

acids by aqueous alkaline permanganate. A scan through existing literature reveals lack of work on permanganate with L(+) Aspartic acid in alkaline medium. Herein we report the results of the study of oxidation of L(+) Aspartic acid by alkaline permanganate.

### EXPERIMENTAL

Reagent grade chemicals and doubly distilled water was used throughout this work. Stock solution of L(+) Aspartic acid (L(+) Asp) (S.D.fine-Chem) is made by dissolving the appropriate amounts of sample in doubly distilled water. The stock solution of potassium permanganate and potassium manganate were prepared and standardized as described in Chapter I (p. 42).

All other reagents were of analytical grade and their solutions were prepared by dissolving requisite amounts of the samples in doubly distilled conductivity water. NaOH and NaClO<sub>4</sub> were used to provide the required alkalinity and to maintain ionic strength respectively.

#### *Kinetic Procedure*

All kinetic measurements were performed under

pseudo-first order conditions where [L(+) Aspartic acid] was at least 10 fold excess over [permanganate ion] at a constant ionic strength of  $2.0 \text{ mol dm}^{-3}$ . The reaction was initiated by mixing previously thermostatted solutions of  $\text{MnO}_4^-$  and L(+) Aspartic acid which also contained required quantities of NaOH and  $\text{NaClO}_4$ . The temperature was uniformly maintained at  $26.7 \pm 0.1^\circ \text{C}$ . The course of reaction was followed by monitoring the decrease in the absorbance of  $[\text{MnO}_4^-]$ , in a 1 cm quartz cell of Hitachi 150-20 spectrophotometer, at its absorption maximum 526 nm where all other constituents of the reaction mixture have negligible absorption, as a function of time. The application of Beer's law for permanganate at 526 nm had earlier been verified, giving  $\epsilon = 2083 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  (literature  $\epsilon = 2200$ ) as in Chapter I (p. 43). The first order rate constants,  $k_{(\text{obs})}$ , were evaluated by plots of  $\log[\text{permanganate}]$  versus time. The reaction was followed more than two half-lives completion of reaction and  $k_{(\text{obs})}$  were reproducible within  $\pm 5\%$  error. An example run is given in Table III(i) (p. 117) and its plot is given in Fig.III(i) (p. 118). The spectral changes during this reaction are shown in Fig.III(ii) (p. 119).

In the course of measurements the colour of the solution

Table III(1)

Alkaline permanganate oxidation of L(+) Aspartic acid at  
26.7°C

Example run

$$[\text{Mn(VII)}] = 3.0 \times 10^{-4};$$

$$[\text{L(+) Asp}] = 3.0 \times 10^{-3};$$

$$[\text{OH}^-] = 1.0;$$

$$l = 2.0/\text{mol dm}^{-3};$$

Time	Optical density	[Mn(VII)]
min.	Abs	$\times 10^4$ mol dm <sup>-3</sup>
0	0.415	1.99
1	0.294	1.41
2	0.208	0.99
3	0.150	0.72
4	0.109	0.52
5	0.081	0.38
6	0.058	0.27
7	0.041	0.19

Figure III(i)

First order plot: on oxidation of L(+) Aspartic acid by  
alkaline permanganate  
(Conditions as in Table III(i) p. 117)

