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Electrolytically Generated Manganese(III) Sulfate for the Oxidation of L-Histidine in Aqueous Sulfuric Acid: A Kinetic Study

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Conditions have been established for the electrogeneration of Mn(III) from Mn(II) in sulfuric acid medium. Mn(III) formed was identified and characterized by UV spectra. Kinetics of Mn(III) oxidation of L-histidine in aqueous sulfuric acid medium has been studied spectrophotometrically. Oxidation followed second order kinetics in [Mn(III)], first order in [histidine] and increase in $[H^+]$ decreased the rate. The reduced product of the oxidant, Mn(II), retarded the rate of reaction. Evidence for the transient existence of the free radical reaction intermediate is given. Effects of ionic strength, solvent composition, HSO_4^- and certain complexing agents like $P_2O_7^{4-}$, Cl^-, F^-, have also been studied. Added complexing agents decreased the redox potential of the Mn(III)/Mn(II) couple, thereby reducing the oxidation rate. Dependence of reaction rate on temperature is examined and activation parameters computed from Arrhenius and Eyring plots. A mechanism consistent with kinetic results has been proposed in which a combined role of Mn(III)aq and $MnOH^{2+}$aq was envisaged.

Manganese occupies a unique place in the first transition series due to its multi valent character. Next to Mn(VII), oxidation state III of manganese has been extensively used as a potent oxidant for studying the oxidation of both organic and inorganic substrates. Equilibria and kinetics in acidic perchlorate solution of Mn(III) were a subject of review by Davies.[1)] Manganese(III) acetate in acetic acid, manganese(III) pyrophosphate in acidic media, and a number of other redox active complexes of Mn(III) are being increasingly used, presumably because of its selectivity in the oxidation of various compounds. However manganese(III) sulfate has been scarcely used[2–9)] in redox studies because of the difficulty in obtaining it in pure and stable form. In this paper we report the preparation of manganese(III) sulfate by the anodic oxidation in an electrochemical cell and its use for mechanistic investigation. The substrate chosen is L-histidine (His), an essential amino acid which serves important function in our biological systems and plays a significant role in metabolism. It is used in biochemical, microbiological, and nutrition investigation and is employed as a dietary supplement. Histidine also finds application in medicine and pharmaceuticals.

Experimental

Several authors have studied the conditions for obtaining high efficiency of oxidation of manganese(II) sulfate to manganese(III) sulfate.[10–12)] As high as 53% sulfuric acid was considered essential for the stability of Mn(III). Preparation of manganese(III) sulfate in the form of a paste, a highly concentrated reagent for organic preparation work has also been worked out.[11,12)] But all these conditions are not amenable to kinetic investigation of Mn(III) reactions in solution. Therefore, the process is suitably modified and adopted to meet the present requirement.

The sources of Mn(II) is special quality (SQ) sample of $MnSO_4 \cdot H_2O$. 0.2 mol dm^{-3} sulfuric acid was prepared and taken in a 500 cm^3 beaker. Spectroscopically pure antimonial lead strips were used as electrodes. To achieve higher current efficiency, ratio of anode to cathode area was maintained at 10 : 1. Direct current was passed from a silicon rectifier unit. Electrolysis was carried out at the cell voltage of 6 V and a current density of 2 mA cm^{-2}, while the solution was stirred with a magnetic stirrer. The electrolysis can be continued till Mn(III) of 0.05 mol dm^{-3} is formed. Further electrolysis may result in a turbid suspension of sparingly soluble manganese(III) sulfate and hence should be stopped at the appropriate stage. The clear cherry red colored solution contained an excess but known concentration of Mn(II) to supress the disproportionation reaction.[13)]

$$\mathrm{Mn(III)} + \mathrm{Mn(III)} \rightleftarrows \mathrm{Mn(II)} + \mathrm{Mn(IV)}. \qquad (1)$$

The solutions were prepared daily, although they appear to be stable for at least one month at $[H^+] > 5.0$ mol dm^{-3}. To ascertain that the presence of lead ions in solution (from the dissolution of lead electrodes) was minimal, a blank electrolysis was carried out under identical conditions in 5.0 mol dm^{-3} sulfuric acid but without Mn(II). The resulting solution was tested for lead ions in Pye Unicam Model Pu 9000/21 atomic absorption spectrophotometer located at chemical laboratory of Mangalore Fertilisers and Chemicals Ltd., Mangalore. The lead ions present were found to be 2.0 ppm, well within the interference limit.

Chromatographically pure L-histidine (Sisco Research Laboratories, India) was further assayed by standard methods.[14)] An aqueous stock solution of the substrate (0.2 mol dm^{-3}) was prepared as and when needed as the reagent is photosensitive. Solution of sodium perchlorate needed to maintain the ionic strength of the reaction mixture was prepared by neutralizing 12 mol dm^{-3} $HClO_4$ with AR sodium carbonate, boiling to dispel CO_2, followed by filtration to remove the precipitated trace impurities.

