Kinetics andmechanism of oxidation of L-cysteic acid by permanganate ion in aqueous acidic medium

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ABSTRACT

Kinetics studies has been carried out on the oxidation of L-cysteicacid (HR'H) by permanganate ion in aqueous acidic medium at $27.0 \pm 1.0^0 C$, $I = 0.5 mol\ dm^{-3}(Na_2SO_4)$, $[H^+] = 1.0 \times 10^{-1} mol\ dm^{-3}$. The stoichiometry of reaction was 2:5 (MnO_4^- :HR'H). The reaction was also found to be first order in $[MnO_4^-]$ and $[HR'H]$ respectively and the reactions conformed to the following rate law.

$$-\frac{2}{5}\frac{d[MnO_4^-]}{dt} = a[H^+][MnO_4^-][HR'H]$$

The rate of reaction displayed negative salt effects. Added anions and cations catalysed the reaction and changes in dielectric constant of the medium had no effect on the rate of the reaction. The results of spectroscopic and kinetic investigation did not indicate intermediate complex formation during the course of the reaction, since there was no change in λ_{max} at 525nm. The outer- sphere mechanism is proposed for these reactions.
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INTRODUCTION

Amino acids are molecules containing an amino group and carboxylic acid and a side chain that varies for different amino acids. Due to the biological and biochemical importance of amino acids, the kinetics and mechanistic studies of their oxidation have received considerable attention [1]. The permanganate oxidation of amino acids in strong acid medium, neutral and weak basic and weak acid medium have also been investigated.[2-7]. Cysteic acid (here and there after referred asHR'H) as an amino acid is an intermediate in cysteine metabolism, [8]. Cysteine metabolism refers to the biological pathways that consume or form cysteine. The pathways of different amino acids and other metabolites interweave and overlap to creating complex system.

Amino acids have numerous applications: in biology, they are used in plants and microorganisms in the synthesis of pantothetic acid (vitamin B_5); a component of coenzyme, in biochemistry they are important in nutrition and are commonly used in food technology and industry as food additives, drugs and plastics [9-12]. We are motivated by the roles of amino acids in studying the kinetics and mechanism of oxidation of $HR'H$. In addition this study will be useful for further understanding of many of its applications. It is structurally shown as below.
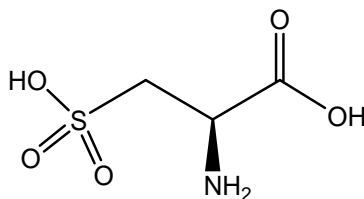
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Figure 1: L-cysteic acid

MATERIALS AND METHODS

Experimental

All chemical used were BDH (analar grades) and were used without further purification. Standard solution of HR'H was prepared with distilled water. Tetraoxosulphate(VI) acid was used as a source of hydrogen ion while the ionic strength of the medium was maintained constant at 0.50mol dm^{-3} using sodium tetraoxosulphate(VI). Standard salt solutions were made by dissolving known amount of the solute in a given volume of distilled water and exact concentration determined by serial dilution method [13].

Stoichiometry

Stoichiometry of the reactions was determined by spectrophotometric titration using the mole ratio method, the absorbance of the solution containing various concentrations of the reductant in the range $(7.5-90.0) \times 10^{-5}$ mol dm^{-3}, at $[H^+] = 1 \times 10^{-1}$ mol dm^{-3} and T = 27.0 ± 1.0^0C 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 oxidant to the reductant plot.

Kinetic Studies:

The kinetics of the reaction was studied by following the decrease in the absorbance of $[MnO_4^-]$ at 27.0 ± 1.0^0C, $[H^+]$ = 1×10^{-1} mol dm^{-3}, I= 0.5mol dm^{-3} using Corning Colorimeter 235 model. The pseudo-first order plots of the log (A_t – A_∞) versus time were made (where A_∞ and A_t are the absorbanceat the end of the reaction and time "t" respectively).

