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Anodically Generated Manganese(III) Oxidation of L-Serine and DL-Threonine in Aqueous Acetic Acid Medium: Kinetics and Mechanism

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ANODICALLY GENERATED MANGANESE(III) OXIDATION OF L-SERINE AND DL-THREONINE IN AQUEOUS ACETIC ACID MEDIUM: KINETICS AND MECHANISM

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ABSTRACT

Manganese(III) acetate solutions were prepared by electrolytic oxidation of $Mn(OAc)_2$ in aqueous HOAc. The electrogenerated Mn(III) species was characterized by spectroscopic and redox potential studies. The kinetics of oxidation of the α -amino acids (AA) L-serine and DL-threonine by Mn(III) ions have been studied in aqueous HOAc medium at 323 K. The reaction follows the following rate law:

rate = k' [Mn(III)]^{1/2} [AA] [H⁺]^{X-} [OAc⁻]^Y where k'= rate constant and x = y = fractional. Variation of the concentration of the reduction product Mn(II) had no effect on the reaction rate. Added anions such as F⁻, Cl⁻ and ClO₄⁻ affected the rate by changing the formal redox potential of the Mn(III)-Mn(II) couple. The effect of varying the solvent composition with HOAc was studied. Kinetic studies showed that the reaction rate

decreased in D₂O (40% v/v) giving solvent isotope effects of k'_{H2O}/k'_{D2O} = 1.46 and 1.69 for serine and threonine, respectively. Activation parameters have been evaluated using the Arrhenius and Eyring plots. A mechanism consistent with the kinetic data has been proposed. The kinetic data for the oxidation of some α -amino acids by various Mn(III) species are summarized and compared.

INTRODUCTION

The oxidations of organic substrates by manganese(III) are of special importance due to their biological relevance^{1,2}. There are several reports on the kinetics of the oxidation of various substrates by manganese(III) in perchlorate, sulfate, acetate, and pyrophosphate media³. The important ones are oximes⁴, vitamins^{5,6} and amino acids⁷⁻¹⁵. Amino acids serve important functions in biological systems and play a significant role in metabolism. They are also used in biochemical, microbiological and nutrition investigations and some of them are employed as dietary supplements. As a part of our broad investigation of the oxidation of amino acids by transition metal ions, we report the kinetics and mechanism of the oxidation of L-serine and DL-threonine by manganese(III) in acetic acid as solvent at 323 K.

EXPERIMENTAL

Solutions of $Mn(OAc)_3$ were prepared by the electrolytic oxidation of $Mn(OAc)_2$. The electrolysis was carried out in an undivided cell with a platinum foil electrode of a generation area of 4.0 cm². The cathode of the generation circuit was a thin platinum spiral of effective area less than 0.2 cm². The electrolyte was a 0.050 mol dm⁻³ solution of $Mn(OAc)_2$ (Glaxo, SQ) in aqueous HOAc (90% v/v) also containing NaOAc (0.050 mol dm⁻³). The presence of NaOAc enhances the conductance of the solution and the solubility of $Mn(OAc)_3$ due to its ability to form the $[Mn(OAc)_4]^-$ complex ion. The optimum conditions for the electrogeneration were HOAc concentrations between 85% and 95% (v/v), current densities of 1-5 mA cm², Mn(II) concentrations of 0.050 mol dm⁻³, and NaOAc concentrations of 0.50 mol dm⁻³. The current efficiency achieved was 79%. It was observed that 0.0100 mol dm⁻³ $Mn(OAc)_3$ solutions in aqueous HOAc (90% v/v) underwent <u>ca</u>. 5% deterioration in 2-3 days. However, freshly prepared solutions were always used for each set of experiments.

Chromotographically pure L-serine and DL-threonine (Sisco Research Laboratories, India) were assayed for amino acid content by standard methods¹⁶. Aqueous stock solutions of the substrates (0.400 mol dm⁻³) were prepared. Glacial HOAc (Glaxo, SQ) was further purified, by refluxing with chromic oxide for 4 h, and distilled. Triply distilled water was used for preparing aqueous solutions. Regression analysis of experimental data was carried out on a statistical calculator SHARP EL-506G D.A.L.

