

Electron tranfer reactions of L- aspartic acid andpermanganate ion in aqueous acidic medium

Idongesit B. Anweting*, Johnson F. Iyun and Sulaiman O. Idris.

Department of Chemistry Ahmadu Bello University, Zaria, Nigeria.

ABSTRACT

Kinetics and mechanistic studies of electron transfer reaction of L- aspartic acid (H_2P) and permanganate ion in aqueous acidic media have been carried out at $29.0 \pm 1.0^\circ C$, $I = 1.0 \text{ mol dm}^{-3}$ (Na_2SO_4), $[H^+] = 2.0 \times 10^{-1} \text{ mol dm}^{-3}$. The reaction is first order with respect to permanganate ion and H_2P concentrations and reaction rate showed dependence on acid concentration. The reaction conforms to the rate equation.

$$-\frac{d}{dt}[MnO_4^-] = (a+b[H^+]^2) [MnO_4^-] [H_2P].$$

The rate of reaction increase with increase in ionic strength. Added cations and anions catalysed the reaction, spectroscopic investigations indicated that precursor complex formation did not precede the electron transfer step, but Michaelis Menten's plot of $1/k_{obs}/k_{obs}$ versus $1/[H_2P]$, showed a positive intercept by least square analysis. A plausible mechanism has been proposed for this reaction.

Keywords: *L-aspartic acid, permanganate ion, mechanism, electron transfer, kinetics.*

INTRODUCTION

Based on the biological and industrial importance of amino acids, the kinetics and mechanistic study of their oxidation (electron transfer reaction) have received considerable attention. [1, 2, 3, 4].

Aspartic acid (here and thereafter refer as H_2P) is one of two acidic amino acid, it plays important roles as general acids in enzyme active centre as well as in maintaining the solubility and ionic character of protein. It is of paramount importance in the metabolism during construction of other amino acids and biochemicals in the citric cycle. Among the biochemicals that are synthesized from H_2P are asparagines, arginine, lysine, methionine, threonine, isoleucine and several nucleotides.

Permanganate ions are widely used as oxidizing agent in synthetic and analytical Chemistry (5). It has several advantages as an analytical reagent e.g. it is strong, vividly colour, serving as its own indicator. In acidic medium it exist in different forms as $HMnO_4$, $H_2MnO_4^+$, $HMnO_3$, Mn_2O_7 and depending on the nature of the reductant, the oxidant has been assigned both inner sphere and outer- sphere pathways in their redox reaction [6].

Despite the fact that the kinetic and mechanism of oxidation of amino acids have received some considerable attention as stated earlier, but the data available for their industrial and Laboratory usage are not sufficient enough. This work may also play an essential role by providing part of the much needed kinetic data.

It is structurally shown as:

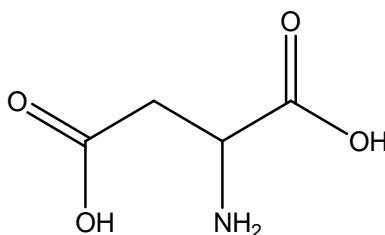


Figure 1: L-aspartic acid

MATERIALS AND METHODS

EXPERIMENTAL

Standard solution of H₂P (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 kept constant at 1.0 mol dm⁻³ using sodium tetraoxosulphate(VI).

Standard salt solutions were prepared by dissolving known amounts of the solute in a given volume of distilled water and the exact concentration determined by serial dilution method(7).

Stoichiometry: The stoichiometry of the reactions was determined by spectrophotometric titration using mole ratio method. The absorbances of the solution containing various concentrations of the reductant in $(3.75-60) \times 10^5$ mol dm⁻³ range and a constant concentration of oxidant 1.5×10^{-4} mol dm⁻³ at

$[H^+] = 2.0 \times 10^{-1}$ mol dm⁻³ and $I = 1.0$ mol dm⁻³ (Na₂SO₄), $T = 29.0 \pm 1.0^\circ C$ 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 oxidant to reductant plot.

