

been reported on the oxidation of L-Alanine by permanganate ion in aqueous alkaline medium, the details of the study is given in this Chapter.

EXPERIMENTAL

Stock solution of L-Alanine (L-Ala) (S.D.fine-Chem) was prepared by dissolving the sample in doubly distilled water. The preparation of stock solution of potassium permanganate and potassium manganate and their standardization was as given in Chapter I (p. 42).

All other reagents were of analytical grade and their solutions were prepared by dissolving the samples in doubly distilled conductivity water. NaOH and NaClO₄ were employed to provide the required alkalinity and to ionic strength.

Kinetic Procedure

All kinetic measurements were carried out under pseudo-first order conditions where [L-Alanine] was at least ten fold excess over [permanganate ion] at a constant ionic strength of 1.0 mol dm⁻³. The reaction was initiated by mixing previously thermostatted solutions of MnO₄⁻ and L-Alanine which also contained the required quantities of NaOH and NaClO₄ to

maintain required alkalinity and ionic strength respectively. The temperature was uniformly maintained at $27.0 \pm 0.1^\circ\text{C}$. The course of reaction was followed by monitoring the decrease in the absorbance of MnO_4^- , in a 1 cm. quartz cell of Hitachi 150-20 spectrophotometer, at its absorption maximum 526 nm as function of time. At this wavelength all other constituents of the reaction mixture have negligible absorbances. The application of Beer's law for permanganate at 526 nm had earlier been verified (giving $\epsilon = 2083 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) as in Chapter I (p. 44). The first order rate constants $k_{(\text{obs})}$ were evaluated by plots of $\log[\text{permanganate}]$ versus time. The reaction was followed in almost all the experiment to more than 90% completion and the first order plots were linear upto 85% completion of the reaction and $k_{(\text{obs})}$ were reproducible within $\pm 5\%$. An example run is given in Table II(i) (p. 83) and its plot is shown in Fig.II(i) (p. 84). The spectral changes during the oxidation of L-Alanine by alkaline permanganate are shown in Fig.II(ii) (p. 85).

In the course of measurements the colour of the solution changed from violet to blue and further to green. The spectrum of green solution was identical to that of MnO_4^{2-} . No

Table II(1)

Oxidation of L-Alanine by alkaline permanganate
at 27.0°c

Example run

$$[\text{Mn(VII)}] = 2.30 \times 10^{-4};$$

$$[\text{L-Ala}] = 2.0 \times 10^{-3};$$

$$[\text{OH}^-] = 0.30;$$

$$l = 1.0/\text{mol dm}^{-3};$$

Time	Optical density	[Mn(VII)]
min	Abs	$\times 10^4$ mol dm ⁻³
0.0	0.469	2.25
0.2	0.446	2.14
0.4	0.427	2.04
0.6	0.410	1.96
0.8	0.395	1.89
1.0	0.381	1.82
2.0	0.322	1.54
3.0	0.275	1.32
4.0	0.238	1.14
5.0	0.207	0.99
6.0	0.181	0.86
7.0	0.160	0.76
8.0	0.141	0.67
10.0	0.115	0.55
11.0	0.105	0.50
12.0	0.097	0.46
13.0	0.088	0.42

Figure II(i)
First order plot: on oxidation of L-Alanine by alkaline permanganate
(Conditions as in Table II(i) p. 83)