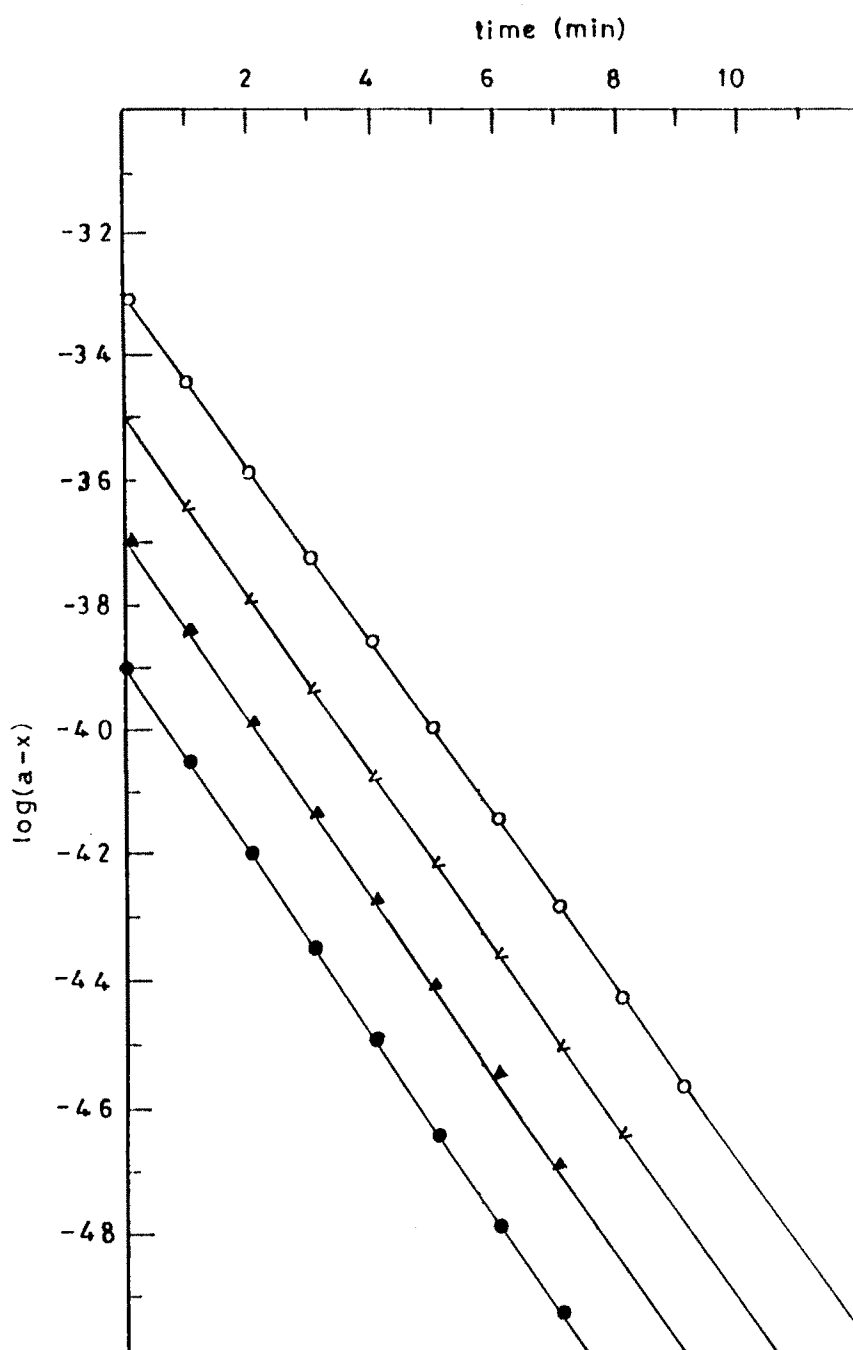
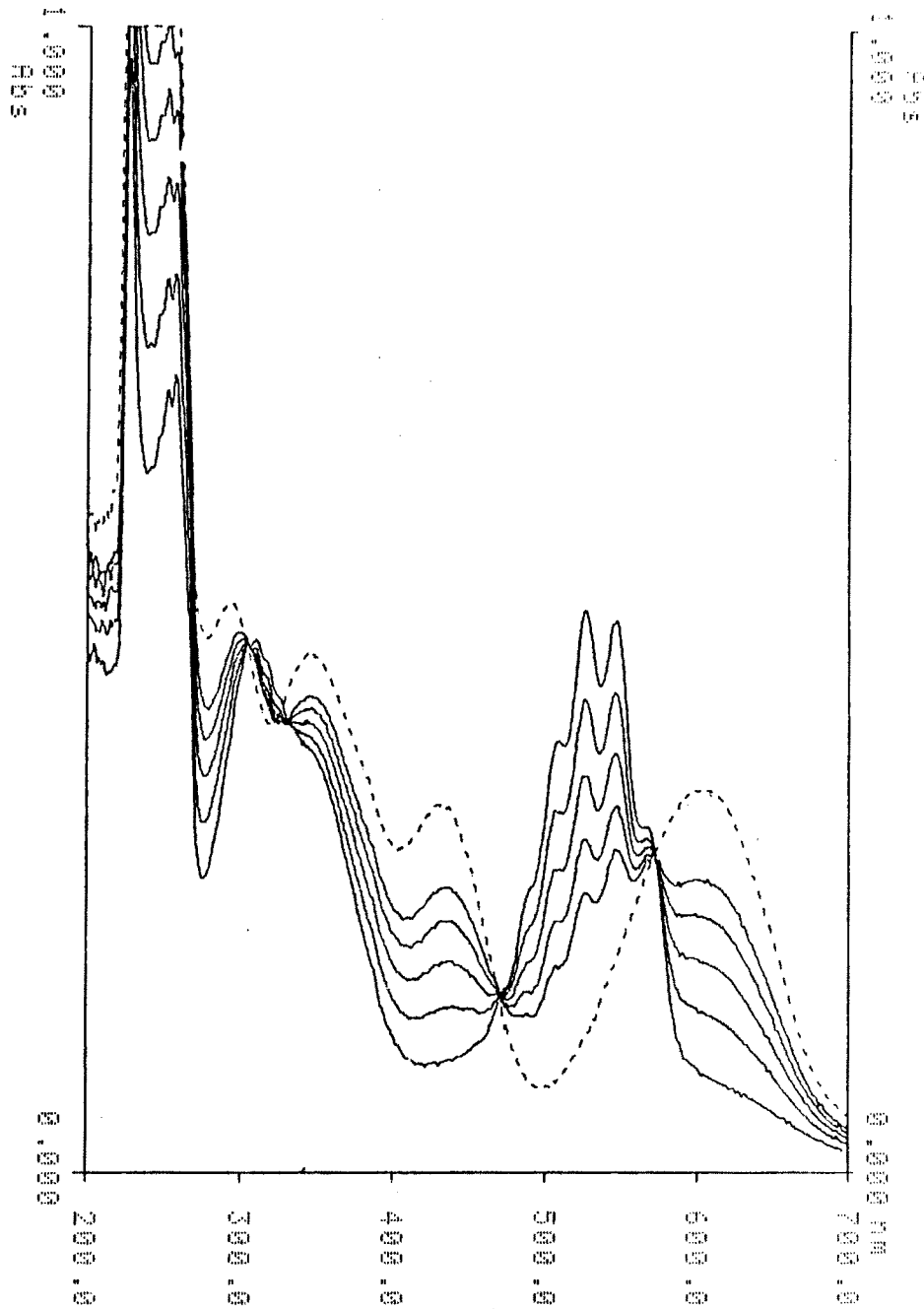


Figure III(11)

Spectral changes during the oxidation of L(+) Aspartic acid  
by alkaline permanganate  
(Conditions as in Table III(i) p. 117)



changed from violet to blue and further to green. The spectrum of green solution was identical to that of  $\text{MnO}_4^{2-}$ . No effect of dissolved oxygen on the rate of reaction was found.