Kinetic Studies: The Kinetics of the reaction was studied by following the decrease in the absorbance due to $[MnO_4^-]$ at λ_{max} 525nm using Corning Colorimeter model 253 spectrophotometer under the pseudo- first order condition with $[H_2P]$ in large excess over $[MnO_4^-]$ at $29.0 \pm 1.0^\circ C$, $[H^+] = 2.0 \times 10^{-1}$ mol dm⁻³ and $I = 1.0$ mol dm⁻³ (Na₂SO₄).

The pseudo-first order plots of the $\log(A_t/A_\infty)$ versus time were made (where A_t and A_∞ are the absorbances at time 't' and the end of reaction respectively) and from the slope of the plots, the pseudo first order rate constants (k_{obs}) were determined, second order rate constants k_2 were obtained from k_{obs} as $k_{obs}/[H_2P]$.

Effect of $[H^+]$: The effect of $[H^+]$ on the rate of the reaction was studied using tetraoxosulphate(VI) acid in the range $(5.0- 30) \times 10^{-2}$ mol dm⁻³, while the concentration of MnO_4^- and H_2P were kept constant at $I = 1.0$ mol dm⁻³ (Na₂SO₄) and $T = 29.0 \pm 1.0^\circ C$. The results are presented in Table 1.

Effect of ionic strength: The effect of ionic strength of the reaction medium on the rate of the reaction was investigated in the range $0.7 \leq I \leq 1.3$ mol dm⁻³ (Na₂SO₄) while the concentrations of MnO_4^- , H_2P and tetraoxosulphate(VI) acid were kept constant. The results are presented in Table 1.

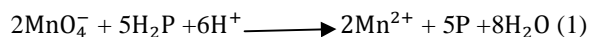
Test for Intermediate Complex Formation

Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture two minutes after the start of the reaction with that of the final product within a wave length of 400- 700nm. Michaelis Menten's plot of $1/k_{obs}$ versus $1/[H_2P]$ were also made.

RESULTS AND DISCUSSION

stoichiometry and product analysis

The Stoichiometry of electron transfer reaction of MnO_4^- and H_2P was found in the ratio of 2:5 (MnO_4^- : H_2P). The overall equation can be represented as



Mn^{2+} was qualitatively identified by addition of KIO_4 then warmed gently and the appearance of characteristic purple colour shows the presence of MnO_4^- indicating that Mn^{2+} have reoxidized to MnO_4^- [8]

Kinetics: Plots of $\log(A_t/A_\infty)$ versus time were linear with more than 70% of the extent of reaction indicating that the reaction is first order dependent on $[\text{MnO}_4^-]$. Also, plot of $\log k_{\text{obs}}$ versus $\log[\text{H}_2\text{P}]$ gave a slope of 0.98 suggesting that the reaction is approximately first order in $[\text{H}_2\text{P}]$. The second order rate constant (k_2) was obtained at constant $[\text{H}^+]$ from $k_{\text{obs}} / [\text{H}_2\text{P}]$ (Table 1) the constancy of the second order rate constant show that the reaction is also first order with respect to $[\text{H}_2\text{P}]$. Therefore the overall order for the reaction is second order the rate equation is:

$$-\frac{d}{dt} [\text{MnO}_4^-] = k_2 [\text{MnO}_4^-][\text{H}_2\text{P}] \quad (2)$$

at $[\text{H}^+] = 2.0 \times 10^{-1} \text{ mol dm}^{-3}$ and $T = 29.0 \pm 1.0^\circ\text{C}$

Where $k_2 = (3.50 \pm 0.06) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

The first order kinetics with respect to both oxidant and substrates were also reported by other researchers[9-12]

Table1: Pseudo first and second order rate constant for redox reaction of MnO_4^- and H_2P , $[\text{MnO}_4^-] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 525\text{nm}$ and $T = 29.0 \pm 1.0^\circ\text{C}$

