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Oxidation of a Dipeptide by Electrolytically Generated Manganese(III) in Aqueous Sulfuric Acid Medium: A Kinetic and Mechanistic Study

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The kinetics of oxidation of the simplest dipeptide, glycylglycine (GG) by electrolytically generated manganese^{III}-sulfate in aqueous sulfuric acid has been studied. The rate shows first order dependence on [Mn^{III}] and a fractional order each on [GG] and [H$^+$]. The reduced product, Mn^{II} has no significant effect on the rate. An increase in ionic strength or decrease in dielectric constant of the medium increases the rate, while addition of complexing agents such as Cl^-, F^-, and $P_2O_7{}^{4-}$ decreases the rate. A Michaelis–Menten type mechanism has been suggested to explain the results. The coefficient of the rate-determining step has been evaluated as a function of temperature, by measuring the rates at different temperatures. The corresponding activation parameters have also been computed. Evidence for transient existence of a free radical reaction intermediate has been given. The kinetics of oxidation of GG have also been compared with those of the monomer amino acid, glycine.

Although extensive work has been reported on the kinetics of oxidation of several amino acids, using a variety of oxidants,[1—4] there is little information in the literature on the kinetics of oxidation of dipeptides. Glycylglycine (GG), the first member of the dipeptide series, has been oxidized by bromamine-T[5] and bromamine-B[6] in acid medium. Metal ions play a dominant role in living organisms. Amino acids and their polymers are the essential parts of biological systems. It is of interest to study the mechanisms of amino acid and peptide reactions with metal ions and hence this investigation. We report herein the kinetics and mechanism of oxidation of GG by Mn^{III} in aqueous sulfuric acid medium.

Experimental

Materials: Manganese^{III} sulfate was anodically generated from Mn^{II} sulfate in an electrolytic cell.[7,8] The electrolytic cell consisted of a 500-cm^3 beaker and pure antimony–lead alloy strips as electrodes. The ratio of anode to cathode area was maintained at 10 : 1 for higher current efficiency. Direct current was passed from a silicon rectifier unit. The electrolyte was a 0.50 mol dm^{-3} solution of Mn^{II} sulfate in 5.0 mol dm^{-3} H_2SO_4. Electrolysis was done at 6.0 V and at a current density of 2.0 mA cm^{-2} with constant stirring of the solution. The process was continued until the concentration of Mn^{III} reached 0.05 mol dm^{-3}, as further electrolysis results in a turbid suspension of sparingly soluble manganese^{II} sulfate.

The resulting clear cherry red solution contained an excess of [Mn^{II}] sufficient enough to suppress the disproportionation of Mn^{III}.[9]

$$2Mn^{III} \rightleftarrows Mn^{IV} + Mn^{II}$$

Although Mn^{III} appeared to be stable at least for a month at [H$^+$]>5.0 mol dm^{-3}, to be on the safe side Mn^{III} was prepared daily. Analysis of the solution for [Pb^{II}] by AAS showed that it was within the tolerance limit.

Chromatographically pure GG was used. The other reagents used were of analytical reagent grade. All solutions were prepared in double-distilled water.

Kinetic Measurements: The kinetic runs were made under pseudo first-order conditions ([GG]≫[Mn^{III}]). The reactions were started by the rapid addition of the required amounts of Mn^{III} solution (0.0005—0.005 mol dm^{-3}), equilibrated at a desired temperature, to a solution containing known amounts of GG, Mn^{III}, sulfuric acid, sodium perchlorate, and water, equilibrated at the same temperature. Progress of the reaction was monitored by measuring the absorbance of Mn^{III} ion at 490 nm (λ_{max}) as a function of time. It was confirmed that there was no contribution to the absorbance by other reagents at this wavelength. Allowing the mixture to react in the light path of the spectrophotometer continuously for a longer duration may induce a photochemical reaction. Therefore the desired samples were withdrawn from the reaction mixture at suitable times and added to 5.0 cm^3 of 2.0 mol dm^3 ice cold H_2SO_4. Absorbance of chilled solutions were immediately measured with a microprocessor-controlled Beckman model DU-6 UV-visible spectrophotometer.