A Hitachi model UV spectrophotometer with 1 cm quartz cells was used for the absorption measurements. Under the experimental conditions, absorption maximum for the elec-

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trolytically generated Mn(III) species occured at 490 nm. Optical density versus concentration plots for manganse(III) sulfate at $[H_2SO_4]=2.0$—5.0 mol dm^{-3} always containing excess but known [Mn(II)], showed that Beer's law is obeyed at wavelength 490 nm. Molar extinction coefficient, ε at 490 nm varied as a function of $[H^+]$ (ε ranged between 131—110 at $[H^+]$, 1.28—2.98 mol dm^{-3}).

Redox Potential Measurements: The standard redox potential of Mn(III)/Mn(II) couple is a measure of the oxidizing power of the oxidant and it generally decreases on complexation. The standard redox potential was measured at the specified experimental conditions. The Nernst equation in which E (V vs. SCE) indicates that equilibrium potential referring to the position of dynamic equilibrium between oxidized and reduced forms, which is established rapidly at the platinum electrode surface coupled to a calomel electrode, can be represented as follows:

$$E\ (\text{V vs. SCE}) = E^\circ_{\text{Mn(III)/Mn(II)}} + \frac{2.303\,RT}{nF} \log \frac{[\text{Mn(III)}]}{[\text{Mn(II)}]},$$

where $R=8.314$ J mol^{-1}, $T=298$ K, $n=1$, $F=96500$ C mol^{-1}. Plot of E (V vs. SCE) against $\log \frac{[\text{Mn(III)}]}{[\text{Mn(II)}]}$ gave a straight line with intercept which equals $[E^\circ_{\text{Mn(III)/Mn(II)}} - E_{\text{calcd}}]$ (Fig. 1). Taking E_{calcd} for saturated KCl at 298 K as 0.241 V, $E^\circ_{\text{Mn(III)/Mn(II)}}$ could be found out (1.52 V). The measurements were made at different $[H_2SO_4]$ and in presence of complexing agents, HSO_4^-, $P_2O_7^{4-}$, F^-, and Cl^- and the redox potentials Mn(III)-Mn(II) couple in the changed environment was computed (1.51, 1.48, 1.44, and 1.42 V respectively), (please see Fig. 1).

Kinetic Measurements: Reactions were carried out under substrate excess conditions. Preliminary experiments indicated that rate of reaction varied with reactant concentration. No spectroscopic change occurred in the absorption spectrum of Mn(III) on addition of histidine. Repetitive scans of the spectra during the course of the reaction showed only decrease in the absorbance with no evidence of the shift in the peaks (Fig. 2).

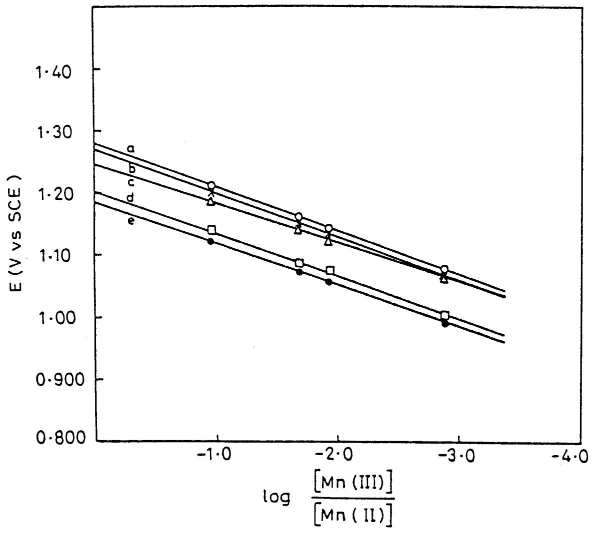


Fig. 1. Plot of E (V vs. SCE) versus log[Mn(III)]/[Mn(II)]. Temp 298 K, $[H_2SO_4]=2.5$ mol dm^{-3}, (a) [Complexing agent]=nil, (b) $[HSO_4^-]=0.1$ mol dm^{-3}, (c) $[P_2O_7^{4-}]=0.1$ mol dm^{-3}, (d) $[F^-]=0.1$ mol dm^{-3}, (e) $[Cl^-]=0.1$ mol dm^{-3}.