$10^2[\text{H}_2\text{P}]$, mol dm^{-3}	$10[\text{H}^+]$, mol dm^{-3}	$[\text{I}]$, mol dm^{-3}	$10^3 k_{\text{obs}}$, s^{-1}	$10^2 k_2$, $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
0.75	2.0	1.0	0.26	3.48
2.25	2.0	1.0	0.85	3.40
3.75	2.0	1.0	1.38	3.66
4.50	2.0	1.0	1.57	3.49
5.25	2.0	1.0	1.67	3.32
6.0	2.0	1.0	2.08	3.46
6.75	2.0	1.0	2.34	3.47
7.50	2.0	1.0	2.62	3.49
11.25	2.0	1.0	3.97	3.53
7.50	0.50	1.0	0.31	0.42
7.50	1.00	1.0	0.70	0.91
7.50	1.50	1.0	1.53	2.04
7.50	2.0	1.0	2.63	3.51
7.50	2.50	1.0	4.09	5.45
7.50	2.70	1.0	4.53	6.04
7.50	3.00	1.0	6.00	8.10
7.50	2.0	0.7	1.98	2.64
7.50	2.0	0.8	2.10	2.80
7.50	2.0	0.9	2.54	3.38
7.50	2.0	1.0	2.65	3.53
7.50	2.0	1.1	2.86	3.81
7.50	2.0	1.2	3.01	4.02
7.50	2.0	1.3	3.38	4.51