And from the slope of the plots, pseudo-first order rate constants (k_{obs}) were determined. The second order rate constant k_2 were obtained as k_{obs}/[HR'H]

Effect of $[H^+]$

The effect of $[H^+]$ on the rate of the reaction was studied using tetraoxosulphate(VI) acid in the range $(1.0-16.0) \times 10^{-2}$ mol dm^{-3} while the concentration of MnO_4^- andHR'H were kept constant at I= 0.50 mol dm^{-3} (Na_2SO_4) and T=27.0 ± 1.0^0C. The results are presented in Table I.

Effect of ionic strength

The effect of ionic strength of reaction medium on the rate of the reaction was investigated in the range $0.4 \leq I \leq 1.0$ mol dm^{-3} (Na_2SO_4) while the concentration of the other reagents were kept constant.

RESULTS AND DISCUSSION

Stoichiometry and products analysis

Mole ratio determination showed that for every two moles of permanganate ion consumed, five moles of HR'Hwere oxidized. A plot of absorbance versus mole ratio of permanganate ion to HR'Hhad a sharp break at about 2.5 corresponding approximately to a mole ratio of 2:5 (Figure 2), this mole ratio is consistent with equation (1)

$$2MnO_4^- + 5HR'H + 6H^+ \longrightarrow 2Mn^{2+} + 5R' + 8H_2O \qquad (1)$$

The ratio of 2:5 is consistent with what has been reported for the reduction of MnO_4^- with some aldehydes [14]. Mn^{2+} was qualitatively identity by the addition of KIO_4 to the reaction mixture, then warmed gently purple colour was formed, the formation of purple colour indicates that Mn^{2+} has been reoxidised to MnO_4^-[15].

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R'was identified to contain carbonyl compound because addition of 2,4-dinitrophenylhydrazine to it gave a yellow precipitate, which is a characteristic test for carbonyl compounds [16].

R' also contain trioxosulphate(VI) ion (SO_3^{2-}). This was confirmed bythe addition of barium chloride solution to the product thereby forming a white precipitate soluble in dilute hydrochloric acid.
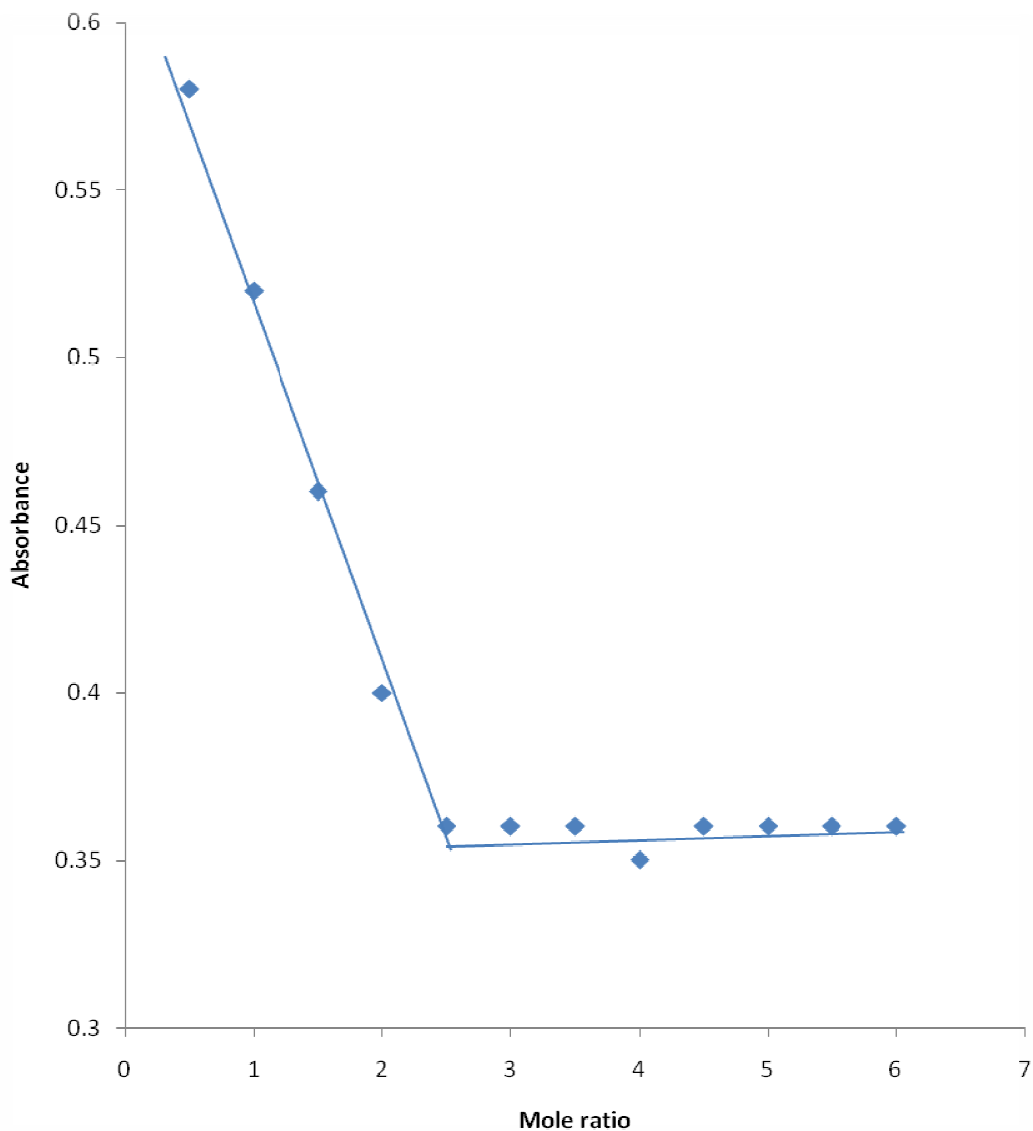