Preliminary Studies

The absorption spectra of freshly prepared Mn(OAc)₃ solutions at different HOAc and NaOAc concentrations were recorded using a Shimadzu 160A UV-Vis. spectrophotometer with a 1 cm quartz cell (Fig. 1). Pure Mn(III) acetate solutions showed a strong band at 446 nm which is probably the undissociated Mn(OAc)₃. Midgley and Thomas¹⁷ noted that when alkali metal acetates are added to manganese(III) acetate in acetic acid, a new peak appears at 417 nm. This has been attributed¹⁷ to the formation of an acetato complex Mn(OAc)⁻4.

Different amounts of manganese(III) were anodically generated in a measured volume of analyte and the electrode potential was measured



Fig. 1. Absorption Spectra of 4.00 mM Manganese(III) Acetate in Aqueous HOAc (v/v). (a) 100% HOAc; (b) 100% HOAc + 0.500 mol dm⁻³ NaOAc; (c) 60% HOAc; d) 70% HOAc; (e)80% HOAc.

each time. The Nernst equation, in which E(V versus SCE) indicates the potential of the dynamic equilibrium between the oxidized and reduced forms established at the electrode surface, can be represented as

$$E = E_0 + (2.303 \text{ RT/nF}) \log ([Mn(III)]/[Mn(II)])$$
(1)

where R = 8.314 JK⁻¹ mol⁻¹, T = 298 K, n = 1 and F = 96,500 C mol⁻¹. Plots of E versus log [Mn(III)]/[Mn(II)] were linear with an intercept equal to $(E_0 - E_{cal})$. Since $E_{cal} = 0.246$ V for the saturated calomel electrode at 298 K, the formal redox potential E_0 of the Mn(III)/Mn(II) couple could be calculated.

The potential measurements were made at different concentrations of HOAc, giving an E_0 value of 1.160 V for the pure Mn(III)-Mn(II) system (<u>i.e.</u>, the one without AA, F⁻, Cl⁻, ClO4⁻ and other impurities). The addition

of anions, namely acetate, chloride, fluoride and perchlorate, gave E_0 values of 1.126, 1.181, 1.140 and 1.169 V, respectively. Hence, there is a small but significant change in the redox potential value in the presence of added anions.

Kinetic Measurements

Mixtures of solutions containing requisite amounts of the substrate (enough AA to maintain a large excess over the oxidant), sodium acetate (to maintain constant ionic strength), manganese(II) and acetic acid were placed in stoppered boiling tubes. The required amount of water was added to maintain a constant total volume. After the mixture was thermally equilibrated in a water bath at 323 K, an aliquot of manganese(III) solution, pre-eqilibrated at the same temperature, was added to give a known overall concentration. The progress of the reaction was monitored for at least two half-lives by withdrawing aliquots at regular time intervals and iodometrically determining the unreacted manganese(III) concentration in each aliquot. Under pseudo-half-order conditions with excess AA, the rate constants kobs were calculated graphically from the integral rate equation for a half-order reaction, k =[2/t] [a^{1/2} (a-x)^{1/2}], where a is the initial concentration of Mn(III) in the reaction mixture and (a-x) is its concentration at time t. A plot of [Mn(III)]^{1/2} versus time gives a straight line with a slope of 1/2. The values of kobs thus calculated were reproducible to within \pm 5% error.

Reaction Stoichiometry and Product Analysis

The reaction stoichiometry was established by preparing solutions of 0.0100 mol dm⁻³ AA and 0.100 mol dm⁻³ Mn(OAc)₃ in the presence of 0.300 mol dm⁻³ NaOAc and maintaining the HOAc concentration at 60% (v/v). The reaction mixture was kept at 323 K in a thermostat. After 24 h, the unreacted [Mn(III)] was determined iodometrically and the mole ratio showed the definite stoichiometry of 2:1 (<u>i.e.</u>, two moles of oxidant

consumed per mole of substrate AA). The product was identified as an aldehyde through its 2,4-dinitrophenylhydrazone derivative, which was isolable up to 90% yield. The observed stoichiometry can be represented by the following equation:

2 Mn(III) + RCH(NH₂)COOH + H₂O
$$\longrightarrow$$
 2 Mn(II) + RCHO +
NH₃ + CO₂ + 2H⁺ (2)

where $R = HOCH_2$ for serine and CH_3CHOH for threonine.

