Preparation of Manganic Sulphate in Sulphuric Acid & Kinetics of Its Reaction with Threonine

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Spectroscopic studies have been made on the equilibrium $Mn(II) + Mn(IV) \rightleftharpoons 2Mn(III)$ in the presence of excess $[Mn(II)]$ and $[H^+]$. Results show that when $[Mn(II)]$ is twice that of $[Mn(IV)]$, $Mn(IV)$ is quantitatively converted into $Mn(III)$ and this principle can be used to prepare manganic sulphate. Oxidation of threonine by $Mn(III)$ follows second order kinetics in [oxidant], first order in [substrate], inverse first order in $[Mn(II)]$ and inverse second order in $[H^+]$. The reaction shows positive salt effect. Suitable mechanism is proposed and discussed based on the kinetic results.

A number of kinetic reports are available on the use of Mn(III) perchlorate in perchloric acid and Mn(III) acetate in acetic acid[1] as oxidants. However, manganic sulphate has been sparsely used as an oxidant because of the difficulty and danger of explosion involved in its preparation[2]. In this paper we report a simple and safe method of preparation of manganic sulphate in sulphuric acid. As a follow up of this preparation, the kinetics of oxidation of threonine by manganic sulphate in sulphuric acid is also studied.

Materials and Methods

Manganese (IV) sulphate in $8 \, \text{mol dm}^{-3}$ sulphuric acid was prepared by the method of Mandal[3] and estimated by iodometry. Threonine (Loba-Chemie) was used as such. All other reagents used were of AR grade. Ionic strength of the medium was maintained using sodium sulphate. UV-visible spectra were recorded on a Perkin-Elmer 402 UV-VIS spectrophotometer equipped with a thermostated cell.

Manganese (III) sulphate was prepared by mixing requisite amounts of manganese (IV) sulphate, sulphuric acid and Mn(II) sulphate and then diluted with water to give the required concentration. Since precipitation was noticed, probably due to MnO_2, when $[H^+] < 4 \, \text{mol dm}^{-3}$, $[H^+]$ was kept preferably above $4 \, \text{mol dm}^{-3}$. For kinetic studies Mn(III) sulphate was prepared in $4 \, \text{mol dm}^{-3} \, H_2SO_4$ and estimated.

The reaction was followed iodometrically upto well over 50% by monitoring the concentration of unreacted manganic sulphate in the reaction mixture the temperature of which was maintained with an accuracy of $\pm 0.1°C$. The pseudo-second order rate constants (k_{obs}) were determined from the slopes of $1/[Mn(III)]$, versus time plots and were reproroducible within $\pm 5\%$.

The stoichiometry of the reaction was determined by mixing Mn(III) and threonine in various proportions under the conditions $[H^+] > [\text{threonine}]$, $[Mn(III)]$ and estimating the unreacted Mn(III) after 24 hr. The stoichiometry can be represented by Eq. (1)

$$\text{Threonine} + 2Mn(III) \rightarrow$$
$$\text{2-hydroxypropanal} + 2Mn(II) + CO_2 + NH_3 \quad \dots (1)$$
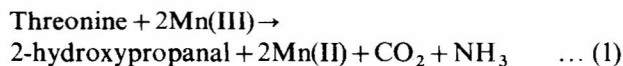
Evolution of CO_2 and NH_3 were detected by lime water and Nessler's reagent respectively. The product was confirmed as lactic aldehyde by comparison of its physical constants and by direct comparison of its derivatives with authentic samples. Further oxidation of lactic aldehyde was noticed on keeping the reaction mixture over a long time