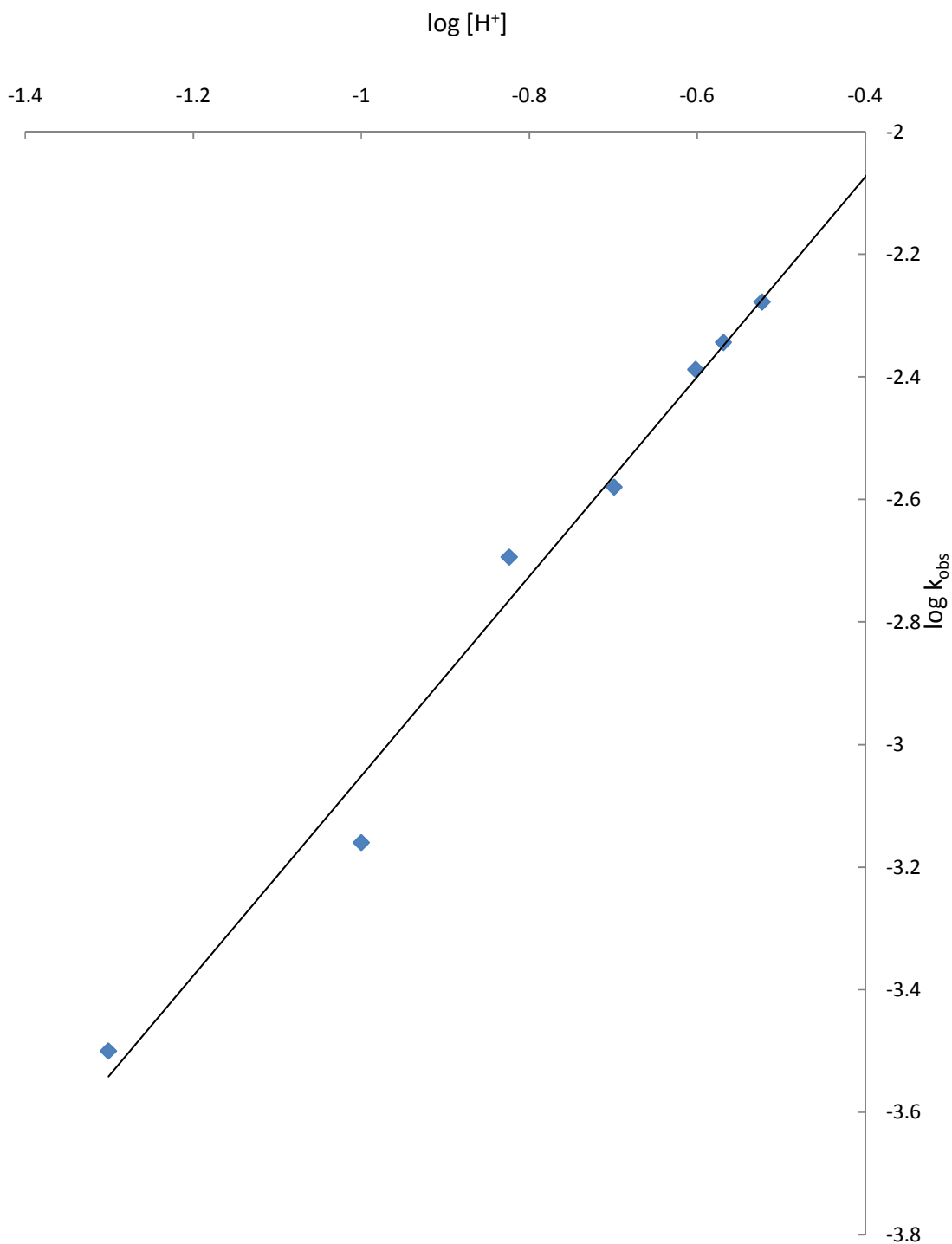


Figure 2: Plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ for the reaction of H_2P and permanganate ion, at $[\text{MnO}_4^-] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{P}] = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 525 \text{ nm}$ and $T = 29.0 \pm 1.0^\circ\text{C}$

Effect of $[\text{H}^+]$: Within the range $(5.0 - 30) \times 10^{-1} \text{ mol dm}^{-3}$, the effect of acid was studied, it was observed that the rate of reaction increases with increase in concentration of hydrogen ions (Table 1). The least square analysis of plot of $\log k_{\text{obs}}$ versus $\log [\text{H}^+]$ gave a slope of 1.70 (Figure 2), this depicts that the order with respect to $[\text{H}^+]$ is approximately 2. Also plot of k_2 versus $[\text{H}^+]^2$ was linear with a positive slope and intercept. (Figure 3).

Therefore the acid dependent rate constant K_H is given as.

