v)

$[\mathrm{Mn(III)}] \times 10^3$ (mol dm^{-3})	$[\mathrm{AA}] \times 10^2$ (mol dm^{-3})	$[\mathrm{Mn(II)}] \times 10^2$ (mol dm^{-3})	$[\mathrm{NaOAc}] \times 10$ (mol dm^{-3})	$k_{obs} \times 10^6$ (mol$^{1/2}$ dm$^{-3/2}$ s^{-1})			
				L-Gly	L-Ala	L-Val	L-Leu
1.0	8.0	4.0	6.0	8.2	10.4	18.1	24.9
2.0	8.0	4.0	6.0	8.3	10.3	18.3	25.4
4.0	8.0	4.0	6.0	7.9	10.5	17.9	25.8
6.0	8.0	4.0	6.0	7.9	10.2	17.9	25.3
2.0	4.0	4.0	6.0	3.4	4.9	10.0	12.5
2.0	6.0	4.0	6.0	5.7	7.0	14.6	18.5
2.0	10.0	4.0	6.0	10.1	11.4	22.0	30.3
2.0	14.0	4.0	6.0	12.2	14.0	29.2	47.2
2.0	8.0	1.0	6.0	11.5	14.8	27.0	36.1
2.0	8.0	4.0	6.0	7.5	10.4	18.3	25.4
2.0	8.0	7.0	6.0	6.6	8.3	15.0	20.0
2.0	8.0	10.0	6.0	5.3	6.8	13.3	17.6
2.0	8.0	4.0	1.0	3.1	5.3	9.2	10.8
2.0	8.0	4.0	2.0	4.2	6.7	12.0	13.8
2.0	8.0	4.0	4.0	5.9	8.3	16.3	20.8
2.0	8.0	4.0	8.0	9.1	11.1	25.0	35.9

of HOAc. Formation of more ordered activated complex is evident from the negative $\Delta S^{\#}$ values. The constancy of $\Delta G^{\#}$ values may indicate the operation of similar mechanism. Decrease of rate with decrease in dielectric constant of the medium (Table 5), observed in all cases is in conformity with Amis concept for dipole-dipole or ion-dipole interactions.

In order to account for the observed half order kinetics for the decay of Mn(III) during the course of the reaction, a combined rate law derived from two seperate schemes, one for the first order kinetics and the other for zero order kinetics is considered. The most likely reaction mechanism which can satisfactorily explains the observed data is as shown in Scheme 1 and 2.



$$\mathrm{Mn(OAc)_3} + \underset{\substack{|\\ \mathrm{NH_3}\\ +\\ (\mathrm{SH^+})}}{\mathrm{R{-}CH{-}COOH}} \overset{K_1}{\rightleftharpoons} \underset{\substack{|\quad \|\\ \mathrm{NH_2}\ \mathrm{O}\\ \searrow\ \swarrow\\ \mathrm{Mn(OAc)_3}\\ (\mathrm{X})}}{\mathrm{R{-}CH{-}C{-}OH}} + \mathrm{H^+} \tag{3}$$

$$\underset{\substack{|\quad \|\\ \mathrm{NH_2}\ \mathrm{O}\\ \searrow\ \swarrow\\ \mathrm{Mn(OAc)_3}\\ (\mathrm{X})}}{\mathrm{R{-}CH{-}C{-}OH}} \xrightarrow[\text{slow}]{k_2} \underset{\substack{|\\ \mathrm{NH_2}\\ (\mathrm{Y})}}{\mathrm{R{-}\dot{C}H}} + \mathrm{CO_2} + \mathrm{Mn(OAc)_2} + \mathrm{HOAc} \tag{4}$$

$$\mathrm{Mn(OAc)_3} + \underset{\substack{|\\ \mathrm{NH_2}}}{\mathrm{R{-}\dot{C}H}} + \mathrm{H_2O} \xrightarrow[\text{fast}]{} \mathrm{R{-}CHO} + \mathrm{NH_3} + \mathrm{Mn(OAc)_2} + \mathrm{HOAc} \tag{5}$$

Scheme 1

Table 3. Effect of variation of [Cl$^-$], [ClO$_4^-$] and [F$^-$] on the reaction rates at 323 K with 60% HOAc (v/v)
[Mn(III)] = 2.0 × 10^{-3}, [AA] = 8.0 × 10^{-2} mol dm^{-3}, [Mn(II)] = 4.0 × 10^{-2} mol dm^{-3}, [NaOAc] = 6.0 × 10^{-1} mol dm^{-3}