Figure 2: A Plot of absorbance against mole ratio for the reaction of MnO_4^- and HR'H

Kinetics

The pseudo-first order plot of log (A_t-A_α) versus time (Figure 3) were linear to about 80% extent of reaction indicating that the reaction is first order in [MnO_4^-] under the experimental conditionat [H^+] = 1×10^{-1} mol dm^{-3}, I= 0.5mol dm^{-3}.

The pseudo – first order rate constants were determined at different concentrations ofHR'H.Least square plot of log k_{obs} versus log [HR'H] gave a slope of 1.06 (Figure 4). This suggest a first order dependence on [HR'H]. The values

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of second order rate constants, k_2 were fairly constant (Table 1), suggesting that the reaction is also first order in $[MnO_4^-]$ and that the reaction is second order overall. The rate equation is

$$-\frac{2}{5}\frac{d[MnO_4^-]}{dt} = k_2 [MnO_4^-][HR'H] \qquad\qquad (2)$$

The first order with respect to amino acids is common as the similar results were obtained when DL – leucine and L – phenylalanine were oxidized by permanganate ion [17-18].

Table 1: Pseudo first and second order rate constants for redox reaction of MnO_4^- and $HR'H$ at $[MnO_4^-]=1.5\times10^{-4}$ mol dm^{-3}, $\lambda_{max} = 525$nm and T= 27.0±1,0^{0}C'