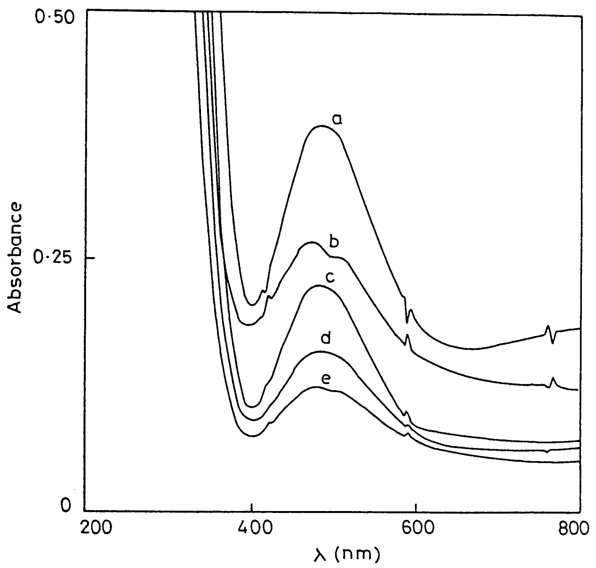


Fig. 2. Sequential scans of the absorption spectrum during the reaction of manganese(III) sulfate with L-histidine. Temp 313 K, $[\text{Mn(III)}]_0=3.0$ mol dm^{-3}, $[\text{His}]_0=0.04$ mol dm^{-3}, $[H_2SO_4]=2.5$ mol dm^{-3}, [Mn(II)]=0.127 mol dm^{-3}, at reaction time (minutes) (a) 0.0, (b) 22, (c) 40, (d) 80, (e) 114.

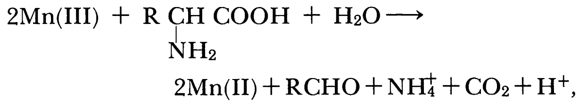
A known amount of Mn(III) solution was thermally equilibrated at the desired temperature, was added to a mixture of appropriate amount of histidine, sulfuric acid, sodium sulfate (for constant sulfate concentration), sodium perchlorate (to keep ionic strength constant), and water (to keep the total volume constant) in another boiling tube thermostated at the same temperature. The course of the reaction was followed by recording the decrease in absorbance of Mn(III) ion at its absorbance maximum of 490 nm as a function of time. It was verified that there was no interference from other reagents at this wavelength. The reaction is sluggish even at 40 °C taking 2—3 hours for 80% of the reaction. Allowing the reaction mixture in the light path of the spectrophotometer continuously for longer duration may induce photochemical reaction. Therefore, aliquot portions were withdrawn from the reaction mixture after suitable time intervals and added to 5.0 cm^3 of 2.5 mol dm^{-3} ice cold H_2SO_4. Absorbance of the chilled solution was measured at 490 nm and [Mn(III)] directly read from the calibration plot.

Under the conditions [His]$\gg$[Mn(III)] and in the presence of excess of Mn(II) required for the stability of Mn(III), the plot of 1/absorbance or 1/[Mn(III))] versus time were linear even beyond 75% of the reaction. The linearity of the plots beyond these points indicated that none of the products formed during the reaction affected the rate. The pseudo-second-order rate constants obtained from the gradients of the above plots were reproducible within ±5%.

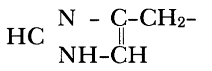
Results

Stoichiometry and Product Analysis. A known amount of histidine was allowed to react completely with 2—4 fold excess of Mn(III) at 40 °C in the presence of 25 fold excess of Mn(II) in 2—3 mol dm^{-3}

H_2SO_4. The Mn(III) remaining after the reaction was estimated by sampling into a freshly prepared ice cold KI in 2.5 mol dm^{-3} H_2SO_4 followed by titration of the liberated iodine with standard sodium thiosulfate. Product analysis was carried out under substrate excess conditions as follows: Reaction mixture containing histidine (0.2 mol dm^{-3}) and manganese(III) sulfate (0.02 mol dm^{-3}) in H_2SO_4 (2.5 mol dm^{-3}) at 40 °C was allowed to react completely. The reaction mixture was extracted with ether. Aldehyde was detected in ether extract by the formation of 2,4-dinitrophenylhydrazone isolable in 85—92% yields. The aqueous layer was neutralised with NaOH, the precitated $Mn(OH)_2$ was filtered off and NH_4^+ was detected in the filtrate with Nessler's reagent. The stoichiometry was found to correspond to;



$$2\mathrm{Mn(III)} + \mathrm{R}\underset{\mathrm{NH_2}}{\mathrm{CH}}\mathrm{COOH} + \mathrm{H_2O} \longrightarrow 2\mathrm{Mn(II)} + \mathrm{RCHO} + \mathrm{NH_4^+} + \mathrm{CO_2} + \mathrm{H^+}, \quad (2)$$

where R is 

The formation of aldehyde, ammonia, and carbon dioxide as reaction products was found to be in accord with the oxidation of histidine in particular by chloramine-T[15] and other amino acids in general by Mn(III) ions.[5—8,16] Further oxidation was noticed on keeping the reaction mixture for a long time.

