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Ruthenium (III) Catalyzed Oxidation of L-Threonine by Manganese (III) in Sulphuric Acid Medium -Kinetics and Mechanism.

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ABSTRACT

The Kinetics of oxidation of L-threonine by manganese (III) in presence of ruthenium (III) in sulphuric acid medium was studied spectrophotometrically at $30 \pm 0.1^\circ\text{C}$ and at a fixed wavelength ($\lambda_{\text{max}} = 500 \text{ nm}$). The reaction is first order dependent on [substrate], [oxidant] and [catalyst]. Ionic strength, $[\text{H}^+]$, $[\text{HSO}_4^-]$ and [manganese (II)] were found to have negligible effect on the reaction rate irrespective of the concentration of manganese (III). The energy of activation, E_a and the entropy of activation, ΔS^\ddagger were computed using linear least squares method and were found to be $42.28 \pm 3.16 \text{ KJmol}^{-1}$ and $-289.71 \pm 10.45 \text{ JK}^{-1}\text{mol}^{-1}$ respectively. A plausible mechanism was proposed based on the observed kinetics.

Keywords: L-threonine, Kinetics, Manganese(III), Ruthenium(III).

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INTRODUCTION

L-threonine(Thr) is an uncharged polar and essential amino acid. It is found in high concentrations in the heart, skeletal muscles and central nervous system. It is important for the formation of tooth enamel, collagen and elastin. It enhances the immune system aiding in the production of antibodies. Many kinetic and mechanistic studies were reported on the oxidation of L-threonine with oxidants like chloramine-T[1], manganese(VII)[2], bis(hydrogenperiodato)argentate(III)[3], N-romonicotinamide [4] and manganese(III) in acetic acid[5] and pyrophosphate[6] media.

Manganese (III) acts as a powerful one electron oxidant and the redox potential of manganese (III)-manganese (II) couple is 1.51V[7] in 7.5 mol dm⁻³ sulphuric acid medium and 1.56V[8,9] in 3.0 mol dm⁻³ perchloric acid medium. Despite of its high redox potential the oxidation of L-threonine by manganese(III) in sulphuric acid medium is observed to be very slow even at 50°C and since ruthenium(III) was found to catalyse the reaction considerably, we have undertaken a detailed kinetic study of the title reaction in 2.0 mol dm⁻³ H₂SO₄ medium.

MATERIALS AND METHODS

An aqueous solution of 0.5 mol dm⁻³ L-threonine(Himedia) was prepared in 0.5 mol dm⁻³ H₂SO₄. A 0.015 mol dm⁻³ solution of manganese(III) of 75 cm³ in 5.0 mol dm⁻³ H₂SO₄ was prepared by slowly adding 2.3 cm³ of 0.1 mol dm⁻³ KMnO₄ solution to an ice cold solution of 50 cm³ of 0.25 mol dm⁻³ manganese(II) sulphate and standardized by titrating against standard Iron(II) using ferroin as indicator. A 0.01 mol dm⁻³ solution of ruthenium(III) sulphate in 0.5 mol dm⁻³ sulphuric acid was prepared from ruthenium trichloride(Johnson Mathey, London) according to surasiti and sandell[10] and was standardized by the method suggested by Beamish and Vanloon[11]. All other chemicals used were of analytical reagent grade.

Kinetic measurements were carried out under the conditions [H₂SO₄] > [Thr] > [Mn^{III}] > [Ru^{III}]. The progress of the reaction was followed by measuring the absorbance of manganese(III) at 500 nm. The plots of log(absorbance) versus time were found to be linear up to 80% completion of the reaction indicating that the reaction is first order with respect to [manganese(III)]. The pseudo-first order rate constants, k', were calculated from the plots of log(absorbance) versus time and the rate constants were found to be reproducible within ±4%.

Absorption measurements were made with a Milton Roy Spectronic-1201 UV-Visible spectrophotometer with 1cm length silica cells. A Siskin-Julabo-V constant temperature liquid circulatory bath was used to maintain constant temperature for all kinetic investigations.

EXPERIMENTAL

Test for free radicals

A freshly prepared acrylamide solution was added to the L-threonine -manganese(III) reaction mixture in 2.0 mol dm⁻³ H₂SO₄ to initiate polymerization by free radicals. The reaction mixture was kept aside and after 24 hours no turbidity was observed indicating the absence of free radicals in the reaction mixture.

Product Analysis

The product analysis was carried out by adopting the following procedure.