The reaction was followed for at least two half-lives. The pseudo-first order rate constants were computed from log (Abs) versus time plots. The plots were linear even beyond 75% of the reaction (r=0.99). The rate constants obtained from the gradients of these plots were reproducible within ±3% error. Identical results were obtained from the plots of log [Mn^{III}] versus time when the reaction was monitored by the iodometric method.

Stoichiometry and Product Analysis: The product analysis was done with an excess of substrate in a reaction mixture containing [GG] (0.10 mol dm^{-3}) and [Mn^{III} (0.01 mol dm^{-3}) in 2.0 mol dm^{-3} H_2SO_4 at 40 °C, allowed to react completely. Aldehyde

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in the reaction mixture was extracted with ether and detected by the formation of 2,4-dinitrophenyl hydrazone, isolable in 90±2% yields. The hydrazone derivative was characterized by its melting point (164 °C) and by recording its IR spectrum. The aqueous layer was treated with NaOH. The precipitated $Mn(OH)_2$ was filtered off and NH_4^+ was detected in the filtrate with Nessler's reagent. Liberation of CO_2 from the reaction mixture was detected by the lime water test. The observed products correspond to 1 : 4 stoichiometry and may be represented by Eq. 1.

$$4Mn^{III} + H_2NCH_2CONHCH_2CO_2H + 3H_2O \rightarrow 4Mn^{II} + 2HCHO + 2CO_2 + 2NH_4^+ + 2H^+ \quad (1)$$

Under these kinetic conditions, the HCHO produced would be of the order of 0.004 mol dm^{-3}. It was observed that the oxidation of HCHO at these concentrations is negligible.

Results

Kinetics of oxidation of GG by Mn^{III} was investigated under varying conditions of [reactant], [Mn^{II}], [H$^+$], solvent composition, and temperature (Tables 1, 2, 3, and 4, Figs. 1 and 2).

Dependence of Rate on [Mn^{III}] and [GG]: Under pseudo-first order conditions {[GG]≫[Mn^{III}]}, plots of log [Mn^{III}] versus time were linear at least for two half-lives and pseudo-first order rate constants were unaffected by the changes in [Mn^{III}]$_o$, establishing first order kinetics in [Mn^{III}] (Table 1). At constant [Mn^{III}], [Mn^{II}], and [H$^+$], the rate increased with increases in [GG]$_o$ with a fractional order kinetics. Further, the plot of k_{obsd} versus [GG] attained the limiting value, while the double reciprocal plot of 1/k_{obsd} versus 1/[GG] was linear, indicating the operation of Michaelis–Menten type kinetics.

Table 1. Pseudo-First Order Rate Constants (k_{obsd}) for the Oxidation[a)]

$10^3\times$[Mn^{III}]$_o$ mol dm^{-3}	$10^2\times$[GG]$_o$ mol dm^{-3}	$10\times$[Mn^{II}]$_o$ mol dm^{-3}	$10^5\times k_{obsd}$ s^{-1}
0.5	2.0	1.2	6.9
1.0	2.0	1.2	7.0
2.0	2.0	1.2	6.9
4.0	2.0	1.2	7.0
6.0	2.0	1.2	7.0
2.0	1.0	1.2	4.4
2.0	4.0	1.2	12.1
2.0	6.0	1.2	16.1
2.0	2.0	0.3	6.7
2.0	2.0	0.6	6.8
2.0	2.0	1.8	7.0

a) [H_2SO_4] = 2.0 mol dm^{-3}, I = 6.51 mol dm^{-3}, and temperature=313 K. (The rate constants are reproducible within ±3% error).

Dependence of Rate on [H$^+$]: Kinetic measurements were made in H_2SO_4–$NaHSO_4$ solutions of different [H$^+$]. The effective hydrogen ion concentrations were then read from the standard curve of [H_2SO_4] versus [H$^+$] prepared from the results of Kemp and waters.[10)] The rate increased with increase in [H$^+$] with a fractional order kinetics.