## RESULTS

### *Stoichiometry*

The reaction mixture containing the excess permanganate concentration over L(+) Aspartic acid in presence of  $1.0 \text{ mol dm}^{-3}$  NaOH adjusted to a constant ionic strength of  $2.0 \text{ mol dm}^{-3}$ , was kept at room temperature. After the elapse of reaction, solid KI was added, following acidification by  $\text{H}_2\text{SO}_4$  (10%). Then remaining permanganate was titrated against standard sodium thiosulphate as in Chapter I (p. 49). The results indicated that two moles of permanganate consumed one mole of L(+) Aspartic acid which is shown by equation (1) (Table III(ii) p. 121). Product identification was done as in Chapter I (p. 50) and identified products are corresponding aldehyde, 2-Carboxyethanal, ammonia and manganese. It is obvious from Fig. III(ii) (p. 119) that the  $[\text{Mn(VII)}]$  decreases at 526 nm where as the  $[\text{Mn(VI)}]$  increases at 608 nm during the course of the reaction. It was further observed that the aldehyde does not undergo further oxidation

**Table III(ii)**  
**Stoichiometry of oxidation of L(+) Aspartic acid by**  
**alkaline permanganate**

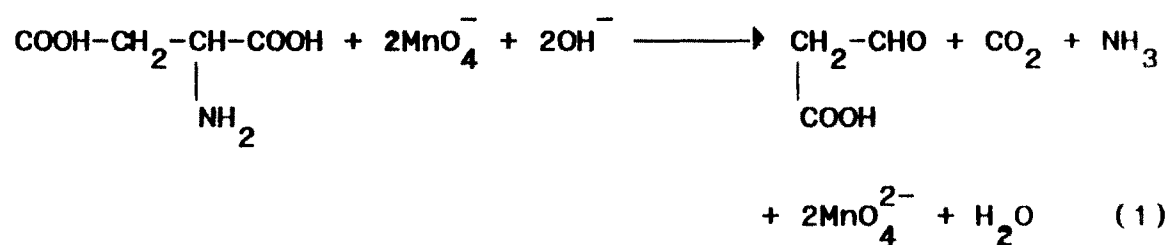
$[\text{OH}^-] = 1.0;$

$I = 2.0/\text{mol dm}^{-3}$

Taken		Found
$[\text{MnO}_4^-]$ $\times 10^4$ $\text{mol dm}^{-3}$	[L(+) Asp] $\times 10^4$ $\text{mol dm}^{-3}$	$[\text{MnO}_4^-]$ $\times 10^4$ $\text{mol dm}^{-3}$
4.0	2.0	0.0
6.0	2.0	2.1
10.0	3.0	3.9
15.0	5.0	5.2

Error  $\pm 5\%$

under the present kinetic conditions. The test for probable oxidation product of aldehyde, acid was negative.



#### REACTION ORDER

The reaction orders were determined from the slopes of  $\log k_{(\text{obs})}$  versus  $\log(\text{concentration})$  plots by varying the concentration of oxidant, reductant and alkali in turn, while keeping others constant.



### *Effect of Varying [Permanganate Ion]*

Keeping constant concentration of L(+) Aspartic acid, sodium hydroxide and sodium perchlorate as given in Table III (iii) (p. 124), the [permanganate ion] was varied in the concentration range  $0.5 \times 10^{-4}$  to  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup> as mentioned in Table III(iii) (p. 124). The constancy in the rate constant ( $k_{(obs)}$ ) values and linearity of the plot of  $\log(\text{concentration})$  against time over more than 90% completion of the reaction as shown in Fig.III(i) (p. 118) indicates the order is unity with respect to [Mn(VII)].

### *Effect of Varying [L(+) Aspartic Acid]*

At various [L(+) Aspartic acid] in the range  $0.6 \times 10^{-3}$  to  $6.0 \times 10^{-3}$  mol dm<sup>-3</sup> and at fixed  $[\text{MnO}_4^-]$ , [alkali] and ionic strength as given in Table III(iii) (p. 124) the order in [L(+) Asp] was found to be unity as the plot of  $k_{(obs)}$  versus [L(+) Aspartic acid] passes through the origin. Also, the slope of  $\log k_{(obs)}$  versus  $\log[\text{L}(+) \text{ Aspartic acid}]$  was found to be unity as shown in Fig.III(iii) (p. 125) which confirms the order in [L(+) Aspartic acid] as unity. Moreover, the values of  $k_{(obs)}/[\text{L}(+) \text{ Aspartic acid}]$  were found to be almost constant at different concentrations of L(+) Aspartic acid.

Table III(iii)

Effects of variation of  $[\text{MnO}_4^-]$ ,  $[\text{L}(+) \text{ Asp}]$  and  $[\text{OH}^-]$  on  
oxidation of L(+) Aspartic acid by alkaline permanganate  
at  $26.7^\circ\text{C}$