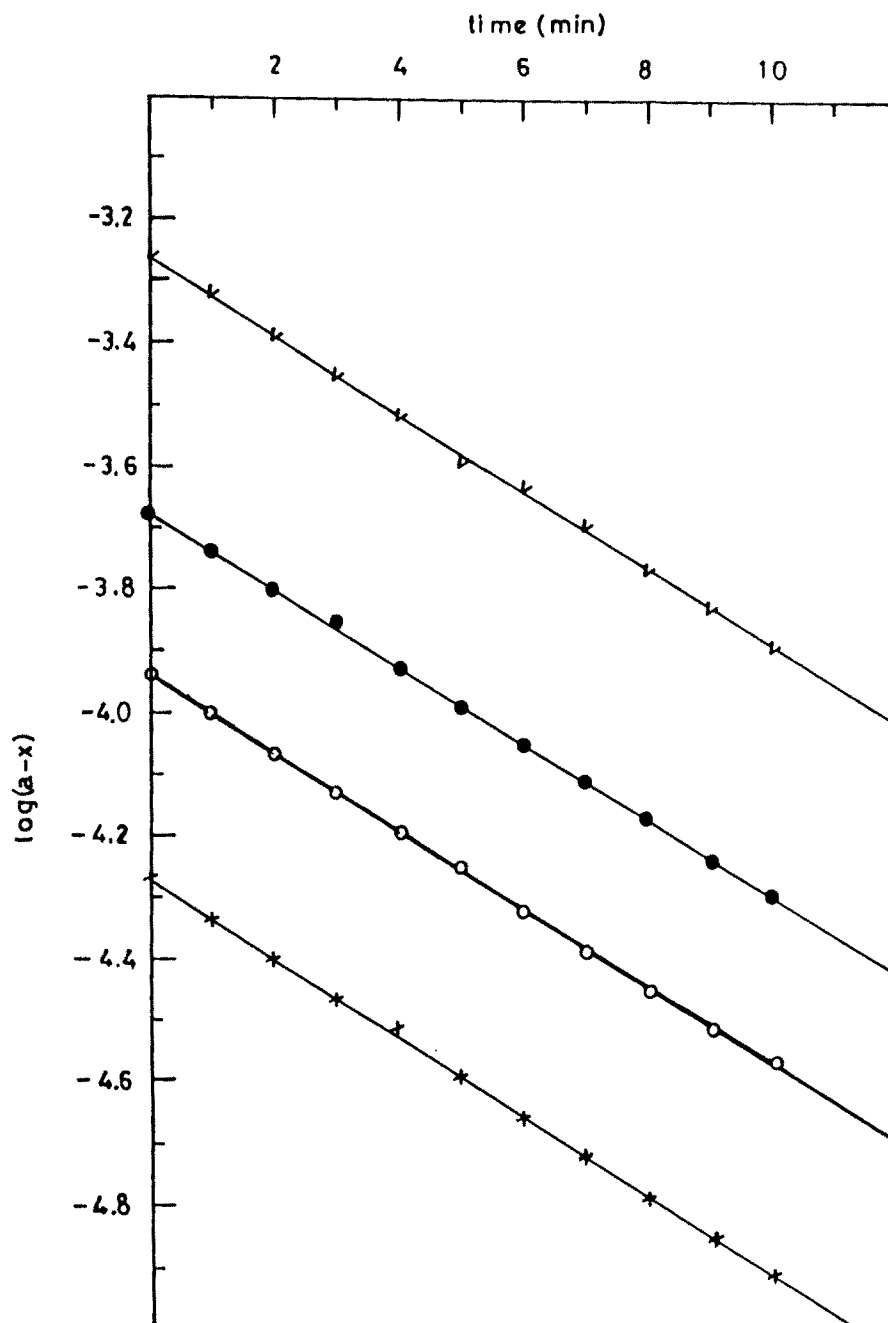