Effects of Varying Ionic Strength and Added Mn^{II}: The reactions were studied at [H_2SO_4]=2.0 mol dm^{-3}. The total ionic strength of the medium amounted to 6.51 mol dm^{-3}. It was therefore varied in the range 6.51—9.01 mol dm^{-3} by adding varying amounts of 5.0 mol dm^{-3} $NaClO_4$ (Table 2). The rate increased with increases in ionic strength, showing a positive salt effect. Variation in [Mn^{II}] had little effect on the rate of oxidation.

Effects of Added Salts: At fixed [reactant], [H_2SO_4], ionic strength, and temperature, the rate decreased with increased addition of SO_4^{2-}, Cl^-, F^-, and $P_2O_7^{4-}$ (Table 3).

The rates were measured at different temperatures (308—323 K) under varying [GG] (0.01—0.06 mol dm^{-3}). Activation parameters were then computed from the constant of the rate-limiting step at different temperatures as described under discussion.

Polymerization Studies: It was observed that the reaction mixture initiate polymerization of monomers like acrylonitrile in less than 15 min and methyl methacrylate in less than 40 min. Since none of the reacting species, either [GG] or [Mn^{III}] does this when added separately to an aqueous

Table 3. Effect of Solvent Composition and [SO_4^{2-}] on the Rate[a)]

$10\times$[SO_4^{2-}] mol dm^{-3}	$10^5\times k_{obsd}$ s^{-1}	[CH_3CO_2H] % v/v	$10^5\times k_{obsd}$ s^{-1}
0	10.5	10	10.9
3	9.3	20	15.0
6	8.1	30	20.0
8	7.5	40	26.9

a) $10^3\times$[Mn^{III}]$_o$ = $10^2\times$[GG]$_o$ = 2.0 mol dm^{-3}, [Mn^{II}]=0.12 mol dm^{-3}, [H_2SO_4]=2.0 mol dm^{-3}, I=9.01 mol dm^{-3}, temp=313 K. (The rate constants are reproducible within ±3% error).

Table 2. Effect of Ionic Strength and Complexing Agents: Cl^-, F^-, and $P_2O_7^{4-}$ on the Rate[a)]

I mol dm^{-3}	$10^5 k_{obsd}$ s^{-1}	$10\times$[Cl^-] mol dm^{-3}	$10^5\times k_{obsd}$ s^{-1}	$10\times$[F^-] mol dm^{-3}	$10^5\times k_{obsd}$ s^{-1}	$10^2\times$[$P_2O_7^{4-}$] mol dm^{-3}	$10^5\times k_{obsd}$ s^{-1}
6.51	7.0	0.05	3.78	0.5	3.8	2.5	5.2
7.21	8.7	1.00	3.41	1.0	3.2	5.0	4.8
8.01	9.4	2.00	3.17	2.0	2.3	7.5	4.3
9.01	10.5	4.00	2.72	4.0	2.0	10.0	3.8

a) $10^3\times$[Mn^{III}]$_o$=$10^2\times$[GG]$_o$=2.0 mol dm^{-3}, [Mn^{II}]=0.12 mol dm^{-3}, [H_2SO_4]=2.0 mol dm^{-3}, I=7.21 mol dm^{-3}, temp=313 K. (The rate constants are reproducible within ±3% error).

mixture of these monomers, it was concluded that the redox steps produce free radicals, which are capable of inducing polymerization.

Discussion

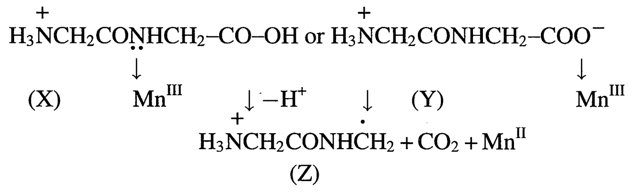
Under these experimental conditions of aqueous sulfuric acid, Mn^{III} aq is the most likely reacting species.[11—13]

Glycylglycine exists in the following protonation equilibrium in acidic solutions.[14]

$$\overset{+}{H_3N}CH_2CONHCH_2COO^- + H^+ \rightleftarrows \overset{+}{H_3N}CH_2CONHCH_2CO_2H$$

$$\text{(Zwitterion } S^\circ\text{)} \qquad \qquad \text{(Cation } SH^+\text{)} \qquad (2)$$