$$I = 2.0 \text{ mol dm}^{-3};$$

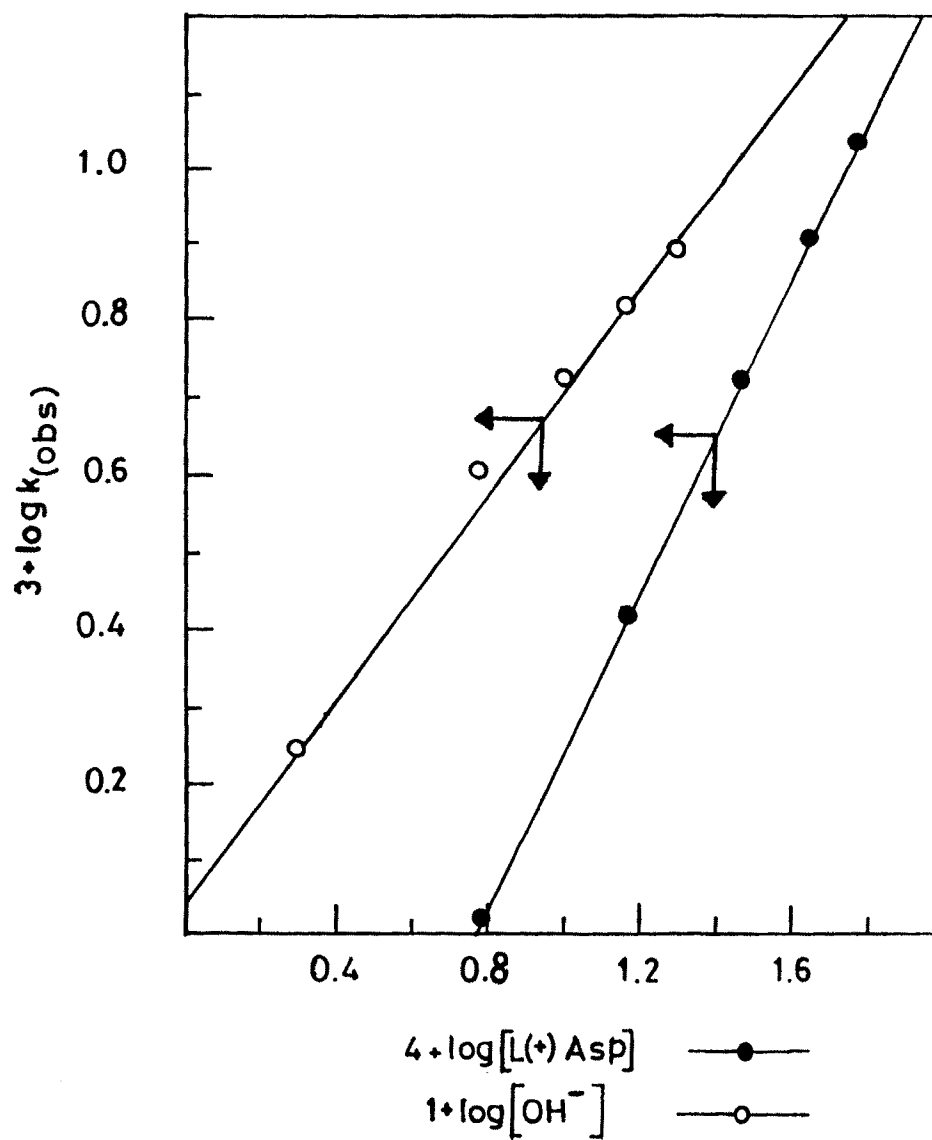
$[\text{MnO}_4^-]$ $\times 10^4$ $\text{mol dm}^{-3}$	$[\text{L}(+) \text{ Asp}]$ $\times 10^3$ $\text{mol dm}^{-3}$	$[\text{OH}^-]$ $\text{mol dm}^{-3}$	$k_{(\text{obs})}$ $\times 10^3$ $\text{s}^{-1}$	
			Expt.*	Calcd.*
0.5	3.0	1.0	5.37	5.36
1.5	3.0	1.0	5.36	5.36
3.0	3.0	1.0	5.32	5.36
4.0	3.0	1.0	5.35	5.36
5.0	3.0	1.0	5.34	5.36
3.0	0.6	1.0	1.06	1.07
3.0	1.5	1.0	2.60	2.68
3.0	3.0	1.0	5.34	5.36
3.0	4.5	1.0	8.10	8.04
3.0	6.0	1.0	10.70	10.70
3.0	3.0	0.2	1.73	1.67
3.0	3.0	0.6	4.01	3.92
3.0	3.0	1.0	5.30	5.36
3.0	3.0	1.5	6.51	6.57
3.0	3.0	2.0	7.57	7.57

Error  $\pm 5\%$ 

\* Experimental and Calculated.

Figure III(111)

Order in  $[L(+)\text{ Asp}]$  and  $[\text{OH}^-]$ : on oxidation of  $L(+)$  Aspartic acid by alkaline permanganate  
(Conditions as in Table III(111) p. 124)



#### *Effect of Varying [Alkali]*

At constant concentration of permanganate, L(+) Aspartic acid and ionic strength, the alkali concentration was varied from 0.20 to 2.0 mol dm<sup>-3</sup> as mentioned in Table III(iii) (p. 124) it is found that the rate of reaction increased with increase in [OH<sup>-</sup>] as shown in Table III(iii) (p. 124). The order with respect to alkali was found to be less than unity from the Fig.III(iii) (p. 125).

#### *Effect of varying ionic strength*

The ionic strength of the reaction medium was varied from 1 to 4 mol dm<sup>-3</sup> by using sodium perchlorate at constant [MnO<sub>4</sub><sup>-</sup>] = 3.0 × 10<sup>-4</sup>, [L(+) Asp] = 3.0 × 10<sup>-3</sup> and [OH<sup>-</sup>] = 1.0/mol dm<sup>-3</sup> as mentioned in the Table III(iv) (p. 127). It was found that rate of reaction enhanced with increasing concentration of NaClO<sub>4</sub> as shown in the Table III(iv) (p. 127) and the plot of log k<sub>(obs)</sub> versus I<sup>1/2</sup> was linear with positive slope as indicated in Fig.III(iv) (p. 128).