The reaction mixture containing 5.0 x 10⁻² mol dm⁻³ threonine, 2.0 mol dm⁻³ sulphuric acid, 2.0 x 10⁻³ mol dm⁻³ manganese(III), 0.2 mol dm⁻³ manganese(II) and 6.0 x 10⁻⁶ mol dm⁻³ ruthenium(III) was allowed to stand at 30°C. After completion of the reaction it is extracted with diethyl ether. The product obtained from the ethereal layer was confirmed as threonine aldehyde from ¹H-NMR and ¹³C NMR spectra.

In the NMR spectrum(Fig.1), the doublet at δ 9.533 ppm corresponds to aldehydic proton, multiplet at δ 5.0412-5.003 ppm corresponds to C-H proton, doublet at δ 2.060 corresponds to alcoholic proton (O-H) and the other doublet at δ 1.163 corresponds to methyl proton respectively.

The product was further confirmed by ¹³C NMR spectrum(Fig.2) showing the methyl carbon at δ 20.25, C-H carbon at δ 98.39 and aldehydic carbon at δ 204.54 ppm respectively.

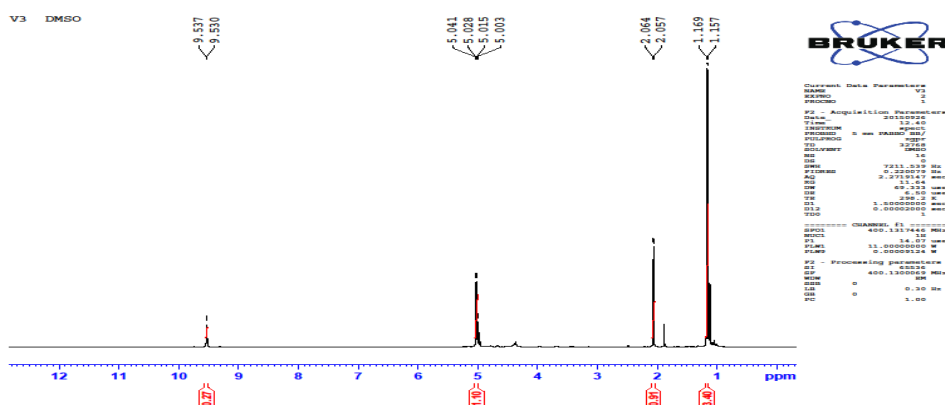


Figure 1: ¹H-NMR Spectrum of Threonine aldehyde

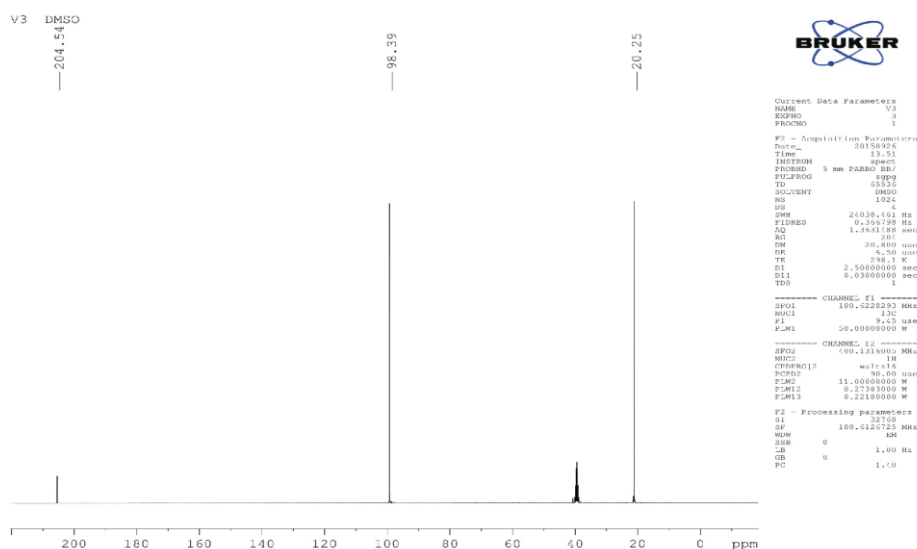


Figure 2: ¹³C NMR Spectrum of Threonine aldehyde

RESULTS AND DISCUSSION

Effect of [manganese (III)]

To resolve the effect of [manganese(III)] on the rate of ruthenium(III) catalysed oxidation of L-threonine, the reaction was studied at various initial concentrations of manganese(III) by varying it from 1.5 - 4.0 x 10⁻³ mol dm⁻³, keeping the concentrations of other species constant. The plots of log(absorbance) versus time were found to be linear upto 75% completion of the reaction indicating that the reaction is first order with respect to [manganese(III)].