10^2[HR'H], mol dm^{-3}	10[H$^+$], mol dm^{-3}	10[I], mol dm^{-3}	$10^3 k_{obs}$, s^{-1}	$10 k_2$, dm^{3}mol^{-1}s^{-1}
0.45	1.0	5.0	0.25	5.50
0.75	1.0	5.0	0.42	5.53
2.25	1.0	5.0	1.24	5.45
3.75	1.0	5.0	2.07	5.52
4.50	1.0	5.0	2.12	5.47
5.25	1.0	5.0	2.90	5.58
6.00	1.0	5.0	3.29	5.48
6.75	1.0	5.0	3.57	5.30
8.25	1.0	5.0	4.53	5.50
9.75	1.0	5.0	5.40	5.57
8.25	0.1	5.0	0.45	0.55
8.25	0.4	5.0	1.31	2.19
8.25	0.6	5.0	2.97	3.60
8.25	0.8	5.0	3.62	4.39
8.25	1.0	5.0	4.51	5.47
8.25	1.2	5.0	5.63	6.82
8.25	1.4	5.0	6.11	7.40
8.25	1.6	5.0	7.24	8.78
8.25	1.0	4.0	4.79	5.80
8.25	1.0	5.0	4.54	5.51
8.25	1.0	6.0	4.13	5.00
8.25	1.0	7.0	3.86	4.68
8.25	1.0	8.0	3.51	4.25
8.25	1.0	9.0	3.15	3.82