#### *Effect of Varying Solvent Polarity*

The effect of dielectric constant (D) of the reaction medium was studied by carrying out the kinetics in presence of

Table III(iv)

Effect of ionic strength (I) and solvent polarity (D) on oxidation of L(+) Aspartic acid by alkaline permanganate at 26.7°C.

$$[\text{Mn(VII)}] = 3.0 \times 10^{-4};$$

$$[\text{L-Glu}] = 3.0 \times 10^{-3};$$

$$[\text{OH}^-] = 1.0;$$

$$I = 2.0/\text{mol dm}^{-3};$$

I	k'	% of	D	k'
mol dm <sup>-3</sup>	× 10 <sup>3</sup> s <sup>-1</sup>	t-Butanol*		× 10 <sup>3</sup> s <sup>-1</sup>
1.0	3.51	1.0	77.82	3.23
1.5	4.10	2.0	77.47	4.75
2.0	5.36	3.0	77.14	7.52
3.0	7.23	4.0	75.79	11.23

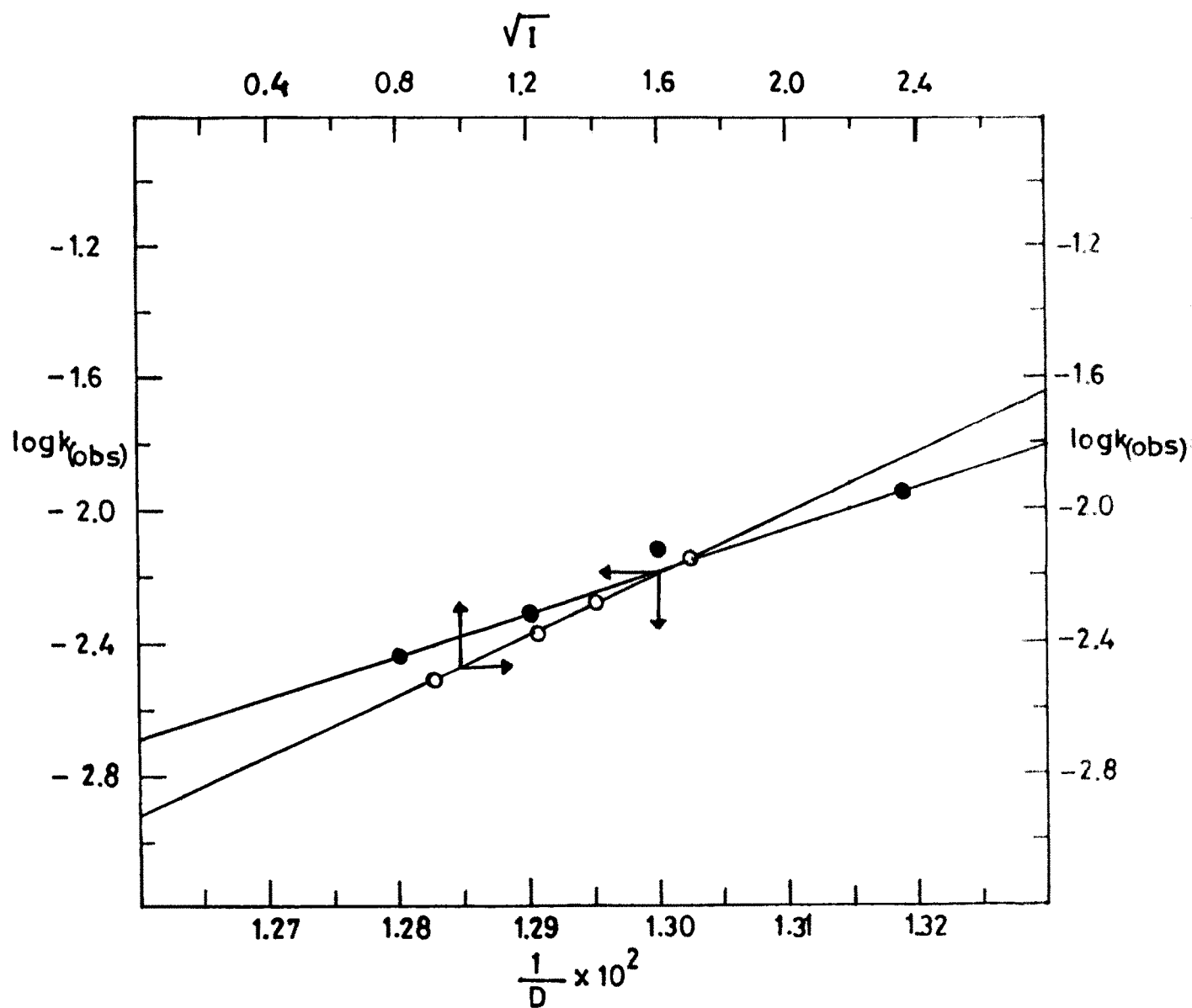
Error ± 5%

\* percentage of t-butanol in water (v/v)

Error ± 5%

Figure III(iv)

Effect of ionic strength (I) and solvent polarity (D): on  
oxidation of L(+) Aspartic acid by alkaline permanganate  
(Conditions as in Table III(iv) p. 127)



different quantities of t-butanol-water content. It was also found that t-butanol was not oxidized to any significant extent by the oxidant at our experimental conditions. During the study of effect of solvent on the kinetics, the ionic strength and rest of the conditions were kept constant. The dielectric constant of the reaction medium at different compositions of water and t-butanol were calculated as given in Chapter I (p. 57) and varied as in Table III(iv) (p. 127). The rate constant,  $k_{(obs)}$ , increased with decrease in dielectric constant of the medium. The plot of  $\log k_{(obs)}$  versus  $1/D$  was linear with positive slope as shown in Fig.III (iv) (p. 128).