[Cl$^-$] × 10^2 (mol dm^{-3})	k$_{obs}$ × 10^6 (mol$^{1/2}$ dm$^{-3/2}$ s^{-1})				[ClO$_4^-$] × 10^2 (mol dm^{-3})	k$_{obs}$ × 10^6 (mol$^{1/2}$ dm$^{-3/2}$ s^{-1})				[F$^-$] × 10^2 (mol dm^{-3})	k$_{obs}$ × 10^6 (mol$^{1/2}$ dm$^{-3/2}$ s^{-1})			
	L-Gly	L-Ala	L-Val	L-Leu		L-Gly	L-Ala	L-Val	L-Leu		L-Gly	L-Ala	L-Val	L-Leu
–	8.3	10.3	18.3	25.4	–	8.3	10.3	18.3	25.4	–	8.3	10.3	18.3	25.4
5.0	8.9	12.3	22.8	28.2	5.0	8.8	11.1	21.2	27.5	5.0	5.8	9.4	15.0	20.8
10.0	10.6	13.7	27.3	33.3	10.0	9.7	12.7	24.4	30.3	10.0	4.5	8.3	13.3	17.4
15.0	10.9	14.2	29.9	43.3	15.0	10.4	13.2	26.7	33.3	15.0	3.9	7.5	12.5	16.7

Table 4. Effect of variation of $[H^+]$ on the reaction rate at 323 K with 60% HOAc (v/v), $[Mn(III)] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[AA] = 8.0 \times 10^{-2}$ mol dm^{-3}, $[Mn(II)] = 4.0 \times 0^{-2}$ mol dm^{-3}, $[NaOAc] = 6.0 \times 10^{-1}$ mol dm^{-3}

$[HClO_4] \times 10^2$ (mol dm^{-3})	pH	$k_{obs} \times 10^6$ (mol$^{1/2}$ dm$^{-3/2}$ s^{-1})			
		L-Gly	L-Ala	L-Val	L-Leu
1.0	3.96	7.7	9.1	16.1	21.7
5.0	3.93	7.3	8.5	14.7	20.2
10.0	3.89	7.1	7.9	13.8	18.9
30.0	3.65	5.0	5.3	9.5	13.0
50.0	3.43	3.3	3.5	7.1	9.5

Table 5. Effect of variation of % of HOAc (v/v) on the reaction rate at 323 K. $[Mn(III)] = 2.0 \times 10^3$ mol dm^{-3}, $[AA] = 8.0 \times 10^{-2}$ mol dm^{-3}, $[Mn(II)] = 4.0 \times 10^{-2}$ mol dm^{-3}, $[NaOAc] = 6.0 \times 10^{-1}$ mol dm^{-3}

% of HOAc (v/v)	$k_{obs} \times 10^6$ (mol$^{1/2}$ dm$^{-3/2}$ s^{-1})			
	L-Gly	L-Ala	L-Val	L-Leu
40	9.7	20.8	33.3	47.6
50	8.8	13.3	24.2	35.5
60	8.3	10.3	18.3	25.4
70	5.8	8.3	13.3	18.1

Table 6. Effect of variation of temperature on reaction rate with 60% HOAc (v/v). $[Mn(III)] = 2.0 \times 10^{-3}$ mol dm^{-3}, $[AA] = 8.0 \times 10^{-2}$ mol dm^{-3}, $[Mn(II)] = 4.0 \times 10^{-2}$ mol dm^{-3}, $[NaOAc] = 6.0 \times 10^{-1}$ mol dm^{-3}

Temp	$k_{obs} \times 10^6$ (mol$^{1/2}$ dm$^{-3/2}$ s^{-1})			
	L-Gly	L-Ala	L-Val	L-Leu
318	4.2	6.6	10.4	13.6
323	8.3	10.3	18.3	25.4
328	14.9	20.0	30.6	46.2
333	27.3	34.3	61.1	85.7
338	52.4	63.3	–	–

Where “X” is the intermediate substrate – manganese(III) acetate complex and “Y” is the free radical.