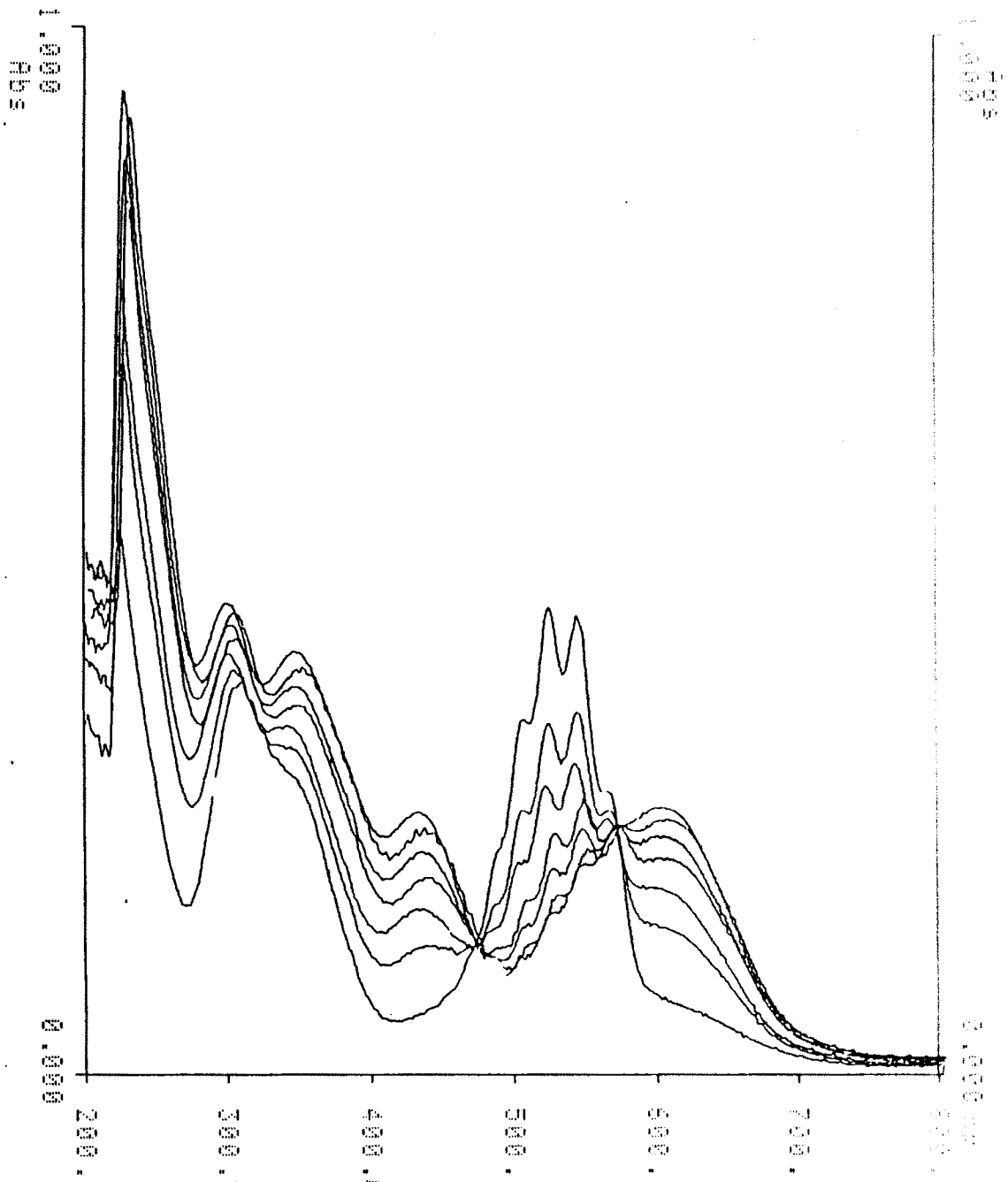