[Mn(III)] and [His] Dependences. The reaction order with respect to Mn(III) ion was determined by studying the oxidation at 40 °C under the conditions $[\mathrm{His}]_0=0.04$ mol dm^{-3}, $[H_2SO_4]=2.5$ mol dm^{-3} and varying $[\mathrm{Mn(III)}]_0=1.0\times10^{-3}$—$6.0\times10^{-3}$ mol dm^{-3}. The disappearance of Mn(III) followed neat second-order kinetics as indicated by the linearity of 1/[Mn(III)] versus time plot even beyond 75% of the reaction with a correlation coefficient of 0.998. However, the values of pseudo-second-order rate constant slightly decreased with increase in initial concentration of Mn(III).

At constant $[\mathrm{Mn(III)}]_0$ and $[H_2SO_4]$, the rate increased with increase in $[\mathrm{His}]_0$. The plot of k_{obsd} versus [His] is linear passing through the origin showing the order in [His] as one.

Dependence of Reaction Rate on Ionic Strength. The reactions were studied at $[H_2SO_4]=2.5$ mol dm^{-3} which amounted to an overall ionic strength of 7.5 mol dm^{-3}. Kinetic runs were performed with increasing addition of $NaClO_4$ till the overall ionic strength reached a value 9.0 mol dm^{-3}. The values of k_{obsd} were found to decrease with increasing ionic strength, showing negative salt effect.

Dependence of Reaction Rate on Added Salts. Mn(II) is the reduced product of the oxidant and its affect on the rate of reaction was investigated. As the initial concentration of [Mn(II)] increased, the rate progressively decreased. The data are summarised in Table 1. The results indicated that Mn(IV) is not involved in the oxidation process.

Table 1. Pseudo-Second Order Rate Constants for the Oxidation of L-Histidine by Mn(III). Temp 313 K, $H_2SO_4=2.5$ mol dm^{-3}, $I=9.05$ mol dm^{-3}

10^3Mn(III)	10^2 [His]	10 Mn(II)	10^2k_{obsd}
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	dm^3 mol^{-1} s^{-1}
2.0	4.0	1.27	9.7
3.0	4.0	1.27	9.3
4.0	4.0	1.27	7.0
5.0	4.0	1.27	6.5
3.0	1.0	1.27	2.4
3.0	2.0	1.27	4.9
3.0	3.0	1.27	7.8
3.0	5.0	1.27	11.9
3.0	6.0	1.27	15.0
3.0	4.0	0.27	16.2
3.0	4.0	0.52	13.7
3.0	4.0	0.77	11.0
3.0	4.0	1.77	6.8
3.0	4.0	2.27	5.1

The effect of complexing agents like pyrophosphate, fluoride, and chloride ions, on the rate of reaction was also investigated. Addition of sodium pyrophosphate, sodium fluoride, and sodium chloride had retardation effect. This may be attributed to the displacement of coordinated SO_4^{2-} ligand leading to the establishment of a new Mn(III)-Mn(II) couple with $P_2O_7^{4-}$, F^-, or Cl^- as ligand, and such redox couples have lower redox potentials, and thereby decreasing the rate. This also means that Mn(III) is the reactive species under the experimental conditions.

Added hydrogensulfate ion (as $NaHSO_4$) in the range 0.05—1.0 mol dm^{-3} at fixed ionic strength and $[H_2SO_4]$ had only negligible affect on the redox potential of Mn(III)-Mn(II) and on the reaction rate (Table

Table 3. Effect of Complexing Agents, $P_2O_7^{4-}$, Cl^-, F^-, and HSO_4^- on the Oxidation of L-Histidine by Mn(III). Temp 313 K, $[\mathrm{Mn(III)}]=3.0\times10^{-3}$ mol dm^{-3}, $[\mathrm{His}]=4.0\times10^{-2}$ mol dm^{-3}, $[\mathrm{Mn(II)}]=1.27\times10^{-1}$ mol dm^{-3}, $[H_2SO_4]=2.5$ mol dm^{-3}, $I=9.05$ mol dm^{-3}

$10^2[P_2O_7^{4-}]$	10^2k_{obsd}	10 $[Cl^-]$	10^2k_{obsd}
mol dm^{-3}	dm^3 mol^{-1} s^{-1}	mol dm^{-3}	dm^3 mol^{-1} s^{-1}
2.5	7.8	0.5	6.3
5.0	7.2	1.0	5.5
7.5	6.8	1.5	5.1
10.0	6.3	2.0	4.7
10 $[F^-]$		$10^2[HSO_4^-]$	
mol dm^{-3}		mol dm^{-3}	
0.5	5.5	1.0	9.2
1.0	4.2	5.0	9.0
1.5	3.6	10.0	8.9
2.0	3.0	—	—