#### *Effect of Initially Added Products*

The effect of initially added products such as potassium manganate, ammonia (in the form ammonium hydroxide) and aldehyde has been examined on the rate of reaction in concentration range  $0.50 \times 10^{-4}$  to  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>,  $0.40 \times 10^{-3}$  to  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup> and  $0.20 \times 10^{-3}$  to  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> as stated in the Table III(v) (p. 130) keeping all other conditions being constant. It was found that added products did not show any significant effect on the rate of the reaction

Table III(v)

Effect of manganate, ammonia and aldehyde: on oxidation  
of L(+) Aspartic acid by permanganate at 26.7° C.

$$[\text{Mn(VII)}] = 3.0 \times 10^{-4};$$

$$[\text{L-Glu}] = 3.0 \times 10^{-3};$$

$$[\text{OH}^-] = 1.0;$$

$$I = 2.0/\text{mol dm}^{-3};$$

$[\text{MnO}_4^{2-}]$ $\times 10^4$ $\text{mol dm}^{-3}$	[Ammonia] $\times 10^3$ $\text{mol dm}^{-3}$	[Aldehyde] $\times 10^3$ $\text{mol dm}^{-3}$	$k'$ $\times 10^3$ $\text{s}^{-1}$
0.5	-	-	5.27
1.5	-	-	5.32
2.0	-	-	5.23
4.0	-	-	5.33
5.0	-	-	5.29
-	0.4	-	5.26
-	0.8	-	5.28
-	1.3	-	5.32
-	2.0	-	5.25
-	3.5	-	5.31
-	-	0.2	5.24
-	-	0.8	5.31
-	-	1.2	5.29
-	-	1.6	5.32
-	-	2.0	5.33



### *Test For Free Radicals*

The intervention of free radicals in the reaction mixture was tested as follows: The reaction mixture to which a known quantity of acrylonitrile was added and kept for an hour in an inert atmosphere. On diluting the reaction mixture with methanol precipitate resulted suggesting the presence of free radical intervention in the reaction.

### *Effect of Temperature*

The rate of reaction was measured at different temperatures under varying  $[\text{OH}^-]$ . The rate of reaction increased with increase in temperature. The rate constant,  $k$ , of the slow step of the scheme 3 were obtained from the slope and intercept of  $L(+)$  Aspartic acid/ $k_{(\text{obs})}$  versus  $1/[\text{OH}^-]$  at different temperatures. The values of  $k$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) were found to be  $4.0 \pm 0.20$ ,  $5.88 \pm 0.30$  and  $7.14 \pm 0.40$  at 299.7, 304.7 and 309.7 K respectively and these values are incorporated in the Table III(vi) (p. 132). From the slope of the plot of  $\log k$  versus  $1/T$  as shown in Fig.III(v) (p. 133) the activation parameters have been calculated as in Chapter I (p. 62) and are given in Table III(vii) (p. 134).

Table III(vi)

Effect of different temperatures on reaction constant of slow step of the mechanism on oxidation of L(+) Aspartic acid by alkaline permanganate

$$[\text{Mn(VII)}] = 3.0 \times 10^{-4};$$

$$[\text{L-Glu}] = 3.0 \times 10^{-3};$$

$$[\text{OH}^-] = 1.0;$$

$$I = 2.0/\text{mol dm}^{-3};$$

T	1/T $\times 10^3$	k	logk
K	K <sup>-1</sup>	dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	
299.7	3.33	4.00	0.602
304.7	3.28	5.88	0.769
309.7	3.22	7.14	0.853

Figure III(v)

Effect of different temperatures on reaction constant of slow step of the mechanism on oxidation of L(+) Aspartic acid by alkaline permanganate

(Conditions as in Table III(vi) p. 132)