Test for Free Radicals

The presence of free radicals in the reaction mixture was tested by adding acrylonitrile and methylmethacrylate to the reaction mixture. Control experiments with solutions of manganese(III) acetate, manganese(II) acetate and AA were also performed under the same experimental conditions. The formation of a polymeric precipitate indicated the generation of free radicals in the reaction mixture.

RESULTS AND DISCUSSION

[Mn(III)] and [AA] Dependence

Plots of log [Mn(III)] versus time and [Mn(III)] versus time were nonlinear. The half-order dependence on manganese(III) was indicated by the linearity of [Mn(III)]^{1/2} versus time plots beyond 75% of the reaction, with a correlation coefficient r > 0.998.

The values of the pseudo-half-order rate constants (k_{obs}) remained constant with an increase in the initial concentration of the oxidant [Mn(III)]₀, (Table I). At constant [Mn(III)]₀, [HOAc], [Mn(II)] and [NaOAc], the rate increased with an increase in [AA]₀ (Table I). The plots of log k_{obs} versus log [AA]₀ were linear (Fig. 2) with a unit slope, indicating a first-order dependence of the rate on [AA].

$10^{3}[Mn(III)]_{o}$	10 ² [AA] ₀	10 ² [Mn(II)] ₀	10[NaOAc] _o	10 ⁶ k _{obs}	$(mo1^{1/2} dm^{-3/2}s^{-1})$	
$(mol dm^{-3})$	(mol dm ⁻	3) (mol dm ⁻³)	$(mol dm^{-3})$	ser.	threo.	
0.50	4.00	1.00	3.00	5.82	21.0	
1.00	4.00	1.00	3.00	5.74	20.9	
2.00	4.00	1.00	3.00	5.72	20.9	
3.00	4.00	1.00	3.00	5.74	21.0	
4.00	4.00	1.00	3.00	5.76	20.9	
1.00	2.00	1.00	3.00	2,95	11.3	
1.00	3.00	1.00	3.00	4.35	15.5	
1.00	4.00	1.00	3.00	5.74	20.9	
1.00	6.00	1.00	3.00	8.18	31.0	
1.00	8.00	1.00	3.00	11.5	40.7	
1.00	4.00	1.00	3.00	5.74	20.9	
1.00	4.00	2.00	3.00	5.68	20.4	
1.00	4.00	3.00	3.00	5.54	20.0	
1.00	4.00	4.00	3.00	5.48	19.6	
1.00	4.00	5.00	3.00	5.44	19.6	
1.00	4.00	1.00	1.00	2.88	11.0	
1.00	4.00	1.00	2.00	4.30	17.6	
1.00	4.00	1.00	3.00	5.74	20.9	
1.00	4.00	1.00	4.00	6.92	23.5	
1.00	4.00	1.00	5.00	7.76	25.7	

Table I. Pseudo-half-order Rate Constants for the Oxidation of L-Serine and DL-Threonine by Manganese(III) Acetate at 323 K with 60% HOAc (v/v).

Dependence of Rate on [H+] and Added Salts

Kinetic measurements were performed using varying perchloric acid concentrations. The effective hydrogen ion concentrations were evaluated from the measured pH values. The rate of reaction decreased



Fig. 2. Plots of Log k_{obs} versus Log $[AA]_o$: (a) L-Serine; (b) DL-Threonine; $[Mn(III)]_o = 1.00 \times 10^{-3} \text{ mol dm}^{-3}; [Mn(II)]_o = 1.00 \times 10^{-2} \text{ mol dm}^{-3};$ $[NaOAc]_o = 0.300 \text{ mol dm}^{-3}; \text{Temp.} = 323 \text{ K}.$

with an increase in [H⁺] (Table II). A plot of log k_{obs} versus log [H⁺] was linear (r > 0.997) with a negative slope (-0.5).

It was found that addition of manganese(II) ion in the form of $Mn(OAc)_2$ had a negligible effect on the rate of oxidation. The effects of the anions CI⁻, F⁻ and CIO₄⁻ on the rate of reaction were also investigated (Table III). Added CI⁻ and CIO₄⁻ increase the redox potential values and also the rate whilst F⁻ decreases the redox potential and also the reaction

Table II. Pseudo-half-order Rate Constants for the Oxidation of L-Serine and DL-Threonine by Manganese(III) Acetate at 323 K with 60% HOAc(v/v) at Different pH Values.