$$K_H = a + b[H^+]^2 \quad (3)$$

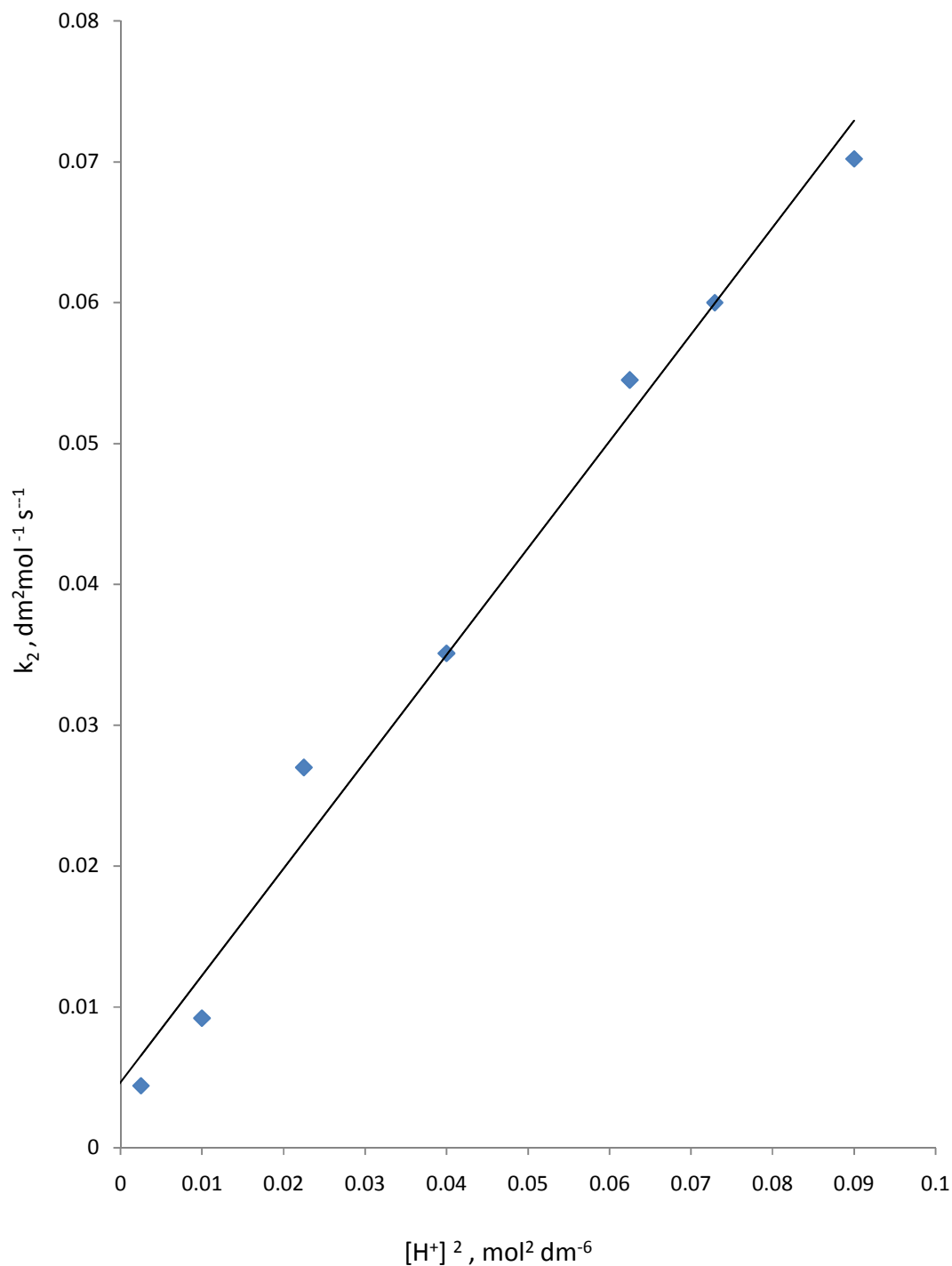


Figure 3: Plot of $\log k_2$ versus $[H^+]$ for the reaction of H_2P and permanganate ion, at $[MnO_4^-] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2P] = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 525 \text{ nm}$ and $T = 29.0 \pm 1.0^\circ \text{C}$

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

$-\frac{d}{dt} [MnO_4^-] = (a+b[H^+]^2) [MnO_4^-][H_2P]$ (4) Where $a=4.0 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $b = 7.58 \times 10^{-1} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. The positive $[H^+]$ dependence on the rate of oxidation of MnO_4^- has been explained in terms of protonation of MnO_4^- in a fast step to give $HMnO_3$ which subsequently reacts with the substrate in a fast step to give the product [13,14].

Effect of ionic strength: The increase in the ionic strength from 0.7 to 1.3 mol dm^{-3} using Na_2SO_4 resulted in an increase in the rate of reaction (Table 1). Plot of $\log k_2$ versus $I^{1/2}$ gave a linear graph with a slope of +0.76, showing positive salt effect, which implies that there is an involvement of like charges in an activated complex. (Figure 4).