8.25	1.0	10.0	2.77	3.36

Effect of hydrogen ion concentration on the rate of the reaction
It was observed that the rate of reaction increased with increase in acid concentration. (Table 1)
The plot of log k_{obs} against log [H$^+$] gave a slope of 1.02.

Also plot of k_2 against [H$^+$] (Figure 4) was linear without intercept, fitted into equation

$k_2 = a[H^+]$ (3)

Least square analysis of the plot gave a= 0.549 dm^{6}mol^{-2}s^{-1} at 27.0$\pm$ 1.0^{0}C therefore the rate equation of the reaction as a function of [H$^+$] can now be written as

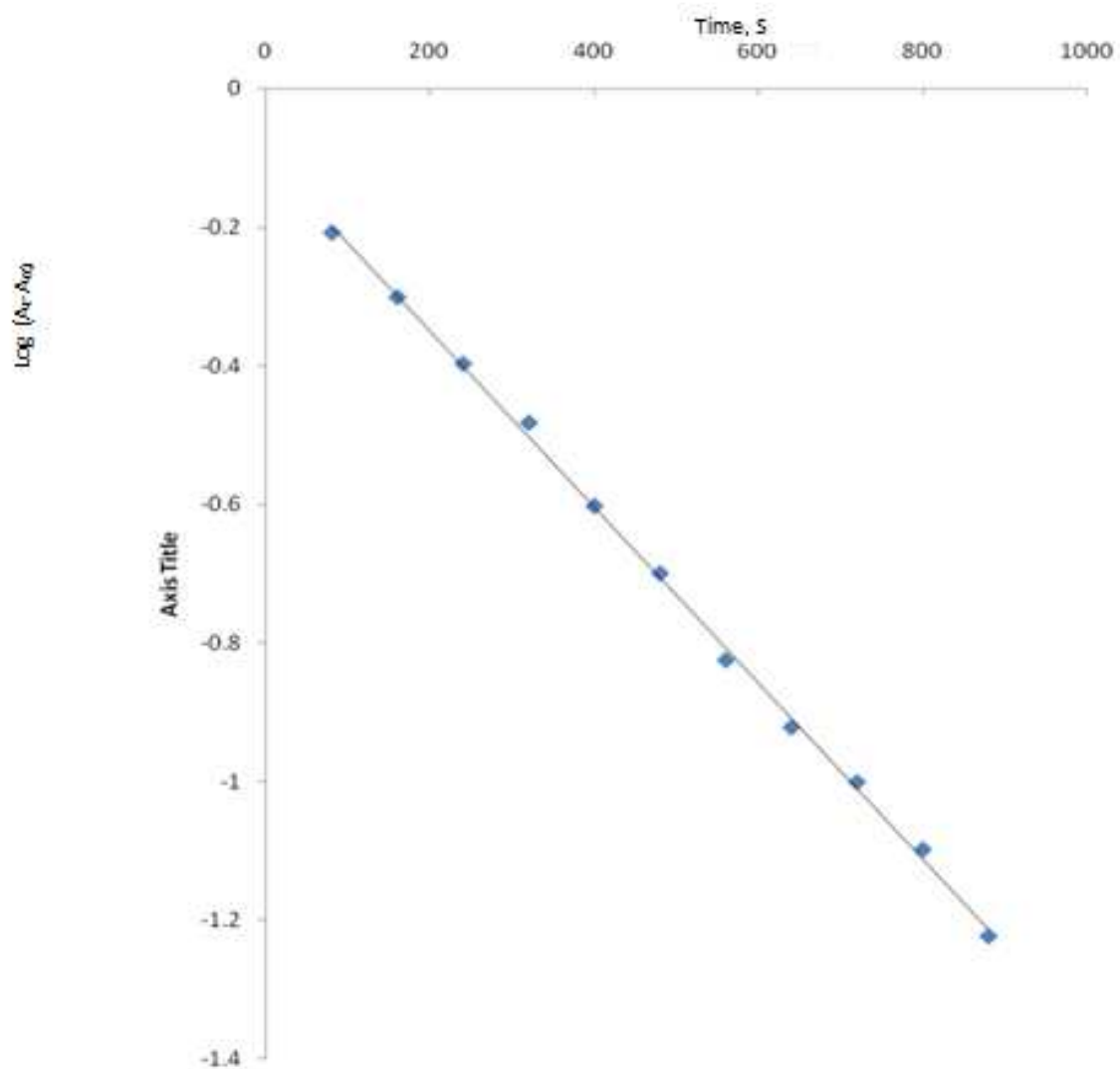$$-\frac{2}{5}\frac{d[MnO_4^-]}{dt} = a[H^+][MnO_4^-][HR'H] \qquad\qquad (4)$$