The zwitterion and the cation are the likely reactive species of GG. In acid medium, Mn^{III} can interact with GG in the following step to produce the intermediate free radical, $\overset{+}{H_3N}CH_2CONH\dot{C}H_2$.



$$\begin{array}{ccc} \overset{+}{H_3N}CH_2CO\underset{\cdot\cdot}{N}HCH_2\text{–}CO\text{–}OH & \text{or} & \overset{+}{H_3N}CH_2CONHCH_2\text{–}COO^- \\ \downarrow & & \downarrow \\ \text{(X)} \quad Mn^{III} \quad \downarrow -H^+ & \downarrow \quad \text{(Y)} & Mn^{III} \\ & \overset{+}{H_3N}CH_2CONH\dot{C}H_2 + CO_2 + Mn^{II} & \\ & \text{(Z)} & \end{array}$$

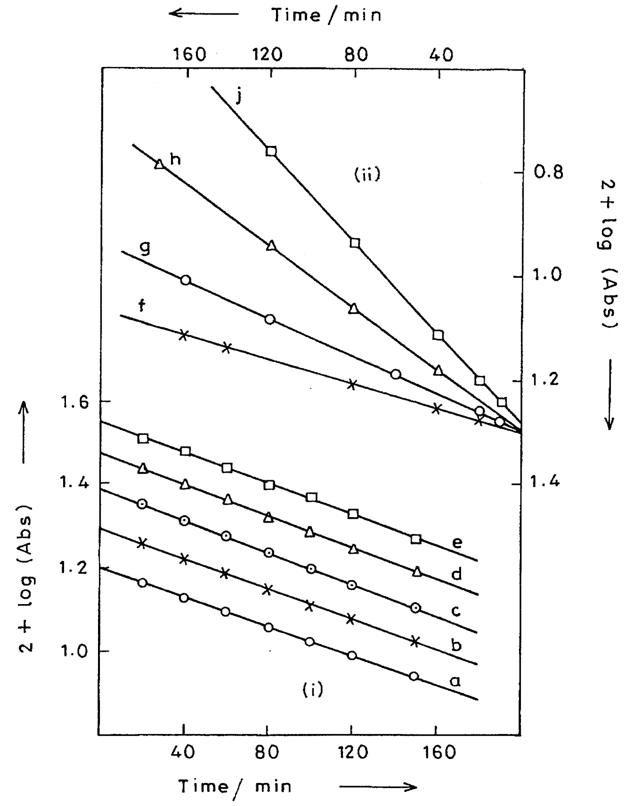


Fig. 1. Plots of $\log[Mn^{III}]$ versus time. $[H_2SO_4]=2.0$ $mol\,dm^{-3}$, $[Mn^{II}]=0.12$ $mol\,dm^{-3}$, $I=6.51$ $mol\,dm^{-3}$, and temperature=313 K. (i) $10^2\times[GG]=2.0$ $mol\,dm^{-3}$, $10^3\times[Mn^{III}]_o/mol\,dm^{-3}=0.05$ (a), 1.0 (b), 2.0 (c), 4.0 (d), 6.0 (e). (ii) $10^3\times[Mn^{III}]_o=2.0$ $mol\,dm^{-3}$, $10^2\times[GG]_o/mol\,dm^{-3}=1.0$ (f), 2.0 (g), 4.0 (h), 6.0 (j).

where X and Y are the metal-substrate complexes. Evidence for discrete metal-substrate complex formation is available in the literature.[15]

Glycylglycine is not expected to undergo hydrolysis before oxidation, as drastic reaction conditions are needed to hydrolyze a dipeptide bond.[16,17] For example, Martin[16] has studied the mechanism of hydrolysis of GG in aqueous acetic acid–perchloric acid mixtures at 120 °C. Synge[17] has used equal volumes of glacial acetic acid and 10 M HCl to cause hydrolysis ($M=mol\,dm^{-3}$). Hence GG is expected to be oxidized rather than hydrolyzed under the conditions in this study.