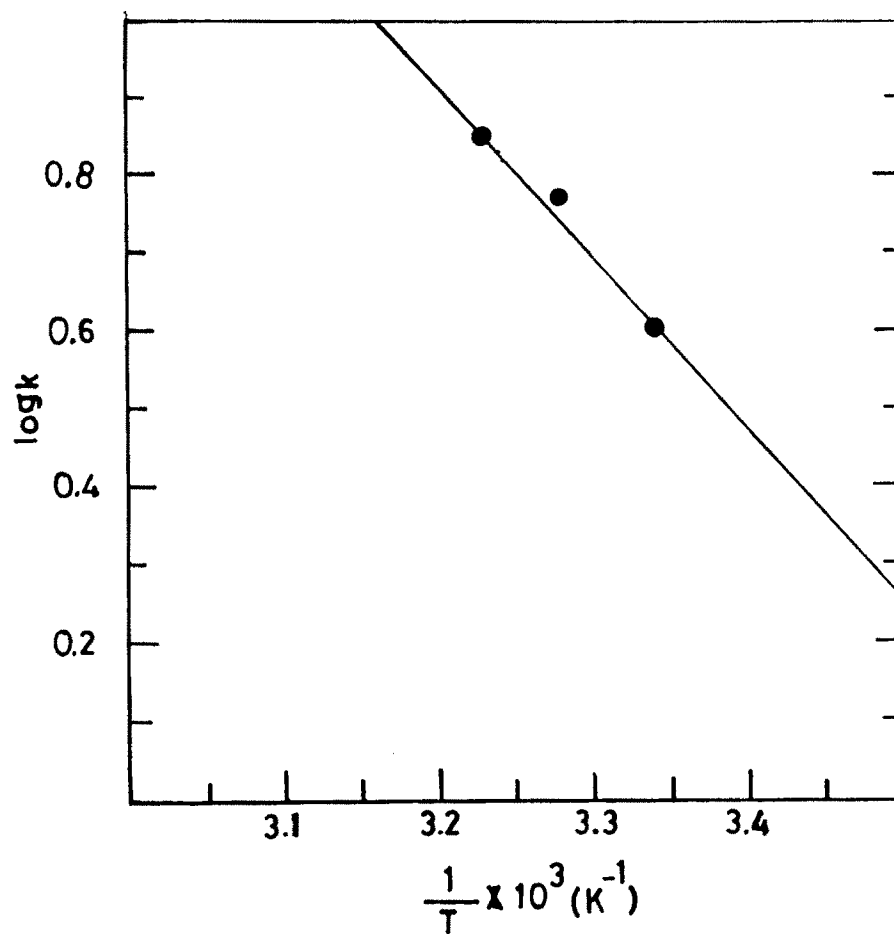


Table III(vii)

Activation parameters for the oxidation L(+) Aspartic acid  
by alkaline permanganate.

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Activation parameters w.r.t. slow step of reaction

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Ea	42.50 ± 2
(kJ mol <sup>-1</sup> )	
logA	7.40 ± 0.4
$\Delta S^\ddagger$	- 99.41 ± 5
(J K <sup>-1</sup> mol <sup>-1</sup> )	
$\Delta H^\ddagger$	39.97 ± 2
(kJ mol <sup>-1</sup> )	
$\Delta G^\ddagger$	69.72 ± 0.5
(kJ mol <sup>-1</sup> )	

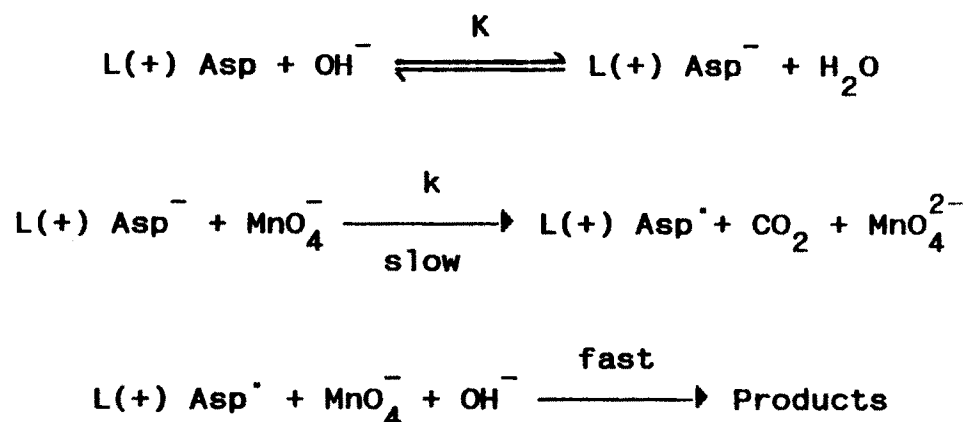
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Error ± 5%

## DISCUSSION

The permanganate ion,  $\text{MnO}_4^-$ , is a powerful oxidant in aqueous alkaline medium. As it exhibits multitude oxidation states, the stoichiometric results and pH of the reaction media play an important role. Under the present experimental condition at  $\text{pH} > 12$ , the reduction product of Mn(VII) being Mn(VI) is stable and further reduction of Mn(VI) might be stopped<sup>8</sup>. The Diode Array Rapid Scan Spectrophotometer (DARSS) studies have shown that at  $\text{pH} > 12$ , the product of Mn(VII) as Mn(VI) and no further reduction was observed as reported<sup>8</sup> by Jaky et al. However, on long standing green coloured Mn(VI) is reduced to tobacco coloured Mn(IV) slowly under our experimental conditions.

The reaction between permanganate and L(+) Aspartic acid in alkaline medium has a stoichiometry of 2:1 with first order dependence each in permanganate ion and L(+) Aspartic acid concentrations. The rate of reaction increased with increase in  $[\text{OH}^-]$ . No products effect has been observed. The observed kinetics and other results may be incorporated by the following mechanism (Scheme 3).



Scheme 3

The observed order of less than unity may be due to the substantial existence of L(+) Aspartic acid as an anionic form in alkaline medium<sup>10</sup>. The anionic form of L(+) Aspartic acid will react with active species of permanganate,  $\text{MnO}_4^-$ , to give a radical of L(+) Aspartic acid with decarboxylation, which further reacts with another molecule of permanganate species in a fast step to yield products. Since permanganate species is one electron oxidant in alkaline medium under the conditions of experiment, the reaction between L(+) Aspartic acid and permanganate ion would afford a radical intermediate. The presence of free radical was evidenced, by the initiation of polymerization of acrylonitrile monomer, which is also observed in earlier works<sup>9</sup> with amino acid as well.