The rate of amino acid oxidation is given by

$$\text{Rate} = -d[Mn(OAc)_3]/dt = k_2[X] \tag{6}$$

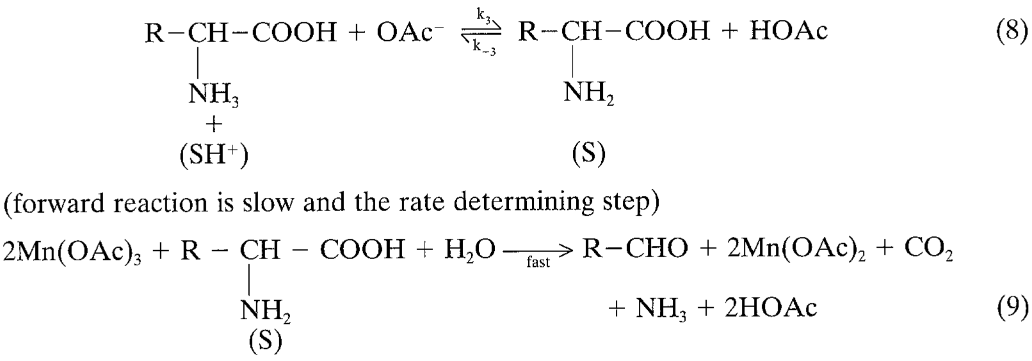
Table 7. Kinetic data and activation parameters for the oxidation of amino acids by manganese(III) acetate

Order	Amino acids			
Observed in	L-Gly	L-Ala	L-Val	L-Leu
[MAc]	0.50	0.50	0.50	0.50
[AA]	1.00	0.95	1.00	1.00
[NaOAc]	0.48	0.35	0.50	0.66
$[H^+]$	−0.76	−0.68	−0.70	−0.69
[Mn(II)]	−0.63	−0.37	−0.33	−0.32
Parameter				
log A	12.90	12.70	11.20	11.20
E_a, $kJ\,mol^{-1}$	111.4	109.7	98.4	97.8
$\Delta H^{\#}$, $kJ\,mol^{-1}$	102.1	100.6	97.1	95.7
$\Delta s^{\ddagger}$, $JK^{-1}mol^{-1}$	−26.7	−34.5	−35.8	−37.2
$\Delta G^{\#}$, $kJ\,mol^{-1}$	110.7	110.6	108.6	107.8

By solving for [Y] with the application of steady state approximation to intermediate X in Scheme 1, we get

$$\mathrm{Rate} = k_1k_2[\mathrm{Mn(OAc)_3}][\mathrm{SH^+}]/k_{-1}[\mathrm{H^+}] + k_2 \qquad (7)$$

The competitive zero order pathway is represented by the following Scheme 2.



$$\underset{(SH^{+})}{\mathrm{R{-}\underset{\underset{+}{NH_3}}{\underset{|}{CH}}{-}COOH}} + \mathrm{OAc^-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{(S)}{\mathrm{R{-}\underset{NH_2}{\underset{|}{CH}}{-}COOH}} + \mathrm{HOAc} \qquad (8)$$

(forward reaction is slow and the rate determining step)

$$\mathrm{2Mn(OAc)_3} + \underset{(S)}{\mathrm{R - \underset{NH_2}{\underset{|}{CH}} - COOH}} + \mathrm{H_2O} \xrightarrow[\text{fast}]{} \mathrm{R{-}CHO + 2Mn(OAc)_2 + CO_2 + NH_3 + 2HOAc} \qquad (9)$$

Scheme 2

Scheme 2 leads to the following rate law.

$$\mathrm{Rate} = -d[\mathrm{Mn(OAc)_3}]/dt = k_3[\mathrm{SH^+}][\mathrm{OAc^-}] \qquad (10)$$

The combined rate law is obtained from,

$$\mathrm{Rate} = \frac{k_1k_2[\mathrm{Mn(OAc)_3}][\mathrm{SH^+}]}{k_{-1}[\mathrm{H^+}] + k_2} + k_3[\mathrm{SH^+}][\mathrm{OAc^-}] \qquad (11)$$

This combined rate law supports the observed kinetic results, including the fractional order on $[\mathrm{Mn(OAc)_3}]$ and $[\mathrm{OAc^-}]$ each, and inverse fractional order on $[\mathrm{H^+}]$.