The observed kinetics of first-order in $[Mn^{III}]$, and a fractional order each in [GG] and $[H^+]$ may therefore be explained by a Michaelis–Menten type mechanism like those shown in Scheme 1 or Scheme 2 by considering the two reactive forms of substrate. The rate law in accordance with Scheme 1 is given by Eq. 3.

$$\frac{d[Mn^{III}]}{dt} = k_3[X] \qquad (3)$$

Applying a steady state approximation to the intermediate X, we have

$$\frac{-d[X]}{dt} = k_2\{[Mn^{III}]_o - [X]\}[SH^+] - k_{-2}[X] - k_3[X] = 0$$

Where $[Mn^{III}]=[Mn^{III}]_o-[X]$ and $[SH^+]\approx[SH^+]_o$ or

$$[X] = \frac{k_2[Mn^{III}]_o[SH^+]}{k_{-2}+k_3+k_2[SH^+]} \qquad (4)$$

k_3 in the denominator can be ignored compared with the other terms. Equation 4 therefore takes the form,

$$[X] = \frac{k_2[Mn^{III}]_o[SH^+]}{k_{-2}+k_2[SH^+]} = \frac{K_2[Mn^{III}]_o[SH^+]}{1+K_2[SH^+]} \qquad (5)$$

Introducing Eq. 5 into Eq. 3, we have

$$\begin{array}{rcll} S^\circ + H^+ & \overset{K_1}{\rightleftarrows} & SH^+ & \text{(fast)} \\ SH^+ + Mn^{III} & \overset{K_2}{\rightleftarrows} & X & \text{(fast)} \\ X & \overset{k_3}{\rightarrow} & \text{Products} & \text{(slow)} \end{array}$$

Scheme 1.

$$\begin{array}{rcll} SH^+ + H^+ + Mn^{III} & \overset{K_4}{\rightleftarrows} & X^\bullet & \text{(fast)} \\ X^\bullet & \overset{k_3}{\rightarrow} & \text{Products} & \text{(slow)} \end{array}$$

Scheme 2.

Table 4. Effect of $[H^+]$ on the Rate[a)]

$\frac{[H_2SO_4]}{mol\,dm^{-3}}$	$\frac{[H^+]}{mol\,dm^{-3}}$	$\frac{10^4\times k_{obsd}}{s^{-1}}$
1.50	1.62	3.18
2.00	2.04	3.42
2.50	2.52	3.72
3.00	2.98	4.01

a) $10^3\times[Mn^{III}]_o=10^2\times[GG]_o=2.0$ $mol\,dm^{-3}$, $[Mn^{II}]=0.12$ $mol\,dm^{-3}$, $[H_2SO_4]=2.0$ $mol\,dm^{-3}$, $[H_2SO_4+NaHSO_4]=3.545$ $mol\,dm^{-3}$, temp=323 K. (The rate constants are reproducible within ±3% error).

$$\frac{-\mathrm{d}[\mathrm{Mn^{III}}]_o}{\mathrm{d}t} = \frac{K_2k_3[\mathrm{Mn^{III}}]_o[\mathrm{SH^+}]}{1+K_2[\mathrm{SH^+}]} \tag{6}$$

Equation 6 may be rearranged as,

$$-\frac{1}{[\mathrm{Mn^{III}}]_o}\frac{\mathrm{d}[\mathrm{Mn^{III}}]}{\mathrm{d}t} = \frac{K_2k_3[\mathrm{SH^+}]}{1+K_2[\mathrm{SH^+}]} \tag{7}$$

But we have,

$$-\frac{1}{[\mathrm{Mn^{III}}]_o}\frac{\mathrm{d}[\mathrm{Mn^{III}}]}{\mathrm{d}t} \approx -\frac{\mathrm{d}\ln[\mathrm{Mn^{III}}]}{\mathrm{d}t} = k_{\mathrm{obsd}} \tag{8}$$

Equation 7 therefore takes the form,

$$k_{\mathrm{obsd}} = \frac{K_2k_3[\mathrm{SH^+}]}{1+K_2[\mathrm{SH^+}]} \tag{9}$$