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Figure 3: A typical pseudo- first order plot for the redox reaction of HR'H and permanganate at $[MnO_4^-]$= 1.5×10^{-4} mol dm^{-3}, [HR'H]= 8.25×10^{-2} mol dm^{-3}, [H$^+$]= 0.1 mol dm^{-3} I= 0.5mol dm^{-3} λ_{max}= 525nm and T= 27.0 ± 1.0^0C

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The nature of acid dependence observed implies that, there is a rapid equilibrium between protonated andunprotonated forms of the reductant (HR'H) prior to the rate determining step and that only the protonated form is reactive [18-20]
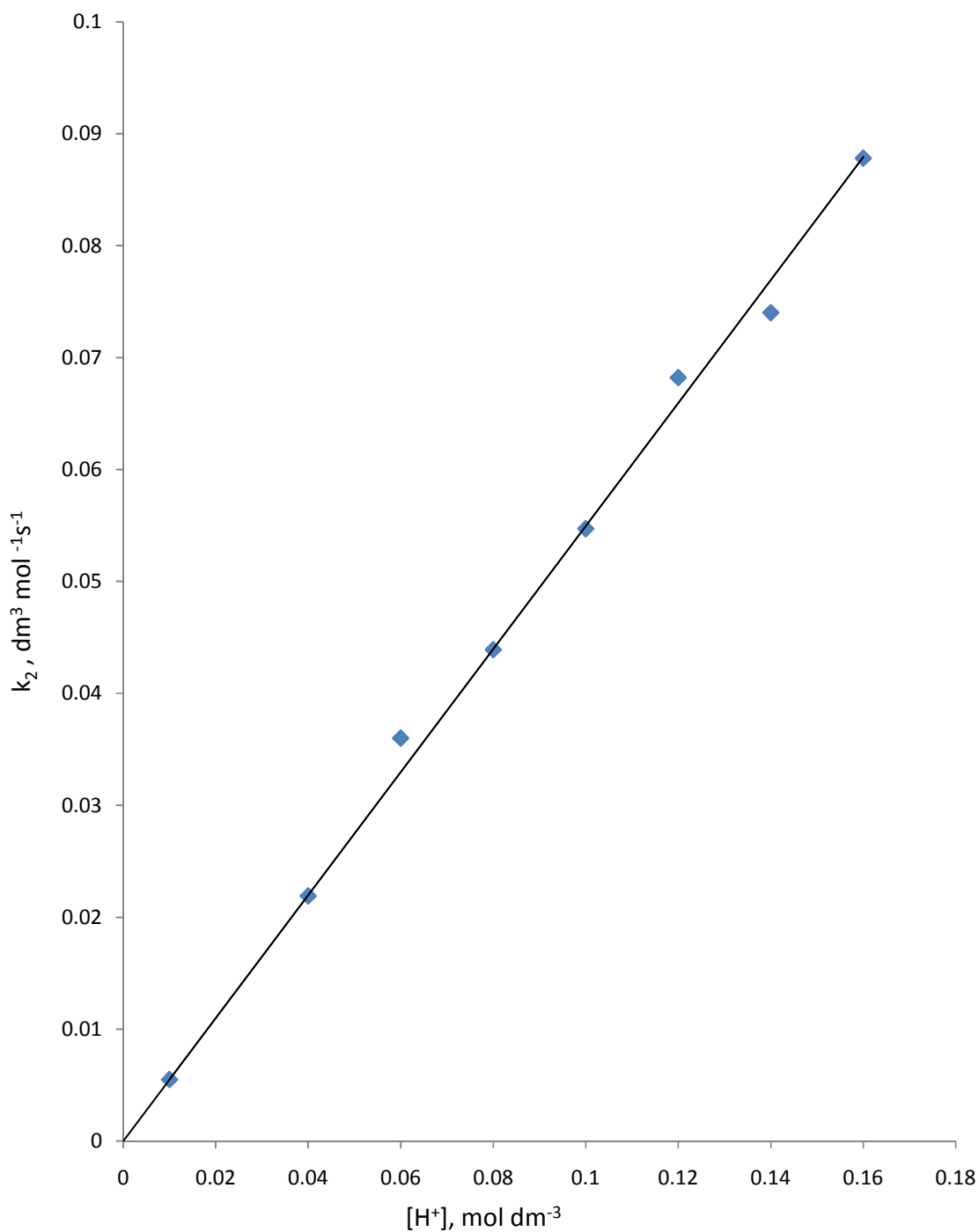

Figure 4: Plot of k_2 versus [H$^+$] at [MnO$_4^-$]= 1.5 x10^{-4} mol dm^{-3}, [HR'H]= 8.25x10^{-2} mol dm^{-3}, 1 = 0.5 mol dm^{-3}

Effect of ionic strength
The rate of reaction was found to decrease with increase in ionic strength of reaction medium. A least square plotof $\log k_2$ versus $I^{1/2}$ gave a slope of -0.60. The negative salt effect observed indicated that the rate determining step involved the reaction of cationic and anionic species [18]. The slope of - 0.60 is an indication that some other interactions might have taken place in the reaction medium to account for the non-integral value of the slope. Similar results were reported by many authors. [21-23].

Effect of added anions and cations
The effect of added cations (Li^+ and Mg^{2+}) and anions (NO_3^- and Cl^-) were investigated by varying the concentration of these cations and anions while keeping [MnO_4^-], [HR'H] and ionic strength constant at 27.0 ± 1.0^0C. The cations and anions were observed to enhance the rate of the reaction within the concentration range studied. The enhancement of the rate by added anions and cations is probably due to columbic factor, because at the activated complex, cationic and anionic species are present. This observation indicate that outer-sphere electron transfer may be significant in this reaction [24].

