

Kinetics and mechanistic approach to the oxidation of L-tryptophan by permanganate ion in aqueous acidic medium

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ABSTRACT

The kinetics of permanganate ion oxidation of L-tryptophan (LT) in aqueous tetraoxosulphate(VI) acid solution at a constant ionic strength of 0.50mol dm^{-3} at $28 \pm 1^\circ\text{C}$ has been investigated spectrophotometrically. The reaction showed a first order dependence on both $[\text{MnO}_4^-]$ and $[\text{LT}]$. The rate of reaction decreased as the ionic strength of the medium increased. Added anions and cations catalysed the reaction, the result of the Michaelis Menten's analysis and spectroscopic investigation gave no evidence of intermediate complex formation. On the basis of the results obtained in this study, the outer sphere mechanism is proposed for the reaction.

Keywords: Kinetics, mechanism, permanganate ion, L- tryptophan

INTRODUCTION

Tryptophan is an essential amino acid that is required in human diet. Only the L-stereoisomer of tryptophan is used in structural or enzyme proteins, but the D-stereoisomer is occasionally found in naturally produced peptides (for instance the marine venom peptide) [1]. Tryptophan function as a biochemical precursor for the production of Serotonin (a neurotransmitter) [2,3], niacin (nicotinic acid) [4] and auxin (a phytohormone) [5]. Commonly used oxidizing agents include potassium permanganate, potassium dichromate, hydrogen peroxide, chromic acid etc. [6-8]. Kinetics is concerned with the rate of reaction [9].

Permanganate ion is a strong oxidizing agent that does not generate toxic by-products. [10] Permanganate ion can also act as an antiseptic, for example, its dilute solutions are used to treat canker sores (ulcers), disinfectant for the hands and treatment for mild pompholyx, dermatitis and fungal infections of hands or feet [11].

Despite the various uses of tryptophan, much has not been done on its kinetics investigation. Our motivation for this work is to probe into the kinetics of oxidation of the reaction of L – tryptophan by permanganate ion with a view of assigning a mechanistic pathway for the reaction. L – tryptophan is structurally shown as:

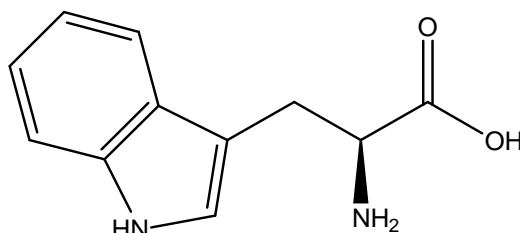


Figure 1: L-tryptophan

MATERIALS AND METHODS

Experimental

Standard solution of L-tryptophan (here and there after referred to as LT), (BDH) was prepared with distilled water. Tetraoxosulphate (VI) acid (analar grade) was used as a source of hydrogen ions while the ionic strength of the medium was maintained constant at 0.5 mol dm^{-3} using sodium tetraoxosulphate (VI).

Standard salt solutions were made by dissolving known amounts of the solute in a given volume of distilled water and the exact concentration determined by serial dilution method [12].

Stoichiometry

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method. The concentration of MnO_4^- was kept constant at $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ while that of LT varied between $(4.0-48) \times 10^{-5} \text{ mol dm}^{-3}$ at $[\text{H}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$, $I = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$ (Na_2SO_4) and $T = 28 \pm 1^\circ\text{C}$ were measured at 525nm after the reaction had gone to completion. The stoichiometry of the reaction was then evaluated from absorbance versus mole ratio of the reductant plot.

Kinetic studies

The kinetics of the reaction was studied by following the decrease in the absorbance due to $[\text{MnO}_4^-]$ at λ_{max} 525nm using Corning Colorimeter model 253 spectrophotometer under the pseudo first order condition with [LT] in large excess over $[\text{MnO}_4^-]$ at $28 \pm 1^\circ\text{C}$, $[\text{H}^+] = 1 \times 10^{-1} \text{ mol dm}^{-3}$ and $I = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$ (Na_2SO_4).