Table 4. Effect of Varying Ionic Strength, Solvent Composition, $[SO_4^{2-}]$, on the Oxidation of L-Histidine by Mn(III). Temp=313 K, $[Mn(III)]=3.0\times10^{-3}$ mol dm^{-3}, $[His]=4.0\times10^{-2}$ mol dm^{-3}, $[Mn(II)]=1.27\times10^{-1}$ mol dm^{-3}, $[H_2SO_4]=2.5$ mol dm^{-3}

I	k_{obsd}	CH_3COOH	10^2k_{obsd}	$[SO_4^{2-}]$[a)]	10^2k_{obsd}
mol dm^{-3}	dm^3 mol^{-1} s^{-1}	% v/v	dm^3 mol^{-1} s^{-1}	mol dm^{-3}	dm^3 mol^{-1} s^{-1}
8.05	15.0	5.0	8.3	2.0	4.6
8.50	13.9	10.0	7.2	2.2	6.0
9.05	9.3	15.0	6.9	2.5	9.3
9.5	7.8	20.0	5.6	2.75	12.0
10.0	6.5	—	—	3.0	16.0

a) $\{[H_2SO_4]+[HClO_4]\}=2.5$ mol dm^{-3}.

3).

It was considered as of interest to know the possible catalytic effect due to Ag(I), Cu(II), and Cr(III). The rate of reaction was found to be unaffected by adding the sulfate salts of Ag(I), Cu(II), and Cr(III), at constant ionic strength, $[SO_4^{2-}]$, and $[H^+]$.

Sulfate ions had catalytic effect on their oxidation reaction. When added $[SO_4^{2-}]$ was varied between 0.1—0.67 mol dm^{-3} at constant ionic strength, $[H^+]$, and temperature, the rate of the reaction showed a regular increasing trend (Table 4). An attempt has been made to explain the affect of $[SO_4^{2-}]$ as due to the presence of an additional equilibrium (Eq. 21).

Dependence of Reaction Rate on the Hydrogen Ion Concentration. Kinetic measurements were performed in H_2SO_4-$NaHSO_4$ solutions of different $[H^+]$. The effective hydrogen ion concentrations were evaluated with the aid of a standard curve of $[H_2SO_4]$ versus $[H^+]$ prepared from the results of Kemp and Waters.[7)] The rate of reaction decreased with increase in $[H^+]$ (Table 2), indicating that hydrolyzed species of Mn(III) are more reactive than unhydrolyzed species (Eq. 3).

These types of redox reactions are expected to be air sensitive. Flushing solutions with nitrogen prior to kinetic runs made some apparant differences in the results. Present investigations are done in aerobic conditions and it is expected that oxidation in anaerobic conditions proceed by quite different mechanism and form a subject of separate study.

Polymerization Studies. It was found that the reaction mixtures initiate polymerization of monomers like acrylonitrile in less than 20 minutes and methyl methacrylate in less than one hour. As neither of the reacting species, histidine or Mn(III), do this when added separately to an aqueous mixtures of these monomers, it can be assumed that the redox steps produce some free radicals which are capable of inducing polymerization. Further, the polymerization product of methyl methacrylate monomer from the above reaction answered the nitrogen test confirming the presence of nitrogen containing end group. NMR spectrum of the polymer product in $CDCl_3$ showed a singlet at $\delta=0.8$ and triplet at $\delta=1.98$ and 3.6 due to one CH_3 and two CH_2 groups respectively. Methoxyl group resonated at $\delta=4.4$. Imidazole protons appeared as two doublets at $\delta=6.8$ and 7.3. Presence of a peak at $\delta=5.6$ and 6.05 confirmed NH_2 and NH protons respectively.

Table 2. Effect of $[H^+]$ on the Oxidation of L-Histidine by Mn(III). Temp=322.5 K, $[Mn(III)]=3.0\times10^{-3}$ mol dm^{-3}, $[His]=4.0\times10^{-2}$ mol dm^{-3}, $\{[H_2SO_4]+[NaHSO_4]\}=3.545$ mol dm^{-3}, $[Mn(II)]=1.27\times10^{-1}$ mol dm^{-3}

$[H_2SO_4]$/mol dm^{-3}	1.0	1.5	2.0	2.5	3.0
$[H^+]$/mol dm^{-3}[a)]	1.2	1.62	2.04	2.5	2.98
10 k_{obsd}/dm^3 mol^{-1} s^{-1}	6.205	5.35	3.715	3.012	2.5

a) $[H^+]$ were evaluated with the aid of a standard plot of $[H_2SO_4]$ versus $[H^+]$, from the results of Kemp and Waters.[7)]