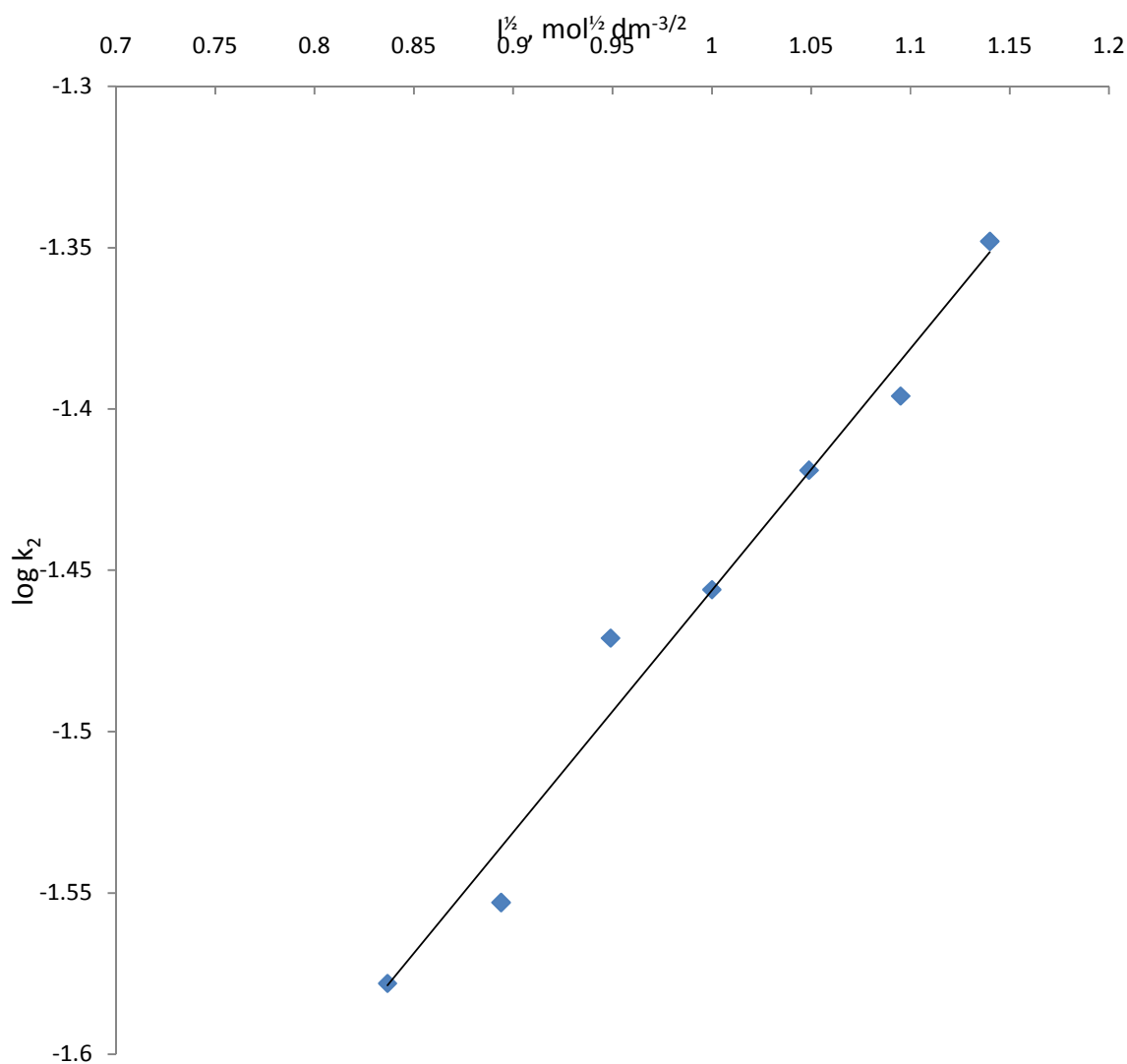


Figure 4: Plot of $\log k_2$ versus $I^{1/2}$ for the reaction of H_2P and permanganate ion, at $[MnO_4^-] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2P] = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 0.2 \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 525 \text{ nm}$ and $T = 29 \pm 1^\circ \text{C}$

Effect of added anions and cations: The results obtained from the effect of added anions and cations on the rate of reaction were presented in Table 2. The reaction was catalysed by the added anions and cations and this is suggestive of outer-sphere mechanism [15,16,17].