The pseudo-first order plots of the $\log (A_t - A_\infty)$ versus time were made (where A_t and A_∞ are the absorbance at time "t" and at the end of reaction respectively) and from the slope of the plots, the pseudo-first order rate constant (k_{obs}) were determined. The second order rate constant (k_2) were obtained from k_{obs} as $k_{\text{obs}}/[\text{LT}]$.

Effect of hydrogen ion concentration

The effect of $[\text{H}^+]$ on the rate of the reaction was studied using H_2SO_4 in the range $(1.0 - 15.0) \times 10^{-2} \text{ mol dm}^{-3}$, while the concentration of MnO_4^- and LT were kept constant at $I = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$ (Na_2SO_4) and $T = 28 \pm 1^\circ\text{C}$. The results are presented in Table 1.

Effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigated in the range $0.4 - 1.0 \text{ mol dm}^{-3}$ (Na_2SO_4) while the concentration of MnO_4^- , LT and H_2SO_4 were kept constant. The results are presented in Table 1.

Test for intermediate complex formation

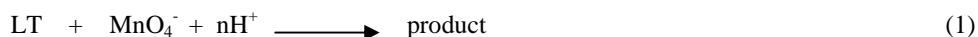
Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture one minute after the start of the reaction with that of the final product within a wavelength range of 400-700nm.

Michealis Menten's plots of $1/k_{\text{obs}}$ versus $1/[\text{LT}]$ were also made. (Figure 5)

RESULTS AND DISCUSSION

Stoichiometry and product analysis.

The stoichiometry of reaction between the MnO_4^- and LT was found in the ratio 1:1. Similar stoichiometry was obtain in the reaction of MnO_4^- with DL- leucine and malachite green [13-14]. The overall equation can be represented as



One of the products of this reaction is Mn^{2+} , this was qualitatively determined by addition of KIO_4 to the reaction mixture then warmed gently, the appearance of characteristic purple colour confirmed the presence of MnO_4^- indicating that Mn^{2+} have reoxidised to MnO_4^- . Also addition of 2,4- dinitrophenylhydrazine gave a yellow precipitate which also confirmed the presence of carbonyl compound as one of the reaction products [15].

Kinetics

Plots of $\log(A_t - A_\infty)$ versus time (Figure 1) were linear to more than 80% extent of reaction suggesting that the reaction is first order in MnO_4^- . Also plot of $\log k_{obs}$ versus $\log [LT]$ gave a slope of 1.03 indicating that the reaction is approximately first order in [LT].

The constancy of the second order rate constant shows that the reaction is also first order in LT. Therefore the overall order for the reaction is second order. the rate law can therefore be written as

$$-d \left[\frac{MnO_4^-}{dt} \right] = k_2 [MnO_4^-] [LT] \quad (2)$$

Table 1: Pseudo first and second order rate constant for redox reaction of MnO_4^- and [LT] at $[MnO_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, and T= $28 \pm 1^\circ \text{C}$

$10^2 [LT]$, mol dm^{-3}	$10 [H^+]$, mol dm^{-3}	$10 [I]$, mol dm^{-3}	$10^2 k_{obs}$, s^{-1}	$10 k_2$, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
2.0	1.0	5.0	1.74	8.72
4.0	1.0	5.0	3.43	8.57
8.0	1.0	5.0	7.09	8.86
10.0	1.0	5.0	8.61	8.61
12.0	1.0	5.0	10.26	8.55
14.0	1.0	5.0	12.4	8.86
18.0	1.0	5.0	16.0	8.88
26.0	1.0	5.0	23.19	8.92
18.0	0.1	5.0	3.69	2.05
18.0	0.3	5.0	6.50	3.61
18.0	0.5	5.0	9.27	5.15
18.0	0.8	5.0	18.75	7.64
18.0	1.0	5.0	16.02	8.90
18.0	1.2	5.0	18.65	10.6
18.0	1.5	5.0	21.83	12.1
18.0	1.0	4.0	17.30	9.63
18.0	1.0	5.0	16.04	8.92
18.0	1.0	6.0	14.40	8.03
18.0	1.0	7.0	14.06	7.84
18.0	1.0	8.0	13.45	7.47
18.0	1.0	9.0	12.71	7.09
18.0	1.0	10.0	11.16	6.02