 $[Mn(III)]_{o} = 1.00 \times 10^{-3} \text{ mol } dm^{-3}; [Mn(II)]_{o} = 1.00 \times 10^{-2} \text{ mol } dm^{-3};$ [AA]_o = 4.00 x 10⁻²; [NaOAc]_o = 0.300 mol $dm^{-3};$ Temp. = 323 K.

	$10^6 k_{obs}/mol^{1/2} dm^{-3/2} s^{-1}$			
рН	serine	threonine		
2.62	5.74	20.9		
2.54	4.92	19.1		
2.45	4.47	15.9		
2.32	3.79	13.8		
2.21	3.31	11.2		
2.08	2.91	9.55		
1.95	2.41	8.32		
1.82	2.11	7.12		

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 Cl⁻, ClO4⁻ and F⁻ as co-ligands.

Dependence of Rate on Dielectric Constant

The effect of the dielectric constant of the medium was studied by varying the percentage of HOAc. The rate decreased with an increase in HOAc content (Table IV). Furthermore, a plot of log k_{obs} versus [HOAc] was linear with a negative slope (r > 0.998). This decrease in rate with a decrease in dielectric constant of the medium is in agreement with the Amis concept for dipole-dipole or ion-dipole interactions¹⁹.

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Table III.	Effect	of Variation	of [C1 ⁻	.], F.	-] and	[C104 ⁻] on	the Ra	te Cor	istant	at 32	23 K 1	with 60	Z HOAc	.(v/v)	
= ⁰ [(III)uW]	1.00 x	10-3 mol dm ⁻	³ ; [Mn(I	. [(I	= 1.00	× 10 ⁻²	mol	ժա-3;	[AA]	= 4.0() x 1()-2 m	ol dm ⁻³	••		
[NaOAc] ₀ = .	300 mol	1 dm ⁻³ .														

1-1-10	1061 / / mo11/	/2 _{dm} -3/2 _c -1)	10[5-]	1001 // 201	1/2 ₄ -3/2 ₂ -1)	10[010]01	10615 / (mol 1/	/24m-3/21
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mol dm ⁻³)	ser.	threo.	(mol dm ⁻³)	ser,	threo.	(mol dm ⁻³)	ser.	threo.
I	5.74	20.9	ł	5.74	20.9	ł	5.74	20.9
0.50	5.98	22.0	0.50	4.60	17.7	0.5	6.49	22.7
1.00	6.63	24.8	1.00	4.08	14.3	1.0	7.80	26.8
1.50	7.73	28.5	1.50	2.63	7.5	1.5	10.65	31.4

% of HOAc	10 ⁶ k _{obs} /(mo	$_{\rm dm}^{-3/2}$ s ⁻¹
(v/v)	serine	threonine
40	8.26	33.8
50	6.68	26.9
60	5.74	20.9
70	4.92	16.0

Table IV. Effect of Variation of Concentration of HOAc (v/v) on the Reaction Rate at 323 K. Other Conditions are the same as in Table II.

Solvent Isotope Studies

The reaction was studied in D₂O as solvent (0.4 atom percent D) for L-serine and DL-threonine and the rate constants k_{D2O} were 3.94 x 10^{-6} and 1.24 x 10^{-5} mol^{1/2} dm^{-3/2} s⁻¹, respectively. The corresponding rate constants k_{H2O} under identical conditions were 5.74 x 10^{-6} and 2.09 x 10^{-5} mol^{1/2} dm^{-3/2} s⁻¹, leading to a solvent isotope effect²⁰ of 1.46 and 1.69.

Dependence of Rate on Temperature

The reactions were carried at 313, 318, 323 and 328 K keeping all other experimental conditions constant. The rate constant so obtained are presented in Table V. The Arrhenius-Eyring plots of log k_{obs} versus 1/T and log k_{obs}/T versus 1/T gave straight lines (r > 0.986). The activation parameters, calculated from the slopes and intercepts of the plots, are summarized in Table VI.