Effect of [threonine]

To observe the dependence of rate on [threonine], kinetic runs were performed by varying the initial concentration of threonine from 3.0-8.0 x 10⁻² mol dm⁻³ keeping the concentration of all other species

constant. The pseudo-first order rate constants obtained were found to increase with increase in [threonine]. Further, the plot of k' versus [threonine] was found to be a straight line passing through origin indicating unit order dependence on [substrate].

Effect of [catalyst]

Kinetic measurements were performed at constant [threonine], $[H^+]$, $[Mn^{III}]$, $[Mn^{II}]$ and temperature by varying the concentration of ruthenium(III) from $4.0 - 9.0 \times 10^{-6} \text{ mol dm}^{-3}$. It was observed that the increase in [ruthenium(III)] enhanced the rate of the reaction and the plot of k' versus [ruthenium(III)] is found to be a straight line passing through the origin (Fig. 3) showing first order dependence on the [catalyst].

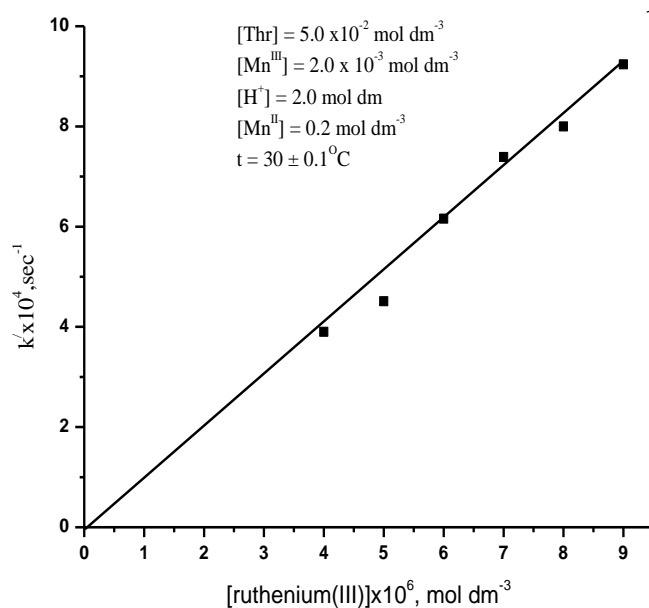


Figure.3: Plot of k' versus [ruthenium(III)]

Effect of [manganese(II)], ionic strength, and $[HSO_4^-]$

The initially added product manganese(II), ionic strength, $[HSO_4^-]$ did not have any significant effect on the rate of the reaction.

Effect of $[H^+]$

The effect of $[H^+]$ on the rate of the reaction was studied by varying $[H^+]$ using perchloric acid and keeping the concentration of all other reactants constant. It was also found that the rate of the reaction is independent of $[H^+]$. A similar observation was made earlier in the oxidation of uronic acids[12] and Ru(III) catalysed oxidation of L-serine[13] by manganese(III).

Effect of temperature

The effect of temperature on the reaction rate was studied at four different temperatures 25, 30, 35 and 40°C keeping the concentration of all other reactants constant. The rate of the reaction was found to increase with increase in temperature. The energy of activation, E_a and entropy of activation, ΔS^\ddagger values were computed using linear least squares method and are found to be $42.28 \pm 3.16 \text{ KJ mol}^{-1}$ and $-289.71 \pm 10.45 \text{ JK}^{-1}\text{mol}^{-1}$ respectively.

In sulphuric acid medium, manganese(III) exists as Mn^{3+} , $MnOH^{2+}$ and $MnSO_4^+$. The absence of bisulphate ion effect on the rate of the reaction indicating $MnSO_4^+$ cannot be reactive species of

manganese(III). As the reaction rate did not alter with $[H^+]$, it was assumed that both Mn^{3+} and $MnOH^{2+}$ to be the reactive species of manganese(III).