Figure II(11)

Spectral changes during the oxidation of L-Alanine by alkaline permanganate
(Conditions as in Table II(1) p. 83)



effect of dissolved oxygen on the reaction rate was found.

RESULTS

Stoichiometry

The reaction mixture containing the excess permanganate concentration over L-Alanine concentration were mixed in presence of 0.3 mol dm^{-3} NaOH adjusted to a constant ionic strength of 1.0 mol dm^{-3} was kept at 27.0° for about an hour. After the completion of reaction, solid KI was added, following acidification by H_2SO_4 (10%). Then remaining permanganate was titrated against previously standardized sodium thiosulphate¹⁰. The results showed that two moles of MnO_4^- consumed one mole of L-Alanine as given by equation (1). (Table II(ii) p. 87). The main oxidation products were identified as acetaldehyde¹¹ by spot test and ammonia¹² by Nessler's reagent and manganate. Such products were also obtained in previous work⁹. It is evident from Fig.II(ii) (p. 85) that the concentration of permanganate decreases at 526 nm where as concentration of manganate increases at 608 nm during the course of the reaction. It was observed that the acetaldehyde does not undergo further oxidation under the

Table II(ii)
Stoichiometry* of oxidation of L-Alanine by alkaline permanganate

$[\text{OH}^-] = 0.30$

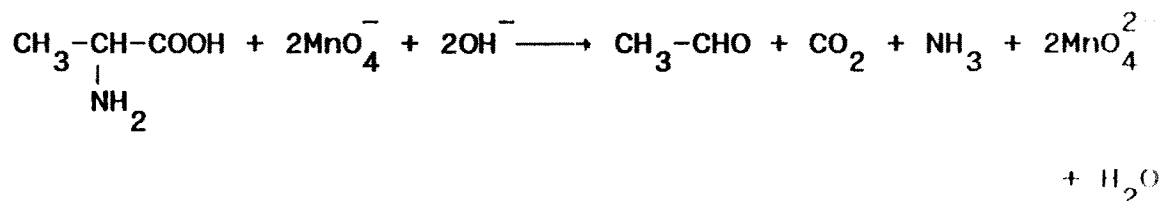
$I = 1.0/\text{mol dm}^{-3}$

Taken		Found
$[\text{MnO}_4^-]$	$[\text{L-Ala}]$	$[\text{MnO}_4^-]$
$\times 10^4$	$\times 10^4$	$\times 10^4$
4.0	1.0	2.0
6.0	2.0	1.9
8.0	2.0	4.1
12.0	3.0	6.0

* All concentrations are in mol dm^{-3}

Error $\pm 5\%$

present kinetic conditions. Test for corresponding 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]

At fixed [substrate], [alkali] and ionic strength, the [oxidant] was varied in the range 5.5×10^{-5} to 5.5×10^{-4} mol dm⁻³ as given in Table II(iii) (p. 90). The non-variation in the rate constant, ($k_{(\text{obs})}$), values as given in Table II(iii) (p. 90) and linearity of the plot of $\log(\text{concentration})$ against time over more than 90% completion of the reaction as shown in Fig.II(i) (p. 84) indicates that the order is unity with respect to [Mn(VII)].

Effect of Varying [L-Alanine]

Keeping all other conditions constant, the substrate, L-Alanine, was varied in the concentration range 5.0×10^{-4} to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ as given in Table II(iii)(p. 90). It was found that rate of reaction increased with increase in concentration of L-Alanine as shown in the Table II(iii) (p. 90). From the plot of $\log(k_{(obs)})$ versus $\log[\text{L-Ala}]$, the order in [L-Alanine] was found to be less than unity as shown in the Fig.II(iii) (p. 91).

Effect of Varying [Alkali]

At constant [oxidant], [substrate] and ionic strength, the [alkali] was varied in the range 0.1 to 1.0 mol dm^{-3} as given in Table II(iii) (p. 90). It was found that rate constant, $k_{(obs)}$, increases with increase in concentration of alkali as shown in Table II(iii) (p. 90) and the from the plot of $\log k_{(obs)}$ versus $\log[\text{OH}^-]$ the order in alkali was found to be less than unity as indicated in Fig.II(iii) (p. 91).

Table II(111)

Effect of variation of [L-Ala], [Mn(VII)] and [OH⁻] on
oxidation of L-Alanine by alkaline permanganate at 27.0°C