Amino acids are known to exist as in the following equilibria in aqueous solution. Table V. Pscudo-half-order Rate Constants (k_{obs}) for the Oxidation of L-Serine and DL-Threenine by Manganese(III) Acetate at Different Temperatures with 60% HOAc (v/v). [Mn(III)]_o = 1.00 x 10⁻³ mol dm⁻³; [AA]_o = 4.0 x 10⁻² mol dm⁻³; [NaOAc]_o = 0.300 mol dm⁻³.

	"obs/mor	
т/к	serine	threonine
313	2.69	7.06
318	3.42	11.9
323	5.74	20.9
328	9.37	32.5

Table VI. Activation Parameters for the Oxidation of L-Serine and DL-Threonine by by Manganese(III) Acetate.

Parameter	serine	threonine
Log A	15.0	21.9
E _a /kJ mol ⁻¹	72.6	87.8
ΔH≭/kJ mol ⁻¹	69.8	150
ΔS≭/JK ⁻¹ mol ⁻¹	-130	-71.8
ΔG≠/kJ mol ⁻¹	112	108

 $[R = HOCH_2$ for serine and CH₃CHOH for threonine]

The dissociation of amino acids depends on the pH of the medium and strongly alkaline and acidic media generally involve the dipolar zwitterion (AA) and the cation (AA⁺).

In our previous studies^{13,15}, we have speculated, based on spectrophotometric and electrochemical evidence, that the reactive species of manganese(III) in aqueous acetic acid-acetate medium are $Mn(OAc)_3$ and $Mn(OAc)_4^-$. In the present study, the kinetic results show a half-order dependence of the rate on $[Mn(OAc)_3]_0$ and $[OAc^-]$, a first-order dependence on $[AA]_0$ and an inverse-fractional-order dependence on $[H^+]$. One explanation for the half-order kinetics involves a fast reversible dissociation prior to the rate-determining step. For example, it is possible that all the manganese(III) is essentially in the form of a dinuclear complex species $[Mn_2(OAc)_5]^+$ with a small equilibrium amount of the kinetically active mononuclear species $[Mn(OAc)_3]$. This is supported by the strong tendency of manganese(III) acetate to form polynuclear complexes^{13,15}. The equilibrium of eq. (4) accounts for the fractional-order observed for acetate ion, as shown in Scheme 1 of the proposed mechanism.

The reaction rate is given by eq. (8).

$$rate = -d[Mn(OAc)_3]/dt = k_3 [X]$$
(8)

By solving the equation for [X] with the application of steady state approximation and substituting in eq. (8), one gets

From the equilibrium of eq. (4), $K_1 = [Mn(OAc)_3]^2 / [Mn_2(OAc)_5^+][OAc^-]$

or
$$[Mn(OAc)_3] = \{K_1 [Mn_2(OAc)_5^+] [OAc^-]\}^{1/2}$$
 (10)

From equations (9) and (10), one gets

rate =
$$\{K_1^{1/2} K_2 k_3 [Mn_2(OAc)_5^+]^{1/2} [OAc^-]^{1/2} [HAA]\}/\{k_2 [H^+] + k_3\}$$
 (11)

The decrease in the reaction rate in D_2O as solvent is consistent with the proposed mechanism. For a fast pre-equilibrium proton transfer, the rate increases by a factor of 2-3 in 100% D_2O as solvent²⁰. Similarly,

$$Mn_{2}(OAc)_{5}^{+} + OAc^{-} + \frac{K_{1}}{(fast)} 2 Mn(OAc)_{3}$$
(4)

$$Mn(OAc)_{3} + R-CH-COOH \xrightarrow{K_{2}}_{(fast)} \begin{pmatrix} R-CH-C-OH \\ H \\ H^{2} \\ OAc & Mn & OAc \\ OAc & (X) \end{pmatrix} + H^{+} (5)$$

$$\begin{bmatrix} R-CH-C-OH \\ I & II \\ NH_2 & O \\ OAc & Mn & OAc \\ I \\ OAc & (X) \end{bmatrix} \xrightarrow{k_3} R-\dot{C}H + Mn(OAc)_2 + HOAc + CO_2 \quad (6)$$

$$\begin{array}{rcl} \mathsf{Mn}(\mathsf{OAc})_3 & + & \mathsf{R-\dot{C}H} & \stackrel{\mathsf{H}_2\mathsf{O}}{\underset{|}{\overset{|}{\mathsf{(fast)}}}} & \mathsf{R-CHO}_+ & \mathsf{Mn}(\mathsf{OAc})_2 & + & \mathsf{NH}_4^+ & + & \mathsf{OAc}^- & (7) \\ & & \mathsf{NH}_2 & \\ & & (\mathsf{Y}) \end{array}$$

Here HAA is the amino acid cation, X is the HAA-Mn(III) acetate chelate and Y is the amine free radical.