We have from the first step of Scheme 1,

$$[\mathrm{SH^+}] = K_1[\mathrm{S}][\mathrm{H^+}].$$

Equation 9 therefore takes the form,

$$k_{\mathrm{obsd}} = \frac{K_1K_2k_3[\mathrm{S}][\mathrm{H^+}]}{1+K_1K_2[\mathrm{S}][\mathrm{H^+}]} \tag{10}$$

$$\frac{1}{k_{\mathrm{obsd}}} = \frac{1}{K_1K_2k_3[\mathrm{S}]}\frac{1}{[\mathrm{H^+}]} + \frac{1}{k_3} \tag{11}$$

The plots of $1/k_{\mathrm{obsd}}$ versus 1/[GG] (Fig. 2, r=0.99) and $1/k_{\mathrm{obsd}}$ versus $1/[\mathrm{H^+}]$ (r=0.98) were linear in accordance with the rate law Eq. 11. The reciprocal of the intercept of the former plot gave k_3.

Further, GG concentrations were varied at different temperatures (308—323 K) and the constant k_3 was calculated at each temperature [Table 5]. Activation parameters corresponding to k_3 have been evaluated from the plots of $\log k_3$ versus $1/T$ and $\log(k_3/T)$ versus $1/T$. The values of E_a (kJ mol^{-1}), A (s^{-1}), $\Delta H^{\neq}$ (kJ mol^{-1}), $\Delta S^{\neq}$ (J K^{-1} mol^{-1}) and $\Delta G^{\neq}$ (kJ mol^{-1}) are 99.3, 3.3×10^{13}, 95.5, 1.2, and 95.1, respectively.

The related rate laws in accordance with Scheme 2 are given by Eqs. 12, 13, and 14.

$$\frac{-\mathrm{d}[\mathrm{Mn^{III}}]}{\mathrm{d}t} = \frac{K_4k_3[\mathrm{Mn^{III}}]_o[\mathrm{SH^+}][\mathrm{H^+}]}{1+K_4[\mathrm{SH^+}][\mathrm{H^+}]} \tag{12}$$

or

$$k_{\mathrm{obsd}} = \frac{K_4k_3[\mathrm{SH^+}][\mathrm{H^+}]}{1+K_4[\mathrm{SH^+}][\mathrm{H^+}]} \tag{13}$$

or

$$\frac{1}{k_{\mathrm{obsd}}} = \frac{1}{K_4k_3}\frac{1}{[\mathrm{SH^+}]}\frac{1}{[\mathrm{H^+}]} + \frac{1}{k_3} \tag{14}$$

Table 5. Coefficient of the Rate Limiting Step and the Equilibrium Constant at Different Temperatures[a]

Temperature	$10^4\times k_3$	K_4
K	s^{-1}	dm^6 mol^{-2}
308	5.0	2.00
313	8.9	2.02
318	16.7	2.04
323	25.0	2.12

a) Please see text. (The computed values are reproducible within ±3% error).

The rate law Eq. 14 is also in accordance with the linearity of the plots, $1/k_{\mathrm{obsd}}$ versus $1/[\mathrm{SH^+}]$ (if $[\mathrm{GG}]=[\mathrm{SH^+}]$) and $1/k_{\mathrm{obsd}}$ versus $1/[\mathrm{H^+}]$. The constant K_4 was calculated from the slope of the former plot by inserting the value of k_3 and $[\mathrm{H^+}]$ (Table 5).

Although the observed results may be explained by either Scheme 1 or Scheme 2 and the related rate laws, Scheme 2 is the most probable one. Under these acidic conditions (2.0 mol dm^{-3} H_2SO_4), it is likely that most of the GG will be in the protonated form. Hence the positive dependance observed in $[\mathrm{H^+}]$ may be due to its catalytic effect instead of its involvement in the protonation equilibrium. So it is most likely that the oxidation of GG goes through the mechanism shown in Scheme 2 under these experimental conditions. We also have

$$\mathrm{H_2SO_4} \overset{K_5}{\rightleftarrows} \mathrm{HSO_4^-} + \mathrm{H^+}$$

$$[\mathrm{H^+}] = K_5[\mathrm{H_2SO_4}]/[\mathrm{HSO_4^-}] \tag{15}$$

Equation 13 therefore takes the form,

$$k_{\mathrm{obsd}} = \frac{K_4K_5k_3[\mathrm{SH^+}][\mathrm{H_2SO_4}]}{[\mathrm{HSO_4^-}]+K_4K_5[\mathrm{SH^+}][\mathrm{H_2SO_4}]} \tag{16}$$

Equation 16 explains the observed rate dependence on $[\mathrm{H_2SO_4}]$ and $[\mathrm{HSO_4^-}]$.