$$I = 1.0/\text{mol dm}^{-3};$$

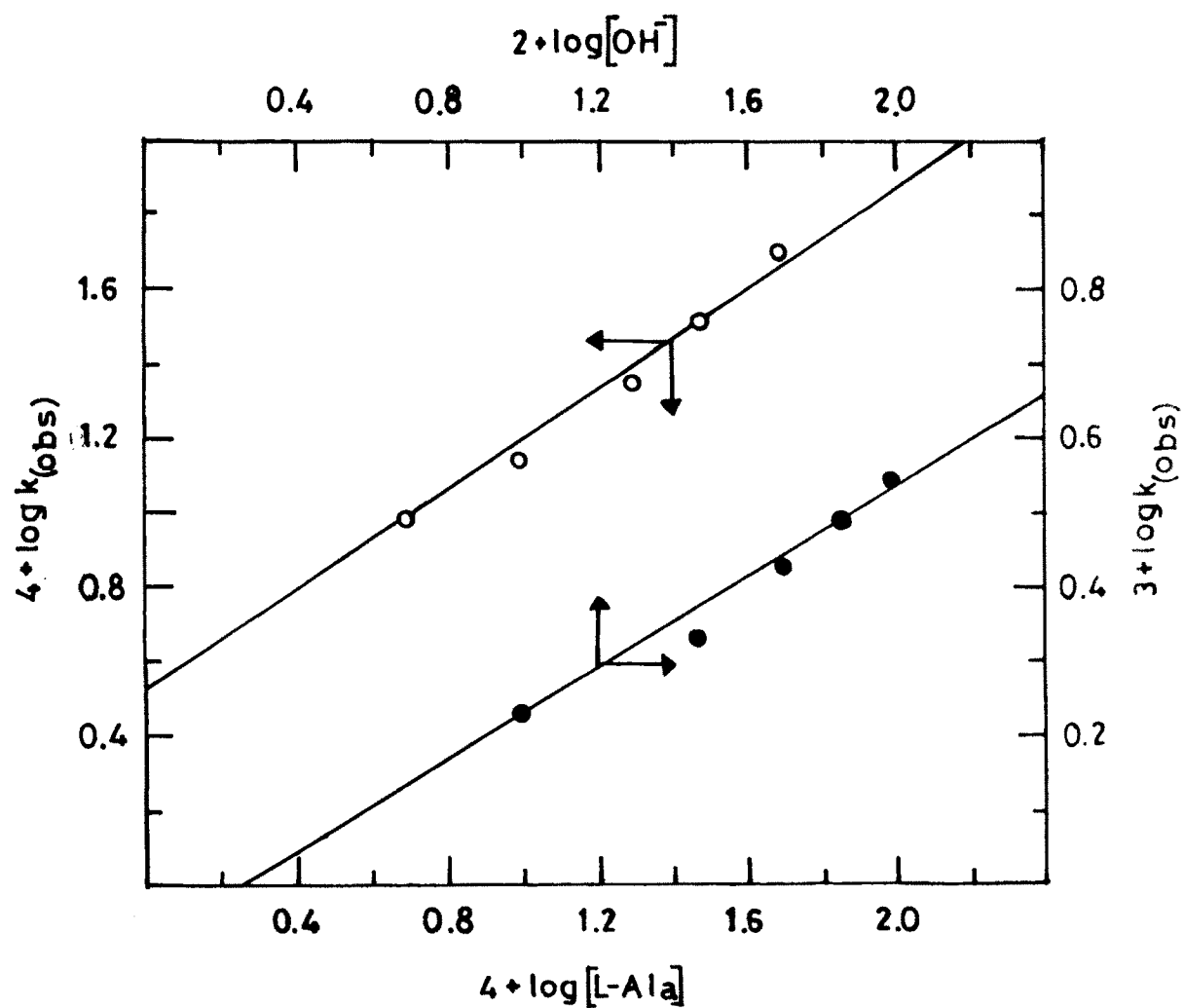
[L-Ala] x 10 ³ mol dm ⁻³	[MnO ₄ ⁻] x 10 ⁴ mol dm ⁻³	[OH ⁻] mol dm ⁻³	k _(obs) x 10 ³ s ⁻¹	
			* Exptl.	* Calcd.
0.5	2.30	0.30	0.96	0.92
1.0	2.30	0.30	1.45	1.39
2.0	2.30	0.30	2.30	2.35
3.0	2.30	0.30	3.30	3.29
5.0	2.30	0.30	5.20	5.18
2.0	0.55	0.30	2.40	2.35
2.0	1.20	0.30	2.35	2.35
2.0	2.30	0.30	2.30	2.35
2.0	3.50	0.30	2.40	2.35
2.0	5.50	0.30	2.40	2.35
2.0	2.30	0.10	1.80	1.80
2.0	2.30	0.30	2.30	2.35
2.0	2.30	0.50	2.70	2.69
2.0	2.30	0.70	3.10	3.02
2.0	2.30	1.00	3.50	3.49

Error ± 5%

* Experimental and Calculated.