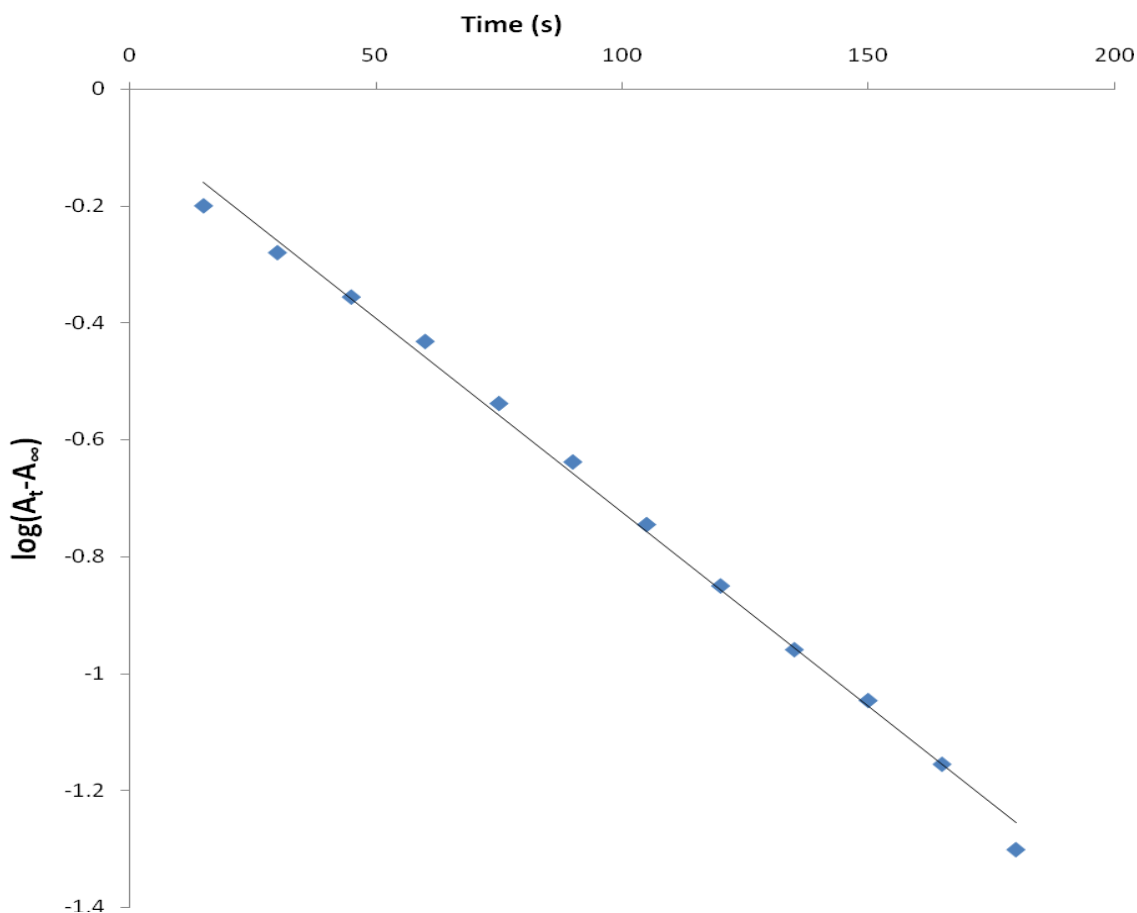


Figure 2: A typical Pseudo- first order plot for the redox reaction of LT and permanganate, at $[MnO_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[LT] = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 0.1 \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 525 \text{ nm}$ and $T = 28 \pm 1^\circ \text{C}$

Effect of $[H^+]$

The rate of reaction increases with increase in concentration of hydrogen ion (Table I). Plot of $\log k_{\text{obs}}$ versus $\log [H^+]$ gave a slope of 0.7. Also plot of k_2 versus $[H^+]$ was linear with a slope of 6.85 and intercept of 0.17 (Figure 3).