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

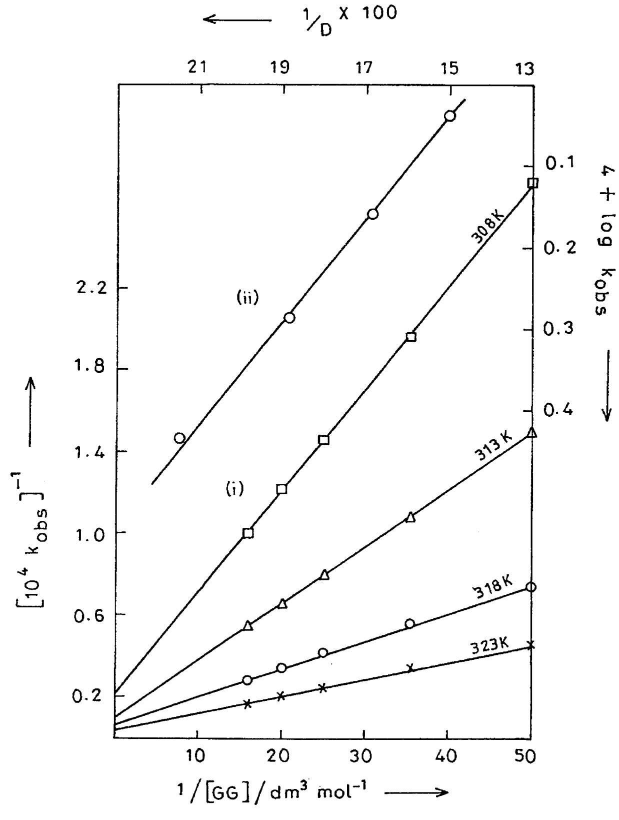
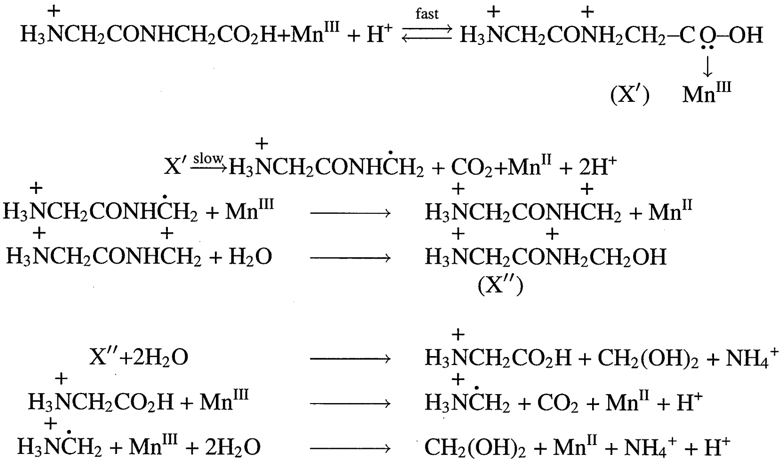


Fig. 2. Plots of (i) $1/k_{\mathrm{obsd}}$ versus 1/[GG] (ii) $\log k_{\mathrm{obsd}}$ versus $1/D$. $10^3\times[\mathrm{Mn^{III}}]_o=[\mathrm{H_2SO_4}]$=2.0 mol dm^{-3}. $[\mathrm{Mn^{II}}]$=0.12 mol dm^{-3}. (i) Aqueous, I=6.51 mol dm^{-3}. (ii) $10^2\times[\mathrm{GG}]$= 2.0 mol dm^{-3}, I=9.01 mol dm^{-3}, temp=313 K.