Scheme 1

the rate decreases in heavy water, where there is a fast proton release as shown in eq. (5).

The rate constant data in Tables I-V show that Mn(III) reacts faster with threonine than with serine under identical conditions. In each case, the negative entropy of activation (ΔS^{\neq}) (Table VI) suggests the involvement of a rigid associated species in the transition state which is probably formed by solvation lowering the entropy of activation. The positive values of ΔG^{\neq} and ΔH^{\neq} indicate that the two amino acids react with Mn(III) via the same mechanism (Table VI).

Spetroscopic Evidence for the Intermediate Complex

The UV-Vis spectrum of pure manganese(III) acetate solution has a λ_{max} at 446 nm. When the amino acid is mixed with manganese(III), the maximum shifts to 434 nm, suggesting a complex formation between manganese(III) and the substrate AA.

<u>Conclusions</u>

The main objective of this study is to arrive at a suitable mechanism of oxidation of amino acids by manganese(III) acetate. The kinetic data for the oxidation of some α -amino acids by manganese(III) species in sulfuric, perchloric and acetic acid and pyrophosphate are summarized in Table VII. The earlier studies (Table VII and references therein) have shown that the dependencies of the oxidation rate on manganese(III) concentration in perchloric acid, sulfuric acid, acetic acid and acidic pyrophosphate media vary implicating different active oxidizing species of manganese(III) in the reactions. There is a similarity in the oxidizing patterns in sulfuric and perchloric acid. The oxidizing species identified in these two media are the ionic forms $Mn^{3+}(aq)$ and

 $MnOH^{2+}(aq)$ and the kinetic order in [Mn(III)] is generally one or two. The order in [AA] is one in all cases while dependencies of inverse orders on [H⁺] and [Mn(II)] are the other common features. However, the studies with manganese(III) acetate in acetic acid medium show a common half-order dependence of the rate on manganese(III) concentration for all amino acids except acidic amino acids such as L-aspartic and L-glutamic acid. It was, therefore, interesting to study the present reaction of neutral