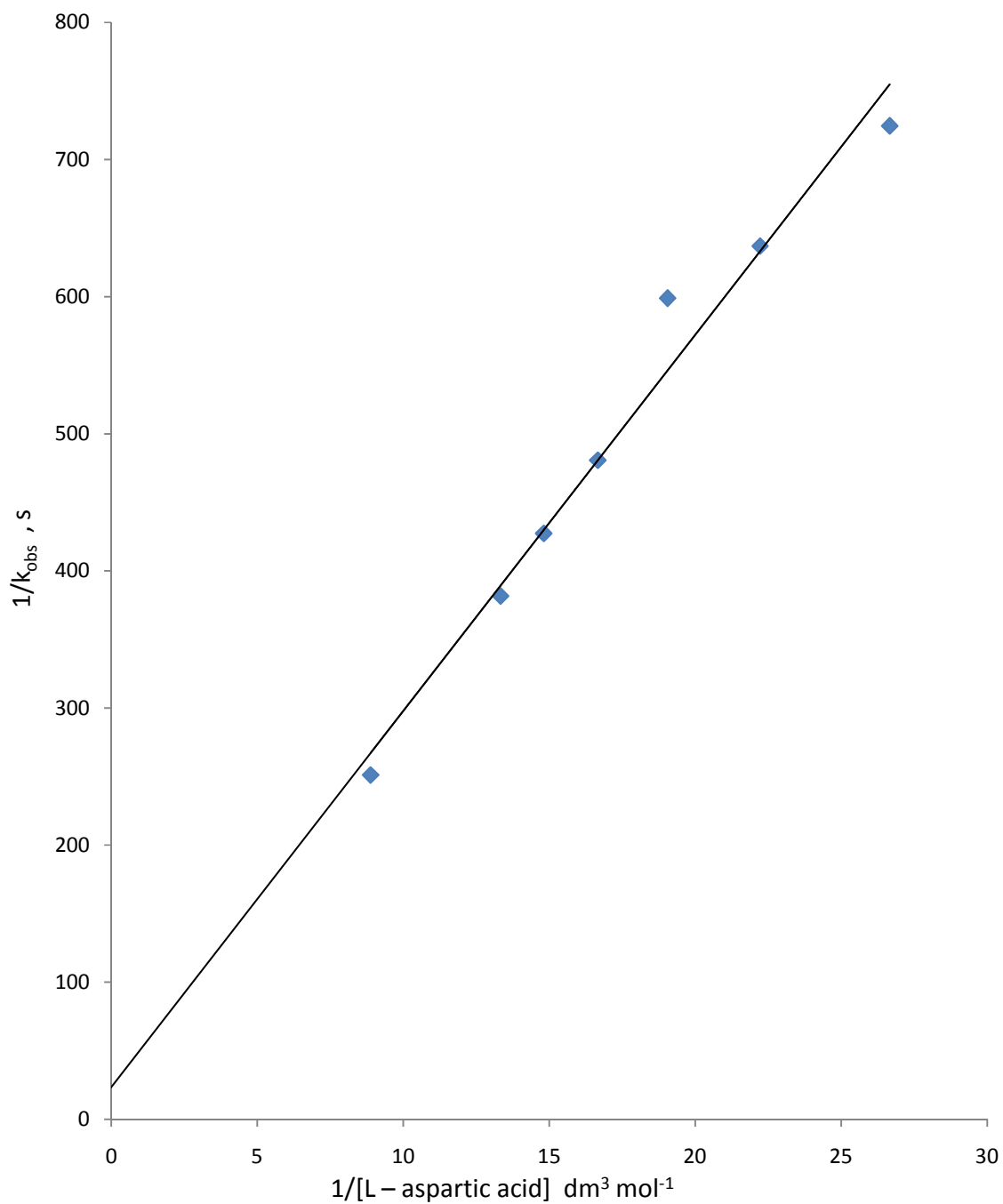


Figure 5: Michaelis – Menten’s plot of $1/k_{obs}$ versus $1/[H_2P]$ for the redox reaction of permanganate ion and H_2P .