$$\overset{+}{H_3N}CH_2CONHCH_2CO_2H+Mn^{III} + H^+ \overset{fast}{\rightleftharpoons} \overset{+}{H_3N}CH_2CO\overset{+}{N}H_2CH_2\text{–}C\underset{\underset{Mn^{III}}{\downarrow}}{\ddot{O}}\text{–}OH \quad (X')$$

$$X' \xrightarrow{slow} \overset{+}{H_3N}CH_2CONH\dot{C}H_2 + CO_2 + Mn^{II} + 2H^+$$

$$\overset{+}{H_3N}CH_2CONH\dot{C}H_2 + Mn^{III} \longrightarrow \overset{+}{H_3N}CH_2CONH\overset{+}{C}H_2 + Mn^{II}$$

$$\overset{+}{H_3N}CH_2CONH\overset{+}{C}H_2 + H_2O \longrightarrow \underset{(X'')}{\overset{+}{H_3N}CH_2CO\overset{+}{N}H_2CH_2OH}$$

$$X''+2H_2O \longrightarrow \overset{+}{H_3N}CH_2CO_2H + CH_2(OH)_2 + NH_4^+$$

$$\overset{+}{H_3N}CH_2CO_2H + Mn^{III} \longrightarrow \overset{+}{H_3N}\dot{C}H_2 + CO_2 + Mn^{II} + H^+$$

$$\overset{+}{H_3N}\dot{C}H_2 + Mn^{III} + 2H_2O \longrightarrow CH_2(OH)_2 + Mn^{II} + NH_4^+ + H^+$$

Where $CH_2(OH)_2$ is the hydrated formaldehyde.
Scheme 3.

$$SO_4^{2-} + H^+ \overset{K_6}{\rightleftarrows} HSO_4^- \quad (17)$$

This brings down the effective $[H^+]$ in the reaction mixture and thereby decreases the rate of reaction.

A detailed mechanism of oxidation of GG is shown in Scheme 3.

Considering the charge distribution in the transition state, Laidler and Eyring[18] deduced Eq. 18 for the reaction between two ions A and B with charges Z_A and Z_B.

$$\ln k_D = \ln k_o + \frac{e^2}{2k_BT}\left\{\frac{1}{D} - 1\right\}\left[\frac{Z_A^2}{r_A} + \frac{Z_B^2}{r_B} - \frac{(Z_A+Z_B)^2}{r_{\neq}}\right] \quad (18)$$

Where k_D is the rate constant in a medium of unit dielectric constant, r_A and r_B are the radii of the ions A and B, respectively, and $r_{\neq}$ is that of the transition state.

In this case for the reaction involving two positive ions, it is likely that the radius $r_{\neq}$ is bigger than that of r_A+r_B, which makes the value of the terms in the parentheses positive. Under these circumstances, the rate constants would be higher in a medium of lower dielectric constant. The observed solvent effect is in conformity with these predictions. Further the plot of $\log k_D$ versus $1/D$ was linear with a positive slope (Fig. 2, r=0.99).

The observed decrease in rate by the added complexing agents like pyrophosphate, fluoride, and chloride ions may be attributed to the displacement of the coordinated SO_4^{2-} ligand due to the establishment of a new Mn^{III}-Mn^{II} couple with $P_2O_7^{4-}$, Cl^-, and F^- as ligands. The latter redox complexes have lower redox potentials and thereby decrease the rate. This also indicates that Mn^{III} is the reactive species under these conditions.

It was thought worthwhile to compare the mechanism of oxidation of GG with that of glycine (Gly) by manganese^{III}-sulfate under similar conditions. Oxidation of glycine shows a second order kinetics in $[Mn^{III}]$, first order in [Gly], and inverse first order each in $[Mn^{II}]$ and $[H^+]$,[19] as compared to first order kinetics in $[Mn^{III}]$, fractional order each in [GG] and $[H^+]$, and negligible dependence of the rate on $[Mn^{II}]$ for the oxidation of GG. Further, the rate of oxidation of Gly ($4.2\ mol\ dm^{-3}\ s^{-1}$) is nearly 10 times faster than that of GG. Glycylglycine (pK_1 3.2 and pK_2 8.2) is weaker both as an acid and as a base with compared to glycine (pK_1 2.4 and pK_2 9.8). The changes may be due to the increased distance between the functional groups and consequently weaker electrostatic affects. Hence the oxidation of dipeptide is expected to be slower than the monomer.

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