Figure II(iii)

Order in [L-Ala] and $[\text{OH}^-]$ on oxidation of L-Alanine by
alkaline permanganate
(Conditions as in Table II(iii) p. 90)



Effect of Initially Added Products

Keeping all other conditions and reactants concentrations being constant, the addition of products manganate, acetaldehyde and ammonia was varied in the concentration range 5.5×10^{-5} to $5.5 \times 10^{-4} \text{ mol dm}^{-3}$, 0.30×10^{-3} to $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ and 0.4×10^{-3} to $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ as given in the Table II(iv) (p. 93). No significant effect is observed on the rate of reaction.

Effect of Varying Ionic Strength

The ionic strength of reaction medium was varied from 0.3 to 1.0 mol dm^{-3} at constant concentrations of permanganate, L-Alanine and alkali as shown in Table II(v) (p. 95). It was found that the rate constant enhances with increasing concentration of NaClO_4 and the plot of $\log(k_{\text{obs}})$ versus $I^{1/2}$ was linear with positive slope as shown in the Fig.II(iv) (p. 96).

Effect of Solvent Polarity

The solvent effect (D) was studied by varying *t*-butyl alcohol content (1 to 5 %) in the reaction mixture keeping all

Table II(iv)

Effect of initially added products $[\text{MnO}_4^{2-}]$, $[\text{CH}_3\text{CHO}]$ and [Ammonia] on oxidation of L-Alanine by alkaline permanganate at 27.0°C

$$[\text{Mn(VII)}] = 2.3 \times 10^{-4};$$

$$[\text{L-Ala}] = 2.0 \times 10^{-3};$$

$$[\text{OH}^-] = 0.30 \text{ and}$$

$$I = 1.0/\text{mol dm}^{-3};$$

$[\text{MnO}_4^{2-}]$ $\times 10^4$ mol dm^{-3}	$[\text{CH}_3\text{CHO}]$ $\times 10^3$ mol dm^{-3}	[Ammonia] $\times 10^3$ mol dm^{-3}	$k_{(\text{obs})}$ $\times 10^3$ s^{-1}
0.55	-	-	2.31
1.50	-	-	2.36
2.50	-	-	2.33
3.50	-	-	2.38
5.50	-	-	2.25
-	0.30	-	2.34
-	0.60	-	2.31
-	1.50	-	2.33
-	2.00	-	2.37
-	3.00	-	2.38
-	-	0.40	2.31
-	-	1.50	2.32
-	-	2.50	2.36
-	-	3.50	2.33
-	-	4.00	2.34

other conditions being constant. There was no reaction of solvent with oxidant under experimental conditions used. It is found that, the rate constants, $k_{(obs)}$, increased with decrease in dielectric constant of the medium as shown in the Table II(v) (p. 95). The dielectric constant of the reaction medium at different compositions of water and t-butanol were calculated as in Chapter I (p. 57). The plot of $\log k_{(obs)}$ versus $1/D$ was linear with positive slope as shown in Fig.II(iv) (p. 96).

Test for Free Radicals

The intervention of free radicals in the reaction was examined as follows: the reaction mixture to which a known quantity of acrylonitrile scavenger had been added initially, was kept for an hour in an inert atmosphere. On diluting the reaction mixture with methanol, a precipitate resulted suggesting the possibility of free radical intervention in the reaction.