## Results and Discussion

Preparation of Mn(III) sulphate

The following disproportionation equilibrium (2) has been recognised by Selim and Ligave[4]

$$2Mn(III) \rightleftharpoons Mn(IV) + Mn(II) \quad \dots (2)$$
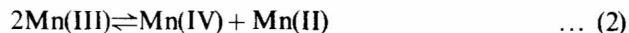
When the concentration of Mn(II) is twice that of Mn(IV) at constant $[H^+]$, an absorption peak occurs at 500 nm and the intensity of this peak remains constant even for a 10-fold change in $[Mn(II)]$. At constant $[Mn(II)]$ and $[Mn(IV)]$, there is no observable change in the intensity, which remains constant till $[H^+] = 4 \, \text{mol dm}^{-3}$. At $[H^+]$ less than $4 \, \text{mol dm}^{-3}$ the absorption peak shifts towards UV region and precipitation occurs. Similarly at constant $[H^+]$ and $[Mn(II)]$ change in $[Mn(IV)]$ is accompanied by a parallel change in the intensity of the absorption peak. This intensity obeys Beer's law. The above results show that in equilibrium (2), when $[Mn(II)]$ is in two-fold excess over $[Mn(IV)]$, all $Mn(IV)$ is

completely converted into Mn(III). This is in accordance with earlier report[4] wherein the equilibrium constant for the disproportionation reaction (2) is reported to be very small, nearly 10^{-3}. Therefore when $[Mn(II)] > [Mn(IV)]$, $[Mn(III)]$ can be calculated if the backward path in Eq. (2) is considered. This fact can be used for the preparation of manganic sulphate in sulphuric acid for kinetic studies since most of the kinetics are carried out in the presence of excess $[Mn(II)]$ in order to suppress the forward path in the disproportionation reaction (2).

Molar extinction coefficient observed for manganic sulphate in sulphuric acid is 105 ± 10. Although the observed value is high for a d-d transition, this value is exactly equal to that reported by Wells and Davies[5] for manganic perchlorate in perchloric acid at $\mu = 4.0 \, mol \, dm^{-3}$ and $25°C$ ($\lambda_{max} = 470 \, nm$). They attributed this high value of ε to the d-d mixing and also to the presence of hydrolysed species of Mn(III) as $Mn(OH)^{2+}$ produced in reaction (3)

$$Mn_{aq}^{3+} \overset{K_h}{\rightleftharpoons} Mn(OH)_{aq}^{2+} + H_{aq}^+ \qquad \ldots (3)$$
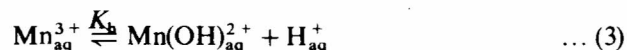
Kinetic results

The disappearance of Mn(III) followed perfect second order kinetics upto 50% of the reaction. The second order rate constants at various $[Mn(III)]$ show that the rate is directly proportional to $[Mn(III)]^2$ (Table 1).

The plot of k_{obs} versus [threonine] is linear passing through the origin showing the order in [threonine] as one.

At constant [threonine] and $[Mn(II)]$, a plot of k_{obs} versus $[H^+]^2$ is linear passing through origin indicating the possibility of interaction between some reacting intermediate and H^+.

The observed rate constant decreases with increase in $[Mn(II)]$ (Table 1). The plot of k_{obs} versus $1/[Mn(II)]$ is linear passing through the origin. These observations show that the rate of disappearance of Mn(III) obeys Eq. (4).

$$-\frac{d[Mn(III)]}{dt} = constant \frac{[Mn(III)]^2 [threonine]}{[Mn(II)][H^+]^2} \ldots (4)$$

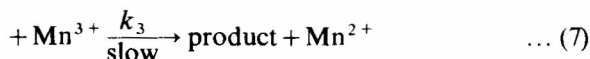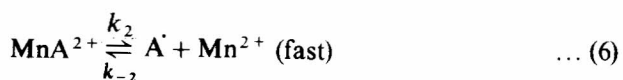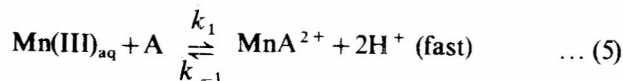Generally amino acids are in equilibrium with its monoprotonated form in acid solutions and under our

Table 1—Pseudo-second Order Rate Constants Under Varying Conditions

[Temp. $= 31°$]