Table 8. Comparison of kinetic data for the oxidation of α-amino acids by manganese (III) in different media

Amino acid	Medium studied	Orders observed in				Reference
		[Mn(III)]	[Sub]	[Mn(II)]	[H^+]	
L-Gly	H_2SO_4 HOAc	2 0.5	1 1	−1 Inverse Fractional	−1	Kamaluddin This work
Dl-α-Ala	H_2SO_4	2	1	−1	−1	Kamaluddin
L-Ala	HOAc	0.5	1	Inverse Fractional		This work
DL-iso-Val	H_2SO_4	1^c or 2^d	1	−1	−1	Beg, Kamaluddin
DL-n-Val	H_2SO_4	1^c or 2^d	1	−1	−1	Beg, Kamaluddin
L-Val	HOAc	0.5	1	Inverse Fractional		This work
L-Leu	H_2SO_4	1^c or 2^d	1	−1	−1	Beg, Kamaluddin
L-Leu	HOAc	0.5	1	Inverse Fractional		This work
L-Thr	H_2SO_4	2	1	−1	−2	Ramachandran et al.
DL-α-amino butyric acid	H_2SO_4	1^c or 2^d	1	−1	−1	Beg, Kamaluddin
L-His	H_2SO_4	2	1	Inverse Fractional	−2	Pinto et al.
L-Asp	H_2SO_4	2	1	Inverse Fractional	−1	Sherigara et al.
L-Asp	HOAc	1	1	Inverse Fractional	0.6	Sherigara et al.
L-Asp	Pyrophosphate	1	1	Inverse Fractional	0	Sherigara et al.
L-Glu	H_2SO_4	1.5	1	Inverse Fractional	−1	Sherigara et al.
L-Glu	HOAc	1	1	Inverse Fractional	0.6	Sherigara et al.
L-Glu	Pyrophosphate	1	1	Inverse Fractional	0	Sherigara et al.
L-Arg	Pyrophosphapte	1	1	−1	0.6	Chandraju et al.
L-Arg	HOAc	0.5	1	0	Inverse Fractional	Chandraju et al.

[a] below 218 K; [b] above 228 K; [c] at lower [Mn(II)]; [d] at higher [Mn(II)].

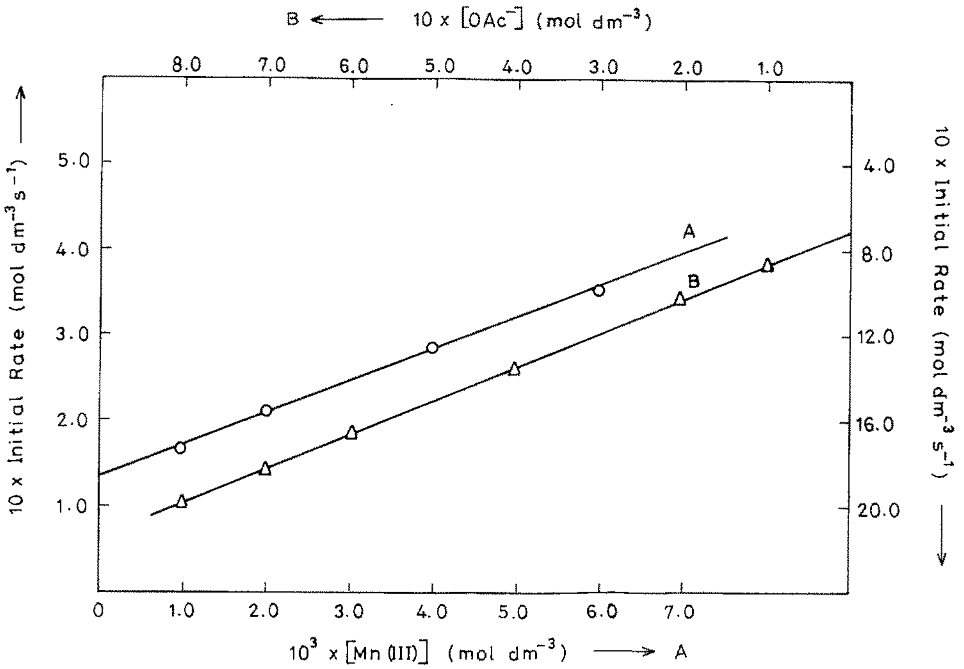


Fig. 3. Plots of: *(A)* Initial rate versus $[\mathrm{Mn(III)}]_0$; and *(B)* Initial rate versus $[\mathrm{OAc}^-]_0$. Temp = 323 K, $10^2[\mathrm{AA}]$ (mol dm^{-3}) = 8.0, $10^2[\mathrm{Mn(II)}]$ (mol dm^{-3}) = 4.0, % of HOAc (v/v) = 60.0

Additionally, the validity of the rate law can be demonstrated as follows: The initial rates, calculated from the runs performed at different initial concentrations of $[\mathrm{Mn(OAc)_3}]_0$ and $[\mathrm{OAc}^-]_0$ with a positive intercept in each case (Fig. 3). The orders with respect to $[\mathrm{Mn(OAc)_3}]$ and $[\mathrm{OAc}^-]$, obtained from the slope of the log-log plots, were 0.46 and 0.39 respectively.