Dependence of Reaction Rate on Temperature. To determine the activation parameters, the reaction was carried at five temperatures 303, 308, 313, 328, and 333 K, and at constant ionic strength and $[H^+]$. A plot of Arrhenius and Eyring equation[19)] gave good straight lines, and from the slopes and intercepts, the energy of activation, Arrhenius frequency factor, and enthalpy, entropy, and free energy of activation were computed. The activation parameters for the overall reaction were $E_a=98.26$ kJ mol^{-1}, $A=2.07\times10^{15}$ s^{-1}, $\Delta H^{\ddagger}=95.6$ kJ mol^{-1}, $\Delta S^{\ddagger}=39.4$ JK^{-1} mol^{-1}, and $\Delta G^{\ddagger}=83.3$ kJ mol^{-1}. These values necessarily substantiate the plausible C-C bond cleavage. As shown in detailed mechanism (Scheme 3), a bulkier metal substrate complex breaks down to simpler intermediates and ions during the stages of activation. This accounts for a positive entropy of activation.

The results reported in this paper is one of the very few cases of redox reaction involving second order dependence in Mn(III). The previous cases involved the oxidation of certain lower amino acids,[5,6,8)] and nitrite ion[17)] by aquamanganese in sulfuric and perchloric acid medium.

It has been observed that Mn(III) ion undergoes considerable hydrolysis even in fairly strong acid medium. The hydrolysis of Mn(III) ion was investigated by Diebler and Sutin,[18)] Fackler and Chawla,[19)] and Wells and Davies.[20)] Reaction (3) has been observed at the initial stages followed by slow formation of dimers or higher polymers.

$$\mathrm{Mn(III)} + \mathrm{H_2O} \rightleftarrows \mathrm{MnOH^{2+}} + \mathrm{H^+}. \qquad (3)$$

By a detailed spectrophotometric investigation of aquamanganese(III) ion in perchlorate media at a ionic strength of 4.0 mol dm^{-3} and temperature 25 °C, Wells and Davies obtained a value K_h=0.93±0.03, which has been used in the present work. Further the spectra of Mn(III)aq and MnOH^{2+}aq have been reported[22] to be similar in both visible and UV region and our observation of the absorbance spectra is consistant with the values reported.

Data published by Diebler and Sutin[18] and the work of Fackler and Chawla[19] have shown, that in the presence of fluoride ions aqueous solution of manganese(III) consists of hexaaquamanganese(III), Mn(III)aq, hydroxopentaaquamanganese(III), MnOH^{2+}aq and MnF^{2+}aq. On the same lines it can be assumed with justification that Mn(III) species present in sulfuric acid medium are Mn(III)aq, MnOH^{2+}aq, and MnSO$_4^+$. Since the affect of HSO$_4^-$ ion on the reaction under investigation is negligible MnSO$_4^+$ cannot be the reactive species. Therefore a combined role of Mn(III)aq and MnOH^{2+}aq can be envisaged as has been observed in many Mn(III) reactions. In fact MnOH^{2+}aq should be considered as more reactive in view of the decrease in rate with increase in [H$^+$]. Formation of dihydroxo species produced by the further hydrolysis of MnOH^{2+} is another possibility.[16]

$$\mathrm{MnOH^{2+}} + \mathrm{H_2O} \longrightarrow \mathrm{Mn(OH)_2^+} + \mathrm{H^+}. \qquad (4)$$

But, fresh solutions of Mn(III) were always prepared and used immediately after cessation of the electrolysis thereby eliminating any reaction with Mn(OH)$_2^+$.

The chemistry of amino acids RCH(NH$_2$)COOH consists of transformations of functional groups already present in them, their hydrocarbon moieties are not usually subjected to chemical reactions due to the high reactivity of the functional groups relative to the inertness of the hydrocarbon chain. The dissociation of amino acid is [H$^+$] dependent.[21]

$$\mathrm{RCH(\overset{+}{N}H_3)COOH} \underset{+\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftarrows}}$$

$\mathrm{SH^+}$
Cation
In strongly
acidic medium

$$\mathrm{RCH(\overset{+}{N}H_3)COO^-} \underset{+\mathrm{H^+}}{\overset{-\mathrm{H^+}}{\rightleftarrows}} \mathrm{RCH(NH_2)COO^-} \qquad (5)$$

$\mathrm{S^\circ}$ $\mathrm{S^-}$
Zwitterion Anion
In strongly
alkaline medium

The most likely reaction mechanism which can satisfactorily explain the observed data is as shown in Scheme 1.

$$\mathrm{Mn^{3+}aq} + \mathrm{LH^+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{X^{2+}} + 2\mathrm{H^+} \qquad (6)$$

$$\mathrm{X^{2+}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \dot{\mathrm{L}} + \mathrm{Mn^{2+}} \qquad (7)$$

$$\dot{\mathrm{L}} + \mathrm{Mn^{3+}} \xrightarrow{k_3} \mathrm{Product} + \mathrm{Mn^{2+}}\ \text{(slow and rds)} \qquad (8)$$

Scheme 1.