[Threonine] (mol dm^{-3})	$[Mn^{3+}] \times 10^3$ (mol dm^{-3})	$[Mn^{2+}] \times 10^2$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	μ (mol dm^{-3})	k_{obs} (dm^3 mol^{-1} min^{-1})
0.015	2.0	2.0	1.612	2.5	22.0*
0.020	2.0	2.0	1.612	2.5	33.0*
0.025	2.0	2.0	1.612	2.5	40.5*
0.030	2.0	2.0	1.612	2.5	52.0*
0.035	2.0	2.0	1.612	2.5	59.0*
0.040	2.0	2.0	1.612	2.5	64.0*
0.020	1.0	2.0	2.014	3.1	31.5
0.020	1.5	2.0	2.014	3.1	31.0
0.020	2.0	2.0	2.014	3.1	31.0
0.020	2.0	2.0	1.612	2.9	41.0
0.020	2.0	2.0	1.612	3.3	60.0
0.020	2.0	2.0	2.014	3.1	31.0
0.020	2.0	2.0	1.772	3.1	45.0
0.020	2.0	2.0	1.611	3.1	53.5
0.020	2.0	2.0	1.450	3.1	68.5
0.020	2.0	4.5	1.612	3.7	47.0
0.020	2.0	7.0	1.612	3.7	32.5
0.020	2.0	9.5	1.612	3.7	25.0
0.020	2.0	12.0	1.612	3.7	18.0
0.020	2.0	17.0	1.612	3.7	13.0
0.015	2.0	7.0	1.612	3.7	21.4
0.020	2.0	7.0	1.612	3.7	30.9
0.025	2.0	7.0	1.612	3.7	36.6
0.030	2.0	7.0	1.612	3.7	42.9
0.035	2.0	7.0	1.612	3.7	49.4
0.040	2.0	7.0	1.612	3.7	57.2
0.020	2.0	7.0	1.450	3.7	35.3
0.020	2.0	7.0	1.772	3.7	22.8
0.020	2.0	7.0	2.014	3.7	17.3

* temp $= 28°$

experimental conditions threonine is almost entirely protonated[6]. In strong acid solutions, presence of more than one species of Mn(II) due to hydrolysis has already been proved[5,7]. Therefore the active form of the oxidant may be $Mn(III)_{aq}$ or the hydrolysed species of Mn(III). Considering the experimental conditions and the observations the most probable mechanistic pathway will be as given in Scheme 1.

$$Mn(III)_{aq} + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MnA^{2+} + 2H^+ \text{ (fast)} \qquad \ldots (5)$$

$$MnA^{2+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^{\cdot} + Mn^{2+} \text{ (fast)} \qquad \ldots (6)$$

$$+ Mn^{3+} \xrightarrow[\text{slow}]{k_3} \text{product} + Mn^{2+} \qquad \ldots (7)$$

Scheme 1

In Scheme 1, A stands for the monoprotonated threonine and $A^{\cdot}$ for the free radical.

In literature[8,9] a second order dependence on $[Mn^{3+}]$ and an inverse first order dependence on $[Mn^{2+}]$ have been explained by suggesting the involvement of a number of rapid equilibria prior to the rate-determining step. Since a high concentration of Mn^{2+} is always maintained, the concentration of radical A becomes too low making reaction (7) rate-determining.

Assuming a steady state approximation for $[A^{\cdot}]$, we get

$$\text{Rate} = \frac{k_1 k_2 k_3}{k_{-1}}$$
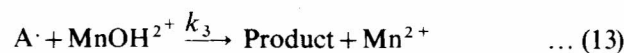$$\times \frac{[A][Mn(III)]^2}{(k_{-2}[H^+]^2[Mn(II)] + k_3[Mn^{3+}][H^+]^2) + k_2 k_3[Mn^{3+}]} \qquad \ldots (8)$$
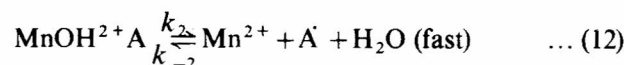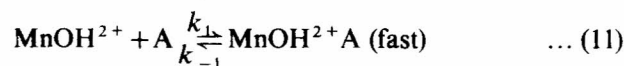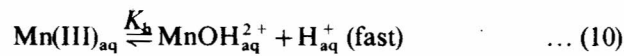
Neglecting the last two terms of the denominator of Eq. (8), we get Eq. (9).

$$\text{Rate} = \frac{k_1 k_2 k_3}{k_{-1}k_{-2}} \frac{[A][Mn(III)]^2}{[H^+]^2[Mn(II)]} \qquad \ldots (9)$$

Equation (9) explains the observed kinetics. The values of $k_1 k_2 k_3/k_{-1}k_{-2}$ obtained at $\mu = 3.7$ mol dm^{-3} and 31°C are 259, 266 and 280 from the variations of [threonine], $[H^+]$ and [Mn(II)] respectively.