Therefore,

$$\text{Rate} = k [\text{L}(+) \text{Asp}^-] [\text{MnO}_4^-] \quad (1)$$

$$\text{and } K = \frac{[\text{L}(+) \text{Asp}^-]}{[\text{L}(+) \text{Asp}] [\text{OH}^-]}$$

$$[\text{L}(+) \text{Asp}^-] = K [\text{L}(+) \text{Asp}] [\text{OH}^-]$$

Therefore equation (1) becomes

$$\text{Rate} = k K [\text{L}(+) \text{Asp}] [\text{OH}^-] [\text{MnO}_4^-] \quad (2)$$

The total concentration of L(+) Aspartic acid is given by

$$\begin{aligned} [\text{L}(+) \text{Asp}]_T &= [\text{L}(+) \text{Asp}]_f + [\text{L}(+) \text{Asp}^-] \\ &= [\text{L}(+) \text{Asp}]_f + K [[\text{L}(+) \text{Asp}] [\text{OH}^-]] \\ &= [\text{L}(+) \text{Asp}]_f \left\{ 1 + K [\text{OH}^-] \right\} \end{aligned} \quad (3)$$

similarly

$$[\text{OH}^-]_T = [\text{OH}^-]_f + [\text{L}(+) \text{Asp}^-]$$

$$\begin{aligned}
&= [\text{OH}^-]_f + K [[\text{L}(+) \text{ Asp}] [\text{OH}^-]] \\
&= [\text{OH}^-]_f + \left\{ 1 + [\text{L}(+) \text{ Asp}] \right\}
\end{aligned} \tag{4}$$

from (3) and (4)

$$[\text{L}(+) \text{ Asp}]_f = \frac{[\text{L}(+) \text{ Asp}]_T}{\{1 + K [\text{OH}^-]\}} \tag{5}$$

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]}{\{1 + K [\text{L}(+) \text{ Asp}]_T\}} \tag{6}$$

substituting equation (5) and (6) in equation (2), we have

$$\text{Rate} = \frac{k K [\text{L}(+) \text{ Asp}]_T [\text{OH}^-] [\text{MnO}_4^-]}{\left\{ 1 + K [\text{OH}^-]_T \right\} \left\{ 1 + K [\text{L}(+) \text{ Asp}]_T \right\}} \tag{7}$$

In equation (7) the term  $(1 + K [\text{L}(+) \text{ Asp}]_T)$  in denominator, in view of low concentration of  $\text{L}(+) \text{ Aspartic acid}$  used in the reaction, it approximates to unity.

$$\text{Rate} = \frac{k K [\text{L}(+) \text{ Asp}]_T [\text{OH}^-]_T [\text{MnO}_4^-]}{1 + K [\text{OH}^-]_T} \tag{8}$$



$$-\frac{d[\text{MnO}_4^-]}{dt} = \text{Rate} = \frac{k K [\text{L}(+) \text{ Asp}]_T [\text{OH}^-]_T}{1 + K [\text{OH}^-]_T} \quad (9)$$

$$\frac{\text{Rate}}{[\text{MnO}_4^-]} = k_{(\text{obs})} = \frac{k K [\text{L}(+) \text{ Asp}]_T [\text{OH}^-]_T}{1 + K [\text{OH}^-]_T} \quad (10)$$

The equation (10) may be rearranged which is suitable for verification as in equation (11).

$$\frac{[\text{L}(+) \text{ Asp}]}{k_{(\text{obs})}} = \frac{1}{k K [\text{OH}^-]} + \frac{1}{k} \quad (11)$$

According to above equation, that is, equation (11), the plot of  $[\text{L}(+) \text{ Asp}]/k_{(\text{obs})}$  against  $1/[\text{OH}^-]$  is expected to be linear with positive intercept which is shown in Fig.III(vi) (p. 140). The slope and intercept of such plot lead to the values of  $k$  and  $K$  at  $26.7^\circ\text{C}$  as  $4.0 \pm 0.20 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $0.809 \pm 0.04 \text{ dm}^3 \text{ mol}^{-1}$  respectively. These constants were used to calculate the rate constants under different experimental conditions. There is a reasonable agreement between the calculated and observed rate constants (Table III(iii) p. 124).

The effect of increasing ionic strength on the rate qualitatively explains the reaction between two negatively charged ions, as seen in scheme 3. However, increasing the content of *t*-butyl alcohol in the reaction medium leads to increase in the rate of reaction, is contrary to the expected slower reaction between like ions in the media of lower relative permittivity. Perhaps the effect is countered substantially by the formation of active reaction species to a greater extent in low relative permittivity media leading to the net increase in rate<sup>11</sup>. The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were both favourable for electron absorption processes. The favourable enthalpy was due to release of energy on solution of changes in the transition state. The values of  $\Delta S^\ddagger$  within the range for radical reactions have been ascribed<sup>12</sup> to the nature of electron pairing and electron unpairing processes, and to the loss of degrees of freedom, formerly available to the reactions on the formation of rigid transition state. It is also interesting to note that, the oxidant species  $[\text{MnO}_4^-]$  required the pH > 12 and below which system gets disturbed and the reaction will proceed further to give reduced product of oxidant as Mn(IV) which develops tobacco coloured turbidity slowly. Thus it becomes apparent that in carrying out this

reaction the role of pH in the reaction medium is crucial.

### Findings

The stoichiometry of this reaction is 2:1 in oxidant to reductant. The order in both oxidant and reductant is unity. Added products have no significant effect on the rate of reaction. However, increase in ionic strength enhances the rate of reaction.

### Importance of the results of Chapter III

It is important note that alkaline permanganate reactions should be carried out at  $\text{pH} > 12$  and below which the reaction system gets disturbed due to the formation of colloidal solution by reductant and the reaction will proceed further to give the reduced product of oxidant as Mn(IV) which turns to tobacco coloured turbidity slowly. Thus it is obvious that in carrying out this reaction the role of pH in the reaction medium is important.

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