Table II(v)

Effect of ionic strength (I) and dielectric constant (D) on
oxidation of L-Alanine by alkaline permanganate
at $27.0 \pm 0.1^\circ\text{C}$

$[\text{Mn(VII)}] = 2.3 \times 10^{-4}$;
 $[\text{OH}^-] = 0.30$;

$[\text{L-Ala}] = 2.0 \times 10^{-3}$;
 $I = 1.0/\text{mol dm}^{-3}$;

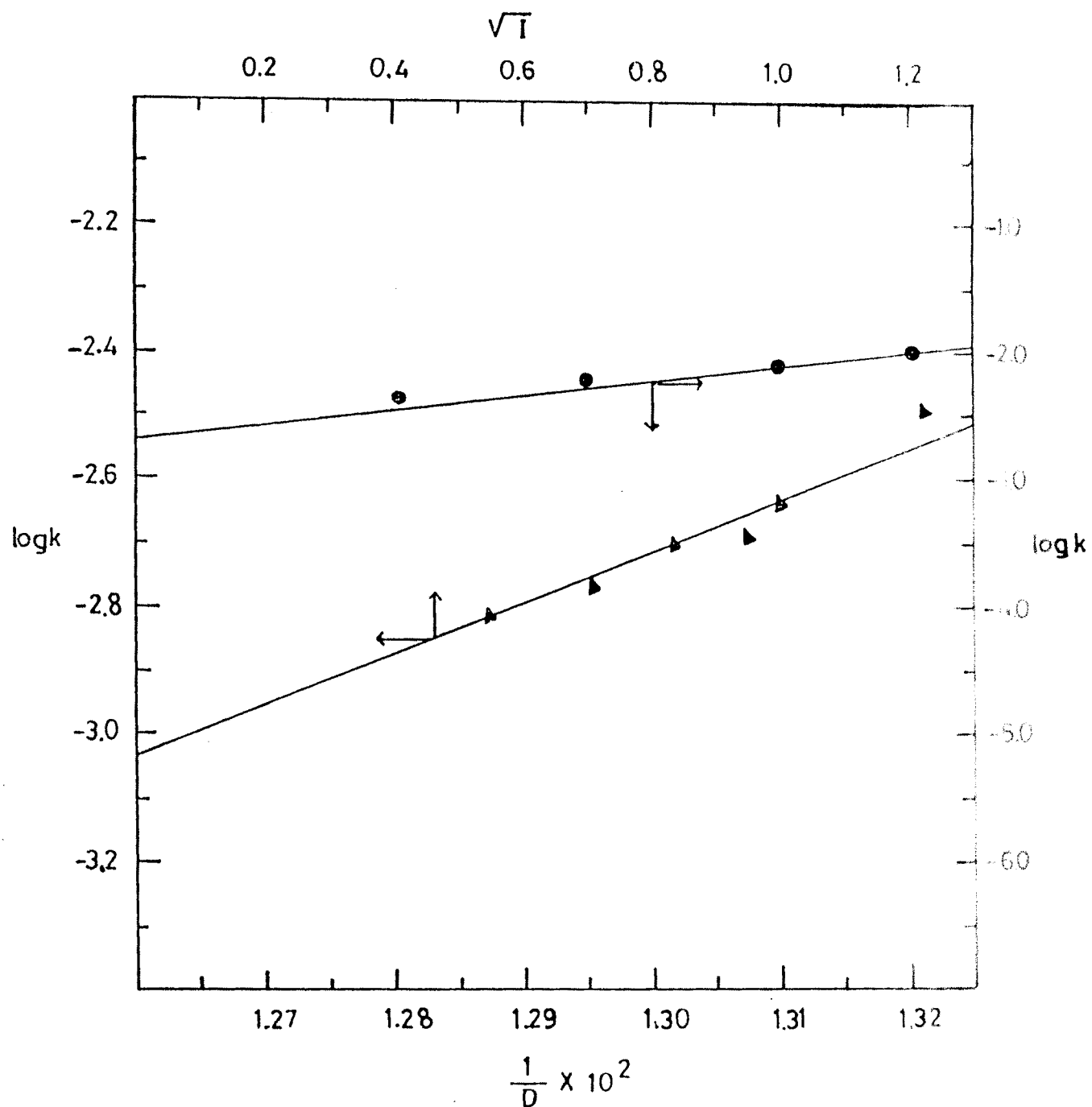
(I) $\times 10^1$ mol dm^{-3}	$k_{(\text{obs})}$ $\times 10^{-3}$ s^{-1}	% t-butanol -water v/v	(D)	$k_{(\text{obs})}$ $\times 10^{-3}$ s^{-1}
3.0	1.53	0.0	78.50	3.35
5.0	1.72	1.0	77.86	3.45
7.0	1.99	2.0	77.18	5.98
9.0	2.04	3.0	76.51	7.96
10.0	2.35	4.0	75.83	8.93
15.0	3.20	5.0	75.15	12.80