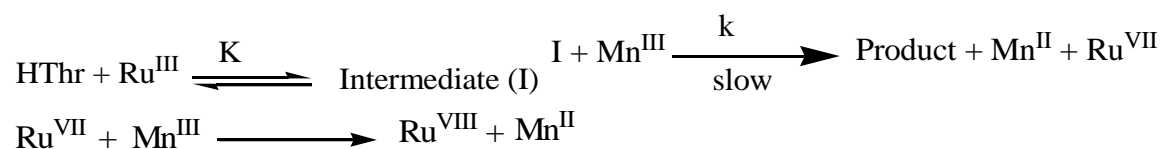
Table 1: Effect of [Threonine], [ruthenium(III)], $[H^+]$ and ionic strength on the pseudo first order rate constant, k' at temp = $30 \pm 0.1^\circ C$

$[Mn(III)] \times 10^{-3}$ mol dm ⁻³	$[Thr] \times 10^{-2}$ mol dm ⁻³	$[Ru(III)] \times 10^{-6}$ mol dm ⁻³	$[H^+]$ mol dm ⁻³	μ mol dm ⁻³	$k' \times 10^{-4}$ sec ⁻¹
2.0	3.0	6.0	2.0	-	3.86
2.0	4.0	6.0	2.0	-	4.72
2.0	5.0	6.0	2.0	-	6.16
2.0	6.0	6.0	2.0	-	7.39
2.0	7.0	6.0	2.0	-	9.24
2.0	8.0	6.0	2.0	-	11.10
2.0	5.0	4.0	2.0	-	3.90
2.0	5.0	5.0	2.0	-	4.51
2.0	5.0	6.0	2.0	-	6.19
2.0	5.0	7.0	2.0	-	7.39
2.0	5.0	8.0	2.0	-	8.0
2.0	5.0	9.0	2.0	-	9.24
2.0	5.0	6.0	2.0	3.5	6.16
2.0	5.0	6.0	2.25	3.5	6.18
2.0	5.0	6.0	2.5	3.5	6.16
2.0	5.0	6.0	2.75	3.5	6.13
2.0	5.0	6.0	3.0	3.5	6.18
2.0	5.0	6.0	3.25	3.5	6.12

Literature reports were available [13-15] on the quantitative oxidation of ruthenium(III) to ruthenium(VIII) in aqueous solution with excess manganese(III) solution. Therefore it may be presumed that ruthenium(VIII) is the reactive species of ruthenium(III) under present experimental study.

In 2.0 mol dm⁻³ sulphuric acid, threonine mainly exists as its protonated species, HThr(>99%).

Based on these observations the following mechanism has been proposed.



Where, HThr = $\text{CH}_3\text{-CH(OH)-CH(NH}_3^+\text{)-COOH}$

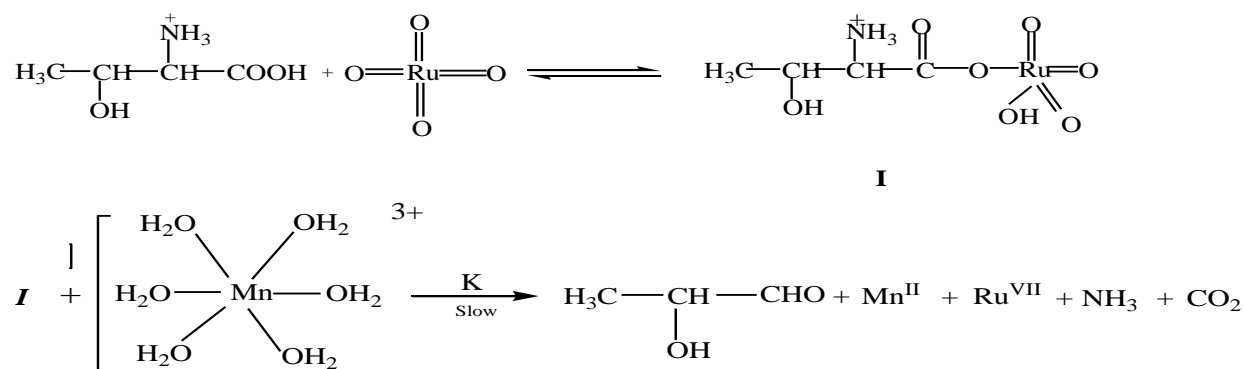
The above mechanism leads to the rate law,

$$\begin{aligned}
 \text{Rate} &= -\frac{d[Mn^{\text{III}}]}{dt} = k [I] [Mn^{\text{III}}] \quad \{\text{since } [I] = K[\text{HThr}][\text{Ru}^{\text{III}}]\} \\
 &= k K [\text{HThr}][\text{Ru}^{\text{III}}][Mn^{\text{III}}]
 \end{aligned}$$

But $[\text{HThr}] = [\text{Thr}]_t$ and $[\text{Ru}^{\text{III}}] = [\text{Ru}^{\text{III}}]_t$

Therefore, rate = $k K [\text{Thr}]_t [\text{Ru}^{\text{III}}]_t [\text{Mn}^{\text{III}}]$.

The above rate equation explains the unit order dependence of rate on [substrate], [oxidant] and [catalyst].

Intimate Mechanism

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