The acid dependent rate constant k_H is therefore

$$k_H = a + b[H^+] \quad (3)$$

The rate equation of the reaction as a function of $[H^+]$ can now be written as

$$-d \left[\frac{MnO_4^-}{dt} \right] = (a + b[H^+]) [MnO_4^-] [LT] \quad (4)$$

where $a = 1.70 \times 10^{-1} \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$

$$b = 6.85 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

The nature of acid dependence observed implies that there are two pathways, one which depends on acid and the other which does not depend on acid. This result depicts that both the protonated and unprotonated forms of the reactant are reactive [16-18].

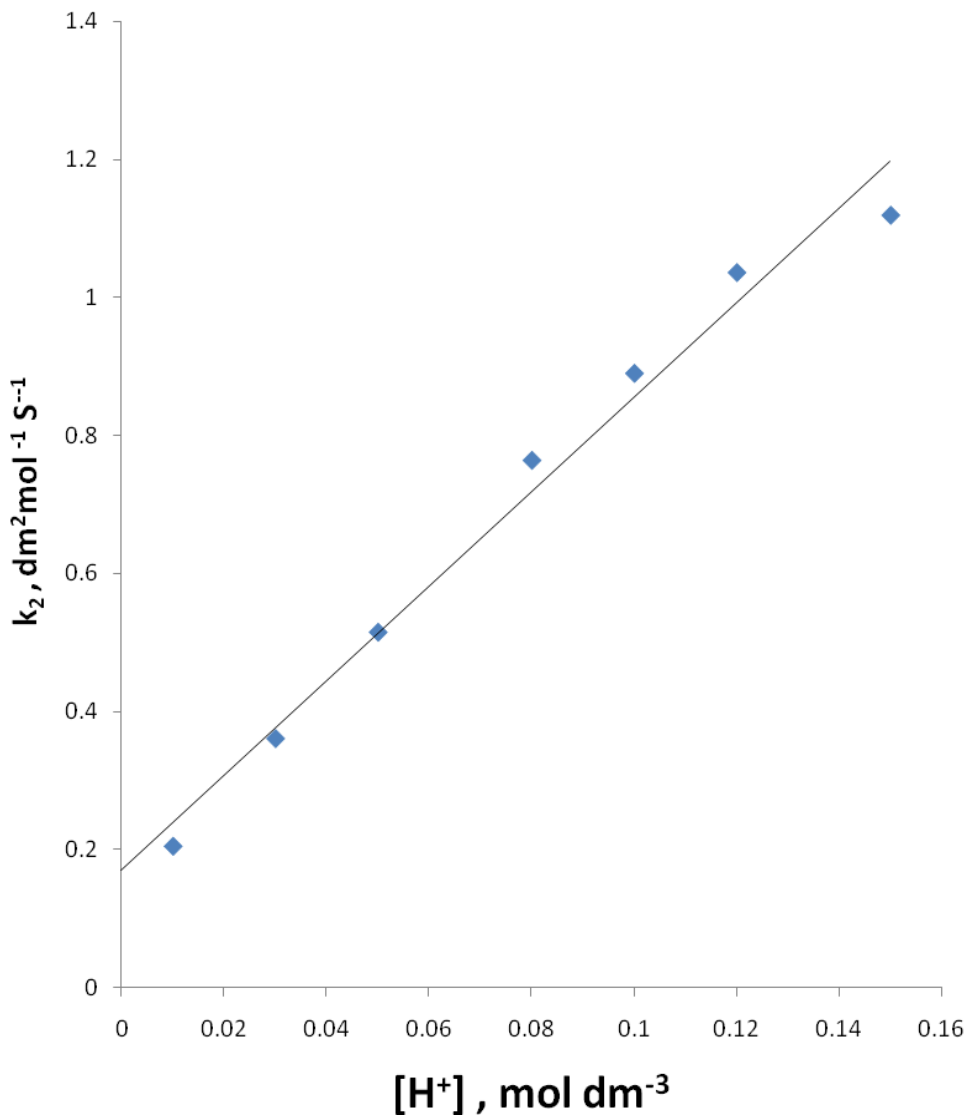


Figure 3: Plot k_2 versus $[H^+]$ at $[MnO_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[LT] = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$

Effect of ionic strength: The increase in the ionic strength from 4.0×10^{-1} to 1.0 mol dm^{-3} using Na_2SO_4 resulted in a decrease in the rate of reaction (Table 1). Plot of $\log k_2$ versus \sqrt{I} gave a linear graph [Fig. 3] with a slope of -0.42 ($R = 0.997$) showing negative salt effect which implies that there is an involvement of unlike charges i.e cationic and anionic species in an activated complex [18-20].