LH$^+$ stands for mono protonated histidine, X for metal-substrate complex and $\dot{\mathrm{L}}$ for the free radical. Evidence for descrete metal-substrate complex formation is available in literature.[22]

The oxidative decay of Mn(III) takes the form

$$-\frac{\mathrm{d[Mn(III)]}}{\mathrm{d}t} = k_3[\mathrm{Mn(III)}]\,[\dot{\mathrm{L}}]. \qquad (9)$$

Applying steady state approximation for the free radical $\dot{\mathrm{L}}$, we get,

$$-\frac{\mathrm{d[Mn(III)]}}{\mathrm{d}t} = \frac{k_1k_2k_3[\mathrm{Mn(III)}]^2[\mathrm{LH^+}]}{k_{-1}k_{-2}[\mathrm{Mn(II)}][\mathrm{H^+}]^2 + k_{-1}k_3[\mathrm{Mn(III)}][\mathrm{H^+}]^2 + k_2k_3[\mathrm{Mn(III)}]}. \qquad (10)$$

Neglecting the last term of the denominator which is negligible in comparison to the first two because the [Mn(III)] is much smaller in comparison to [Mn(II)] and [H$^+$], one arrives at

$$-\frac{\mathrm{d[Mn(III)]}}{\mathrm{d}t} = \frac{k_1k_2k_3[\mathrm{Mn(III)}]^2[\mathrm{LH^+}]}{k_{-1}k_{-2}[\mathrm{Mn(II)}][\mathrm{H^+}]^2 + k_{-1}k_3[\mathrm{Mn(III)}][\mathrm{H^+}]^2}, \qquad (11)$$

or

$$k_{\mathrm{obsd}} = \frac{k_1k_2k_3[\mathrm{LH^+}]}{\{k_{-1}k_{-2}[\mathrm{Mn(II)}] + k_{-1}k_3[\mathrm{Mn(III)}]\}[\mathrm{H^+}]^2}. \qquad (12)$$

[Mn(III)] appearing in the denominator of the rate expression provides a convincing explanation for slight inverse dependence on Mn(III). Plot of k_{obsd} versus [amino acid] was linear passing through the origin showing order in amino acid as one. Plots k_{obsd} versus 1/[H$^+$] and 1/[H$^+$]^2 are shown in Fig. 3, the latter gives a better fit into the rate equation (12). A mechanism involving MnOH^{2+} is also suggested as shown in Scheme 2.

$$\mathrm{Mn^{3+}aq} + \mathrm{H_2O} \overset{K_h}{\rightleftarrows} \mathrm{MnOH^{2+}aq} + \mathrm{H^+aq} \qquad (13)$$

$$\mathrm{MnOH^{2+}} + \mathrm{LH^+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{X^{2+}} + \mathrm{H^+} \qquad (14)$$

$$\mathrm{X^{2+}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{Mn^{2+}} + \dot{\mathrm{L}} + \mathrm{H_2O} \qquad (15)$$

$$\mathrm{MnOH^{2+}} + \dot{\mathrm{L}} \xrightarrow{k_3} \mathrm{Mn^{2+}} + \mathrm{Products}\ \text{(slow and rds)} \qquad (16)$$

Scheme 2.

The rate of oxidation is given by

$$-\frac{\mathrm{d[Mn(III)]}}{\mathrm{d}t}=k_3[\mathrm{MnOH}^{2+}][\dot{\mathrm{L}}]. \tag{17}$$

Applying steady state approximation to $\dot{\mathrm{L}}$ and X.

$$-\frac{\mathrm{d[Mn(III)]}}{\mathrm{d}t}=\frac{K_\mathrm{h}^2k_1k_2k_3[\mathrm{Mn(III)}]^2[\mathrm{LH}^+]}{k_{-1}k_{-2}[\mathrm{Mn(II)}][\mathrm{H}^+]^2+K_\mathrm{h}k_{-1}k_3[\mathrm{Mn(III)}][\mathrm{H}^+]^2+k_1k_2k_3[\mathrm{Mn(III)}][\mathrm{H}^+]}. \tag{18}$$