acid L-Gly HCl(HQS(HOA DL-α-Ala HQS(L-Ala HOA DL-iso-Val H2S(DL-n-Val H2S(L-Val HOA L-Leu HQS(L-Leu HOA DL-a-amino butyric acid H2S(L-His H2S(04 04 c 04 c	[Mn(III)] 1 2 0.5	[AA] 1 1	[Mn(II)] 0	[H ⁺] -1 ^a and -2 ^b	8
L-Gly HCli H2Si H0Ai DL- α -Ala H2Si L-Ala H0Ai DL-iso-Val H2Si DL-n-Val H2Si L-Val H0Ai L-Leu H2Si L-Leu H0Ai L-Leu H0Ai L-Leu H2Si L-Leu H0Ai L-Thr H2Si DL- α -amino butyric H2Si acid H2Si	04 04 c 04 c	1 2 0.5	1 1	0	-1^a and -2^b	8
H ₂ Si HOA DL-α-Ala H ₂ Si L-Ala HOA DL-iso-Val H ₂ Si DL-n-Val H ₂ Si L-Val HOA L-Leu HOA L-Leu HOA L-Thr H ₂ Si DL-α-amino butyric H ₂ Si acid H ₂ Si	04 c 04 c	2 0.5	1	-1		
HOA $DL-\alpha-Ala H_2S$ $L-Ala HOA$ $DL-iso-Val H_2S$ $DL-n-Val H_2S$ $L-Val HOA$ $L-Leu HOA$ $L-Leu HOA$ $L-Leu HOA$ $L-Thr H_2S$ $DL-\alpha-amino butyric H_2S$ $L-His H_2S$	с 0 ₄ с	0.5	-	T	-1	7
$\begin{array}{cccc} DL-\alpha-A1a & H_2S^{\prime\prime}\\ L-A1a & HOA^{\prime\prime}\\ DL-iso-Va1 & H_2S^{\prime\prime}\\ DL-n-Va1 & H_2S^{\prime\prime}\\ L-Va1 & HOA^{\prime\prime}\\ L-Leu & HOA^{\prime\prime}\\ L-Leu & HOA^{\prime\prime}\\ L-Thr & H_2S^{\prime\prime}\\ DL-\alpha-amino \\ butyric & H_2S^{\prime\prime}\\ acid & L-His & H_2S^{\prime\prime}\\ L-Acp & H^{\prime}S^{\prime\prime}\\ \end{array}$	0 ₄ c	-	1	Inverse	fractional	9
L-Ala HOAd DL-iso-Val H ₂ SC DL-n-Val H ₂ SC L-Val HOAd L-Leu H ₂ SC L-Leu HOAd L-Thr H ₂ SC DL- α -amino butyric H ₂ SC acid H ₂ SC L-His H ₂ SC	c	2	1	-1	-1	7
DL-iso-Val H ₂ SC DL-n-Val H ₂ SC L-Val HOAG L-Leu H ₂ SC L-Leu HOAG L-Thr H ₂ SC DL-α-amino butyric H ₂ SC acid H ₂ SC L-His H ₂ SC		0.5	1	Inverse	fractional	9
DL-n-Val $H_2S'_1$ L-ValHOAdL-Leu $H_2S'_1$ L-LeuHOAdL-Thr $H_2S'_2$ DL- α -aminobutyric $H_2S'_2$ acidL-HisL-His $H_2S'_2$	04	1 ^c or 2 ^d	1	-1	-1	10
L-Val HOAd L-Leu HOAd L-Leu HOAd L-Thr H ₂ SC DL- α -amino butyric H ₂ SC acid L-His H ₂ SC	04	1^{c} or 2^{d}	1	-1	-1	10
L-Leu H_2SC L-Leu $HOAG$ L-Thr H_2SC DL- α -amino butyric H_2SC acid L-His H_2SC	c	0.5	1	Inverse	fractional	9
L-Leu HOAd L-Thr H ₂ SC DL-\arguma-amino butyric H ₂ SC acid H ₂ SC L-His H ₂ SC	04	1^{c} or 2^{d}	1	-1	-1	10
L-Thr H_2SC DL- α -amino butyric H_2SC acid L-His H_2SC	с	0.5	1	Inverse	fractional	9
DL-a-amino butyric H ₂ SC acid L-His H ₂ SC	04	2	1	-1	-2	11
L-His H ₂ S	04	1 ^c or 2 ^d	1	-1	-1	10
I-Acr N-S(04	2	1	Inverse fractional	2	12
ц-жэр п <u>2</u> эс	04	2	1	Inverse fractional	-1	13
НОА	с	1	1	Inverse fractional	0.6	13
Pyre	ophosphate	1	1	Inverse fractional	0	13
L-Glu H ₂ SO	04	1.5	1	Inverse fractional	-1	13
HOA	с	1	1	Inverse fractional	0.6	13
Pyre	ophosphate	1	1	Inverse fractional	0	13
L-Arg Pyre	ophosphate	1	1	-1	0.6	14
НОА	c	0.5	1	0	Inverse fractional	14
L-Lys HOAd	с	0.5	1	0	Inverse fractional	15
L-ph.ala HOA	с	0.5	1	0	lnverse fractional	15
L-ser HOAd	с	0.5	1	0	Inverse fractional	This work
DL-threo HOA						

Table VII. Comparison of Kinetic Data for the Oxidation of α -Amino Acids by Manganese(III) in Different Media.

amino acids, L-serine and DL-threonine, with manganese(III) acetate. In the present study, the observed half-order dependence on the oxidant concentration indicates the existence of a fast pre-equilibrium [step (4) in Scheme I] forming the active oxidant species $Mn(OAc)_3$. This observation supports the earlier finding that there is a common mechanism operative in the oxidation of neutral amino acids⁷⁻¹⁵.

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