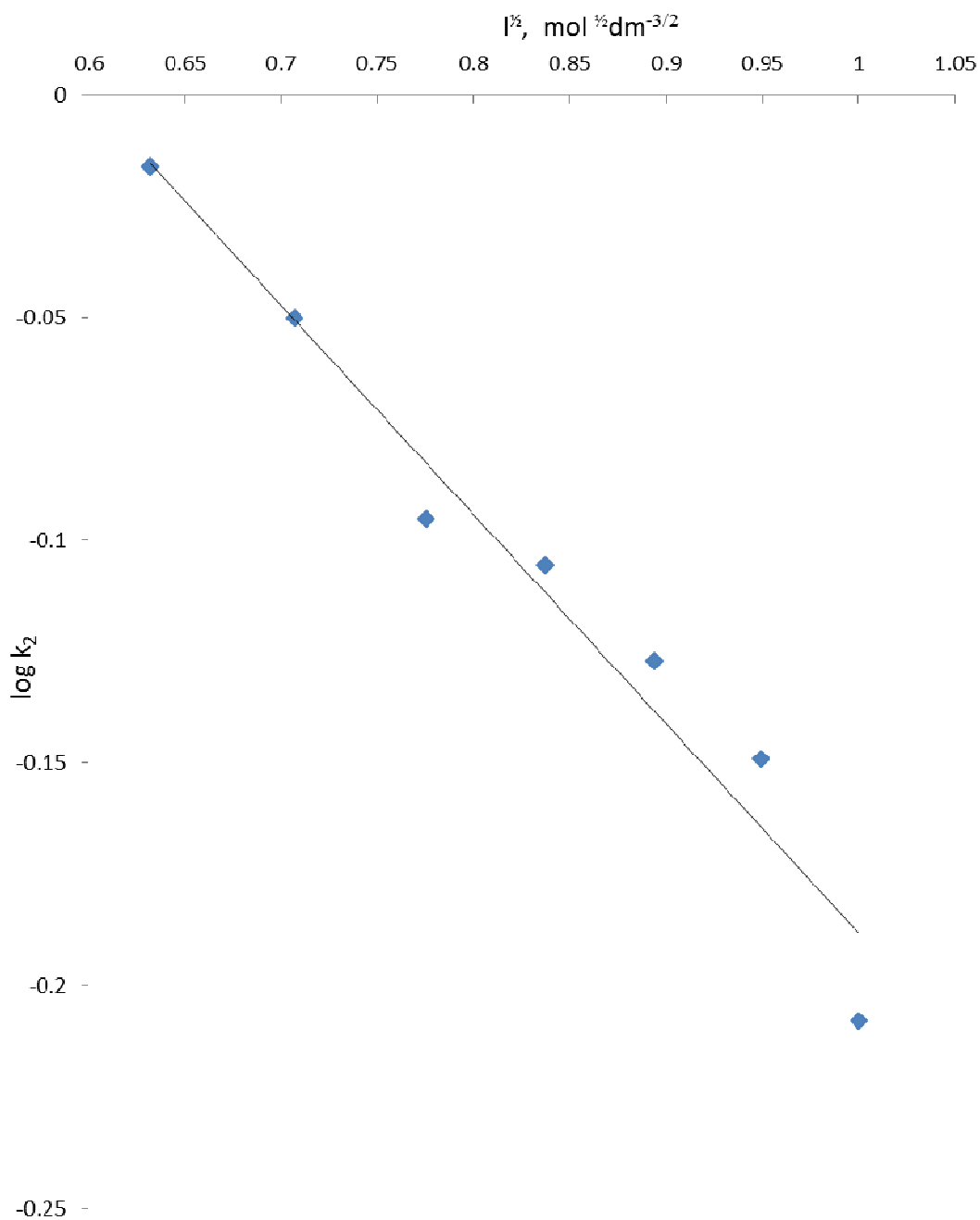


Figure 4: Plot of $\log k_2$ versus $I^{1/2}$ at $[\text{MnO}_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{LT}] = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$ $I = 0.5 \text{ mol dm}^{-3}$