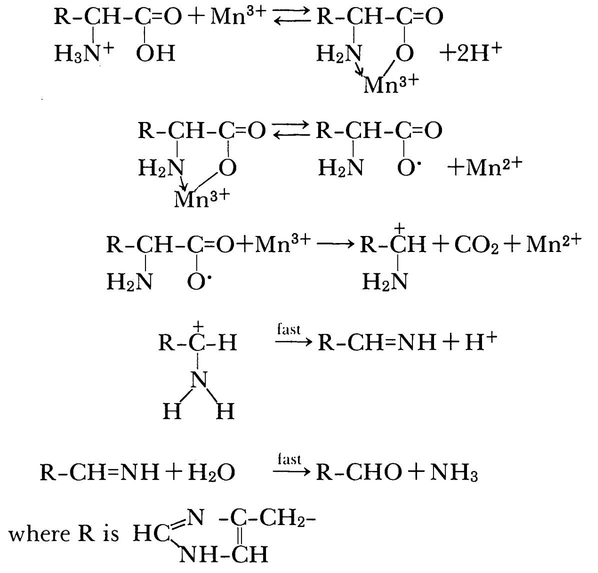
Neglecting the last term of the denominator as it is negligible in comparison to the first two.

$$-\frac{\mathrm{d[Mn(III)]}}{\mathrm{d}t}=\frac{K_\mathrm{h}^2k_1k_2k_3[\mathrm{Mn(III)}]^2[\mathrm{LH}^+]}{k_{-1}k_{-2}[\mathrm{Mn(II)}][\mathrm{H}^+]^2+K_\mathrm{h}k_{-1}k_3[\mathrm{Mn(III)}][\mathrm{H}^+]^2}, \tag{19}$$

or

$$k_\mathrm{obsd}=\frac{K_\mathrm{h}^2k_1k_2k_3[\mathrm{LH}^+]}{\{k_{-1}k_{-2}[\mathrm{Mn(II)}]+K_\mathrm{h}k_{-1}k_3[\mathrm{Mn(III)}]\}[\mathrm{H}^+]^2}. \tag{20}$$

The detailed mechanism of oxidation is shown in Scheme 3.



Scheme 3.

The oxidizing ion-substrate complex formed disproportionates to give the free radical, and as one more Mn^{3+} interacts oxidatively, the free radical undergoes decarboxylation and deamination process to give the reaction products.

The increase in rate due to the addition of SO_4^{2-} may be due to the presence of an additional equilibrium.

$$\mathrm{SO}_4^{2-}+\mathrm{H}^+ \rightleftarrows \mathrm{HSO}_4^-. \tag{21}$$

This brings down the effective $[\mathrm{H}^+]$ in the reaction mixture thereby increasing the rate of reaction.

The observed decrease of rate with decrease of dielectric constant of the medium (Table 4) in conformity with Laidler Eyring equation[23] for ion-ion interactions.

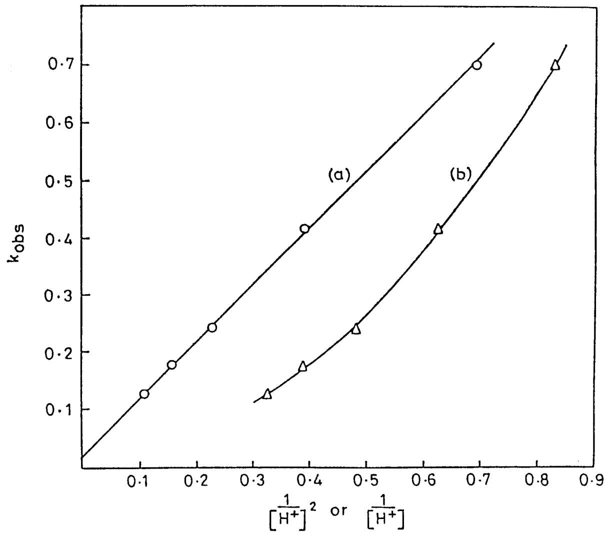


Fig. 3. Plot of (a) k_obsd versus $1/[\mathrm{H}^+]^2$, (b) k_obsd versus $1/[\mathrm{H}^+]$. Temp 322.5 K, $[\mathrm{Mn(III)}]_\mathrm{o}=3.0\times10^{-3}$ mol dm^{-3}, $[\mathrm{His}]_\mathrm{o}=4.0\times10^{-2}$ mol dm^{-3}, $\{[\mathrm{H_2SO_4}]+[\mathrm{NaHSO_4}]\}=3.545$ mol dm^{-3}, $[\mathrm{Mn(II)}]_\mathrm{o}=0.127$ mol dm^{-3}.

$$\ln k=\ln k_\infty-\frac{e^2}{2D\,k_\mathrm{B}T}\left[\frac{(Z_\mathrm{A}+Z_\mathrm{B})^2}{r_\ddagger}-\frac{Z_\mathrm{A}{}^2}{r_\mathrm{A}}-\frac{Z_\mathrm{B}{}^2}{r_\mathrm{B}}\right], \tag{22}$$

k_∞ is the rate constant in a medium of infinite dielectric constant, Z_A and Z_B are the charge on the ion A and B of radii r_A and r_B, D the dielectric constant of the medium, k_B=Boltzman constant, and $r_\ddagger$ is radius of the transition state.

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