Table 2: Rate constant for the effect of cations and anions in redox reaction between MnO_4^- and L-aspartic acid, at $[MnO_4^-] = 1.5 \times 10^{-4} \text{ mol dm}^{-3}$, $[H_2P] = 7.50 \times 10^{-2} \text{ mol dm}^{-3}$, $I = 1.0 \text{ mol dm}^{-3}$, $[H^+] = 0.2 \text{ mol dm}^{-3}$ at $T = 29.0 \pm 1.0^\circ\text{C}$

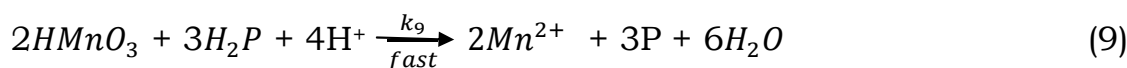
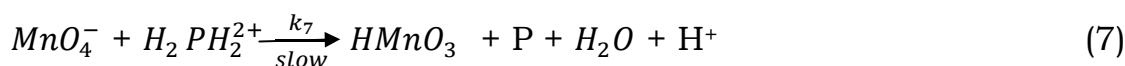
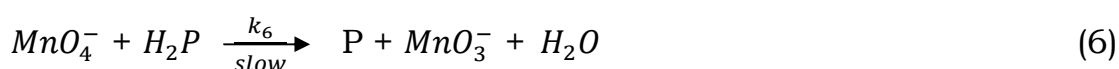
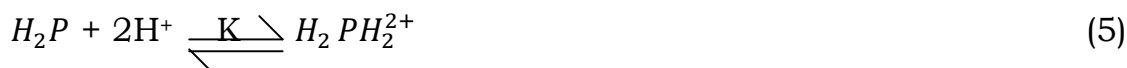
$10^4 [NO_3^-]_{\text{mol dm}^{-3}}$	$10^3 k_{\text{obs}}, s^{-1}$	$10^2 k_2, \text{dm}^3 \text{mol}^{-1} s^{-1}$
5	2.49	3.32
25	2.28	3.04
75	2.06	2.75
100	1.65	2.20
$10^4 [Cl^-]$		
5	2.53	3.37
25	2.35	3.13
75	2.12	2.83
100	1.82	2.43
$10^4 [Li^+]$		
5	2.88	3.84
25	3.32	4.43
75	3.57	4.76
100	3.60	4.80
$10^4 [Mg^{2+}]$		
5	2.83	3.77
25	3.16	4.21
75	3.39	4.52
100	3.27	4.36

Test for intermediate complex formation:

Spectroscopic studies indicate no shift from the absorption maxima of 525nm characteristic of MnO_4^- . This indicated absence of the formation of an intermediate complex suggesting probably the presence of outer-sphere mechanism in the reaction. Plot of $1/k_{\text{obs}}$ versus $1/[H_2P]$ as linear with an intercept, this suggest the presence of inner-sphere electron transfer in the system (Figure 5).

Polymerization test: Acrylamide was added to the partially oxidized reaction mixture of the MnO_4^- and H_2P . No gel formation was observed even on addition of a large excess of methanol. This suggests absence of free radical in the reaction mixture.

Proposed Mechanism: Based on the result of our investigation under the acid condition used for the stoichiometry and kinetic studies, the reaction scheme consistent with the observed data proposed for the reaction is as below.



Equation 6 and 7 are the rate determining steps

$$\text{Rate} = k_6[\text{MnO}_4^-][\text{H}_2\text{P}] + k_7[\text{MnO}_4^-][\text{H}_2\text{PH}_2^{2+}] \quad (10)$$

From equation(5)

$$[\text{H}_2\text{PH}_2^{2+}] = K[\text{H}_2\text{P}][\text{H}^+]^2 \quad (11)$$

Substitute $K[\text{H}_2\text{P}][\text{H}^+]^2$ for $[\text{H}_2\text{PH}_2^{2+}]$ in equation(10)
Therefore:

$$\text{Rate} = (k_6 + Kk_7[\text{H}^+]^2)[\text{MnO}_4^-][\text{H}_2\text{P}] \quad (12)$$

Equation(12) is similar to equation(4) Mechanisms which is similar to above were proposed by earlier researchers[18-20].

CONCLUSION

The electron transfer reaction of H_2P and MnO_4^- in tetraoxosulphate(VI) acid have been carried out. There was consistency between the proposed mechanism and the empirical kinetic data, there was catalysis of rate when NO_3^- , Cl^- , Li^+ and Mg^{2+} were added and the reaction displayed positive salt effect. The reaction followed both outer and inner-sphere mechanistic pathways.

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