Effect of added anions and cations: The results obtained from the effect of added anions and cations on the rate of reaction are presented in Table 2. The reaction was catalysed by the added anions and cations and this suggest that the reaction occurs by the outer-sphere mechanism [20-22].

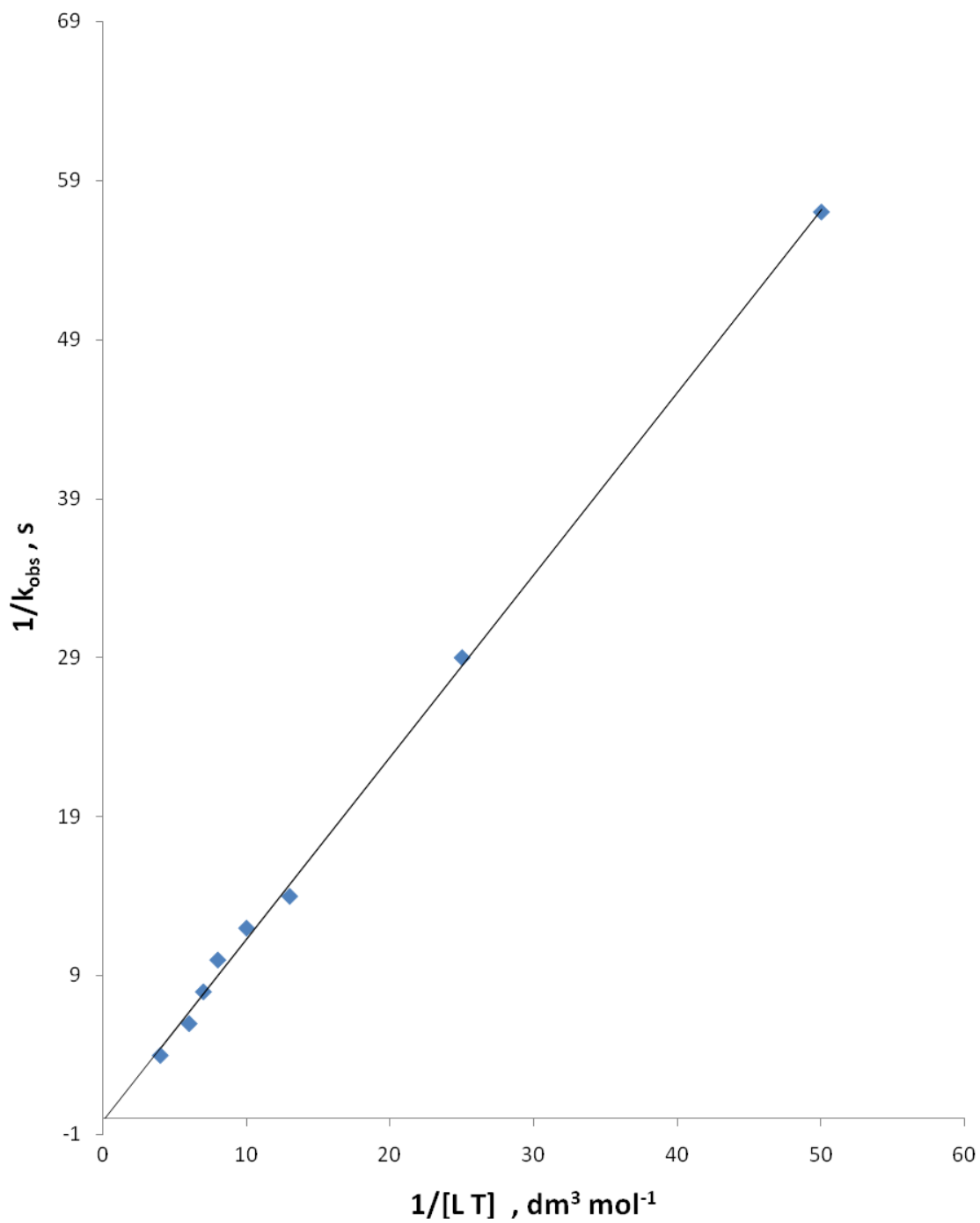


Figure 5: Michaelis Menten's plot of $1/k_{obs}$ versus $1/[L T]$, $[MnO_4^-] = 2.0 \times 10^{-4} mol dm^{-3}$, $I = 0.5 mol dm^{-3}$, $[H^+] = 0.1 mol dm^{-3}$ at $T = 28 \pm 1^\circ C$,

Table 2: Rate constants for the effect of cations and anions in oxidation reaction between MnO_4^- and LT
 $[MnO_4^-] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $[LT] = 1.8 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, $[H^+] = 0.1 \text{ mol dm}^{-3}$ at $T = 28 \pm 1^\circ C$,

$10^4 [NO_3^-]_{\text{mol dm}^{-3}}$	$10^2 k_{obs}, s^{-1}$	$10^2 k_2, \text{dm}^3 \text{mol}^{-1} s^{-1}$
5	1.59	8.83
25	1.56	8.67
75	1.50	8.33
100	1.47	8.16
$10^4 [Cl^-]$		
5	1.58	8.78
25	1.53	8.50
75	1.41	7.83
100	1.86	7.56
$10^4 [Mg^{2+}]$		
5	1.61	8.94
25	1.63	9.06
75	1.67	9.28
100	1.7	9.44

Test for intermediate complex formation: Spectroscopic studies of the reaction indicate no shift in the absorption maxima of 525nm characteristic of $[MnO_4^-]$. This indicated absence of the formation of an intermediate complex in the course of the reaction and the absence of inner-sphere mechanism in the reaction.

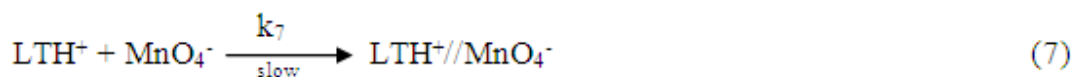
The Michaelis Menten's plots of $1/k_{obs}$ versus $1/[LT]$ were linear without intercept [Fig.5]. Both results suggest the absence of intermediate complex formation prior to the electron transfer step in the reaction. A similar observation was reported for reduction of MnO_4^- by L-ascorbic acid [17].