Conclusions

Kinetics data for the oxidation of some of α-amino acids by manganese(III) in sulphuric, perchloric and acetic acid are computed in Table 8. It is evident from the kinetic data that, there is a greater similarity in the oxidation pattern in sulphuric and perchloric acid media. The oxidising species identified in these two acid media are, the ionic forms, $\mathrm{Mn^{3+}}_{(aq)}$ or $\mathrm{MnOH^{2+}}_{(aq)}$ and as such the kinetic orders in [Mn(III)] are either 1 or 2, order with respect to [amino acid] is generally one and inverse dependence in $\mathrm{H^+}$ and [Mn(II)] are the other common features. Manganese(III) acetate in aqueous acetic acid behaves in a quite different manner in these oxidation, as the oxidising species involved are undecomposed $\mathrm{Mn(OAc)_3}$ or the acetato complex, $\mathrm{Mn(OAc)_4^-}$ as evident from the spectral and redox potential studies.

References

Beg MA, Kamaluddin (1975) Kinetics of oxidation of glycine and DL-α-alanine with manganese(III) sulphate. Indian J Chem 13: 1167–1169

Bhat IK, Sherigara BS, Pinto I (1992) Potentiometric studies on electrolytically generated manganese(III) acetate in aqueous acetic acid: oxidation of thiosemicarbazide, its metal complexes and thiosemicarbazones. Indian J Chem 31A: 49–53

Boucher J (1972) Manganese porphyrin complexes. Coord Chem Rev 7: 289–329

Chandraju, Sherigara BS, Gowda NMM (1994) Oxidation of arginine by manganese(III) in pyrophosphate and acetate media: a kinetic study. Intern J Chem Kinet 26: 1105–1119.

Davies G (1969) Some aspects of the chemistry of manganese(III) in aqueous solution. Coord Chem Rev 4: 199–224

Gopalakrishnan G, Hogy JL (1985) Kinetic and mechanistic studies of the N-bromosuccinimide – promoted oxidative decarboxylation of glycine, DL-alanine and DL-valine. J Org Chem 50: 1206–1212

Gowda BT, Mahadevappa DS (1983) Chloraminometric reactions: kinetics and mechanisms of oxidation of amino acids by sodium N-chlorotoluene-p sulphonamide in acid and alkaline media. J Chem Soc Perkin Tras 2: 323–334 and references therein

Kamaluddin (1980) Kinetics and mechanisms of oxidation of some α-amino acids with manganic sulphate. Indian J Chem 19A: 431–434

Midgley G, Thomas CB (1984) Factors governing product distribution in the oxidation of alkenes by manganese(III) acetate in acetic acid and acetic anhydride. J Chem Soc Perkin Trans 2: 1537–1544

Pinto I, Sherigara BS, Udupa HVK (1990) Electrolytically generated manganese(III) sulphate for the oxidation of L-histidine in aqueous sulphuric acid: a kinetic study. Bull Chem Soc Jpn 63: 3625–3631

Rajanna KC, Saiprakash PK (1979) Kinetics and mechanisms of oxidative decarboxylation and deamination of glycine and DL-α-phenylglycine by lead tetraacetate. Indian J Chem 18A: 412–415

Ramachandran MS, Vivekanandan TS, Syed Kadar S (1984) Preparation of manganic sulphate in sulphuric acid and kinetics of its reaction with threonine. Indian J Chem 23A: 379–382

Reddy MK, Reddy S, Sundram EV (1984) Kinetics and mechanism of N-bromoacetamide oxidation of glycine – a study of pH and general base catalysis. Indian J Chem 23A: 197–199

Sherigara BS, Bhat IK, Pinto I, Gowda NMM (1994) Kinetics and mechanism of oxidation of L-aspartic acid and L-glutamic acid by aquomanganese(III) ions in aqueous sulphuric acid and by complexed manganese(III) ions in acetic acid and pyrophosphate media. Intern J Chem Kinet 27

Srivastava SP, Singhal SK, Mathur BBL (1978) Kinetics of peroxy disulphate oxidation of aspartic acid. Indian J Chem 16A: 899–900

Upadhyay SK, Agrawal MC (1978) Os (VIII) and ferrocyanide catalysed oxidation of alanine, phenylalanine and valine by ferricyanide. Indian J Chem 16A: 39–42

Vogel AI (1958) Quantitative organic analysis. Longman and Green, London

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