In the oxidation of glycine by Mn(III) perchlorate in $HClO_4$, Varadarajan *et al.*[7] observed that at 45°C the rate is proportional to $[H^+]^{-1}$ whereas at 55 and 65° the rate is proportional to $[H^+]^{-2}$. They explained this by suggesting that at 45° the active oxidant speceis is $Mn(OH)^{2+}$ produced by the hydrolysis of Mn(III) (see Eq. 3) whereas at 55 and 65° the dihydroxo species, produced by the further hydrolysis of $Mn(OH)^{2+}_{aq}$ to give $Mn(OH)^+_{2aq} + H^+$ is the active one. Under our experimental conditions the reaction involving the oxidant species $Mn(OH)^+_2$ can be eliminated since a high $[H^+]$ is always maintained throughout the reaction. A mechanism involving $Mn(OH)^{2+}$ to explain the observed fact can be incorporated, as in Scheme 2, since a combined role of Mn^{3+} and $MnOH^{2+}$ was proposed in most of the reactions involving Mn(III) in acid media and in fact $MnOH^{2+}$ is more reactive than Mn(III)(ref. 7).

$$Mn(III)_{aq} \overset{K_h}{\rightleftharpoons} MnOH^{2+}_{aq} + H^+_{aq} \text{ (fast)} \qquad \ldots (10)$$

$$MnOH^{2+} + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MnOH^{2+}A \text{ (fast)} \qquad \ldots (11)$$

$$MnOH^{2+}A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Mn^{2+} + A^{\cdot} + H_2O \text{ (fast)} \qquad \ldots (12)$$

$$A^{\cdot} + MnOH^{2+} \xrightarrow{k_3} \text{Product} + Mn^{2+} \qquad \ldots (13)$$

(rate-determining)

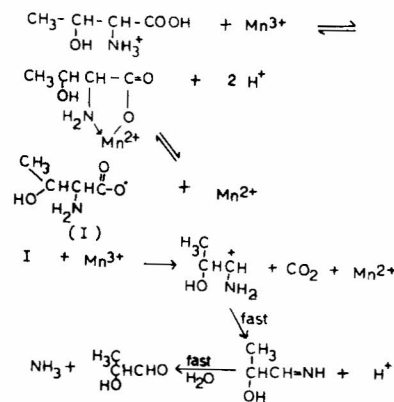### Scheme 2

The rate law, in consonance with Scheme 2 is given by Eq. (14)

$$-\frac{d[Mn(III)]}{dt} = \frac{K_h^2 k_1 k_2 k_3}{k_{-1}k_{-2}} \frac{[A][Mn(III)]^2}{[H^+]^2[Mn(II)]} \qquad \ldots (14)$$

Of the two schemes, for electrostatic reasons alone we can say that Scheme 1 is more plausible.

In the oxidation of some α-amino acids by $K_2S_2O_8$ (ref. 10), chloramine-T (ref. 11), $KMnO_4$ (ref. 12) and Mn(III) (ref. 9) in moderately acidic solutions, the suggested mechanism involved oxidative decarboxylation followed by a deaminative step. However, in the oxidation of several α-amino acids, corresponding α-keto acids were detected as intermediates[13-16] and hence the process was considered to be an oxidative deamination accompanied by fast decarboxylation. In the present investigation we could not detect the intermediate α-keto acid. However, it looks more likely that in cases where we failed to detect the keto acid a

Scheme 3

probable mechanism may be as represented in Scheme 3.

The activation parameters (28-45°C) for overall reaction are $\Delta H^{\neq} = 88.7$ kJ mol^{-1} and $\Delta S^{\neq} = 110.0$ JK^{-1} mol^{-1} (at $\mu = 2.5$, [H$^+$] = 1.612, [Mn(II)] = 0.02 and [threonine] = 0.02 mol dm^{-3}).

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