Free radical test

Acrylamide was added to the partially oxidized reaction mixture of MnO_4^- and LT. No gel formation was observed even on addition of large excess of methanol. This suggests absence of free radical in the reaction mixture.

Reaction Scheme

On the basis of the results of this investigation the following plausible Mechanism is proposed.



$$\text{Rate} = (k_6 + Kk_7[H^+]) [LT] [MnO_4^-] \quad (10)$$

Equation (10) is similar to equation(4), where $k_6 = a$, and $Kk_7 = b$

Where $a = 1.70 \times 10^{-1} \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$
 $b = 6.85 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

Also equation (7) is consistent with the fact that at activated complex there is an involvement of anionic and cationic species.

The mechanism of the reaction is the one that involved two pathways; the acid dependent and acid independent pathways, which are apparent in the rate law. Similar Mechanism was proposed in the reaction that involved MnO_4^- [14].

CONCLUSION

The kinetic of the oxidation of L- tryptophan by permanganate ion in aqueous tetraoxosulphate(VI) acid medium showed a stoichiometry of 1:1, a first order with respect to both L-tryptophan and permanganate ion, similar first order kinetics with respect to both oxidant and substrate has been reported by earlier researchers[8,23]. The rate of reaction was enhanced by increase in the acid concentration, but inhibited as the ionic strength increased. Added anions and cation were observed to catalyze reaction rate. Therefore outer-sphere mechanistic pathway is proposed for this reaction.

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