Table 2: Rate constant for the effect of cations and anions in oxidation reaction between MnO_4^- andHR'H
[MnO_4^-]= 1.5x10^{-4} mol dm^{-3}, [HR'H] = 8.25x10^{-2} mol dm^{-3}, I = 0.5 mol dm^{-3}, [H$^+$] = 0.1 mol dm^{-3} at T = 27.0$\pm$ 1.0^{0}C,

$10^4 \left[NO_3^- \right]$, mol dm^{-3}	$10^3 k_{obs}$, s^{-1}	$10^2 k_2$, dm^3 mol^{-1} s^{-1}
5	4.60	5.58
50	5.23	6.34
75	5.68	6.89
100	5.92	7.17
10^4 [Cl$^-$]		
5.	4.64	5.62
50	5.52	6.70
75	6.02	7.30
100	5.86	7.10
10^4 [Li$^+$]		
5	4.61	5.59
50	5.45	6.60
75	5.65	6.85
100	6.27	7.60
10^4 [Mg^{2+}]		
5	4.64	5.62
50	6.06	7.35
75	7.30	8.85
100	7.59	9.20

There was no shift in λ_{max} from 525nm when the absorbance of the partially reaction mixture was monitored between 400-700 nm.

A plot of $1/k_{obs}$ versus 1/[HR'H] was linear without intercept (Figure 5). This indicates that there was absence of intermediate complex formation during the course of the reaction. Similar result was obtained in the reaction between MnO_4^- and L – ascorbic acid [25].
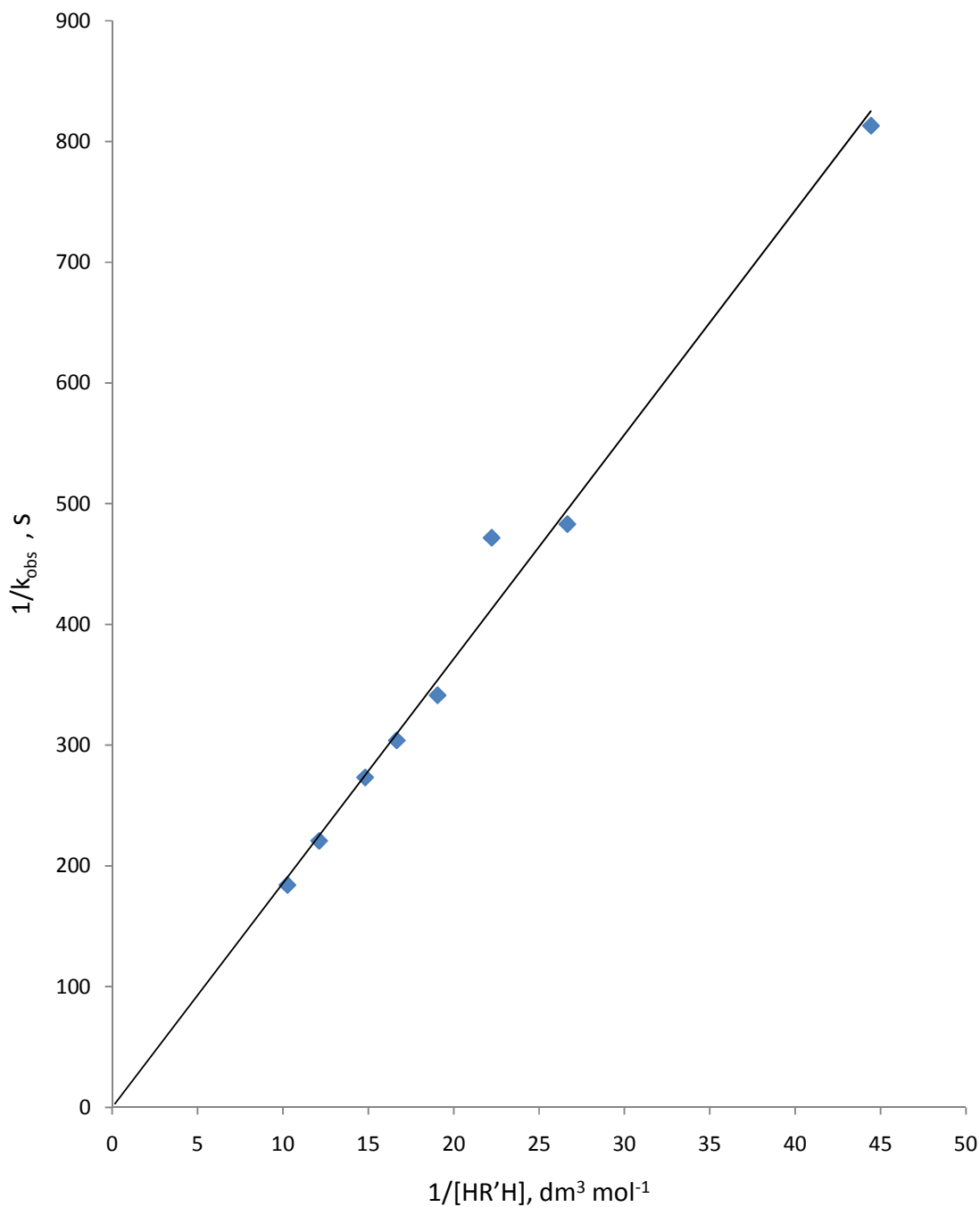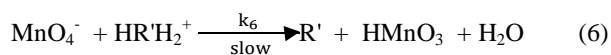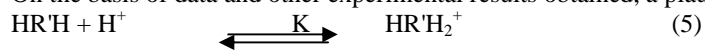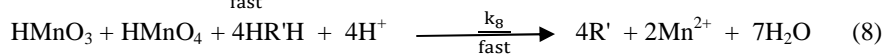
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Figure 5:MichaelisMenten'splot of 1/k$_{obs}$ versus 1/[HR'H]
[MnO$_4^-$]= 1.5x10^{-4} mol dm^{-3}, I = 0.5 mol dm^{-3}, [H$^+$] = 0.1 mol dm^{-3} at T = 27.0$\pm$ 1.0^{0}C,

Reaction scheme

On the basis of data and other experimental results obtained, a plausible reaction mechanism is proposed as follows

$$HR'H + H^+ \underset{}{\overset{K}{\rightleftarrows}} HR'H_2^+ \qquad (5)$$

$$MnO_4^- + HR'H_2^+ \xrightarrow[slow]{k_6} R' + HMnO_3 + H_2O \qquad (6)$$

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$$MnO_4^- + H^+ \xrightarrow[\text{fast}]{k_7} HMnO_4 \qquad (7)$$

$$HMnO_3 + HMnO_4 + 4HR'H + 4H^+ \xrightarrow[\text{fast}]{k_8} 4R' + 2Mn^{2+} + 7H_2O \qquad (8)$$
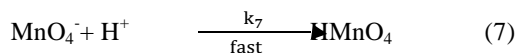
Equation (6) is the rate determining step.

$$Rate = k_6[MnO_4^-][HR'H_2^+] \qquad\qquad\qquad\qquad\qquad (9)$$

From equation (5), substitute for $[HR'H_2^+]$ in equation (9)

$$Rate = k_6K[H^+][MnO_4^-][HR'H] \qquad\qquad\qquad\qquad (10)$$

Equation (10) is analogous to equation (4), the observed rate law.
Where $k_6K = a = 5.49 \times 10^{-1} dm^6 mol^{-1} s^{-1}$.

In equation (6), which is the rate determining step there is an interaction of both negative and positive charges, describing the negative salt effect displayed by changed in the ionic strength of the reaction medium. This suggest that there is an agreement between the proposed mechanism and the empirical kinetic data.

CONCLUSION

In the redox reaction of L- cysteic acid and permanganate ion, two moles of permanganate ion were consumed by five moles of L-cysteic acid. The reaction showed first order with respect to permanganate ion and L-cysteic acid, the rate of reaction increased with increase in hydrogen ion concentration but decrease as the ionic strength of the medium increased. Added cations and anions were found to enhance the reaction rate. There was no evidence of intermediate complex formation in the course of the reaction. Based on the empirical results obtained from this study, the reaction probably followed an outer-sphere mechanistic pathway.

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