Error $\pm 5\%$

Error $\pm 5\%$

Figure II(iv)

Effect of ionic strength (I) and dielectric constant (D) on
oxidation of L-Alanine by alkaline permanganate
(Conditions as in Table II(v) p. 95)



Effect of Temperature

The rate constants (k_1 and k_2) of the slow step of the scheme 3 were obtained from the slopes and intercepts of $k_{(obs)}$ versus concentration of L-Alanine and $1/k_{(obs)} - k_2$ $[OH^-]$ versus $1/[OH^-]$ at different temperatures. The values of k_1 ($dm^3 mol^{-1} s^{-1}$) were 1.02, 1.37 and 1.75 and k_2 ($dm^3 mol^{-1} s^{-1}$) were 1.5×10^{-3} , 2.66×10^{-3} and 4×10^{-3} at 300, 305 and 310 K respectively. These data were subjected to least square analysis and are tabulated in Table II(vi) (p. 99). From the slopes of the plot of $\log k$ versus $1/T$ as shown in the Fig.II(v) (p. 100), the activation parameters have been computed as in Chapter I (p. 62) and are given in the Table II(vii) (p. 101). Two sets of activation parameters (for path I and path II of scheme 3) corresponding to these constants were evaluated from the plots of $\log(k_1$ or $k_2)$ versus $1/T$ and are given in Table II(vii) (p. 101) and the details of calculation of activation parameters are given in Chapter I (p. 62).

DISCUSSION

The permanganate ion, MnO_4^- , exhibits multitude oxidation states, whereby 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 stopped⁸. 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 reported⁸ by Jaky et al. However, when long standing Mn(VI) is slowly reduced to Mn(IV) under our experimental conditions.

The reaction between permanganate and L-Alanine in alkaline medium has a stoichiometry of 2:1 with fractional order dependence on alkali and L-Alanine concentrations and first order on permanganate concentration. No products effect has been observed. The direct plot of $k_{(\text{obs})}$ versus [L-Alanine] gave better correlation than the reciprocal plot as shown in Fig.II(vi) (p. 102). The observed kinetic and other results may be explained by two path way mechanism, one a [substrate] dependent path and the other a [substrate] independent path as detailed in scheme 3.

Table II(vi)

Effect of different temperature on slow step of the mechanism
on oxidation of L-Alanine by alkaline permanganate

$$[\text{Mn(VII)}] = 2.3 \times 10^{-4};$$

$$[\text{L-Ala}] = 2.0 \times 10^{-3};$$

$$[\text{OH}^-] = 0.30;$$

$$I = 1.0/\text{mol dm}^{-3};$$

Temp.	k_1	$\log k_1$	k_2	$\log k_2$	$1/T$
	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		$\times 10^3$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$		$\times 10^{-3}$ K^{-1}
300	1.02	0.008	1.50	- 2.823	3.30
305	1.36	0.136	2.66	- 2.575	3.27
310	1.75	0.243	4.00	- 2.379	3.22

Figure II(v)

Effect of different temperature on slow step of the mechanism
on oxidation of L-Alanine by alkaline permanganate
(conditions as in Table II(vi) p. 99)

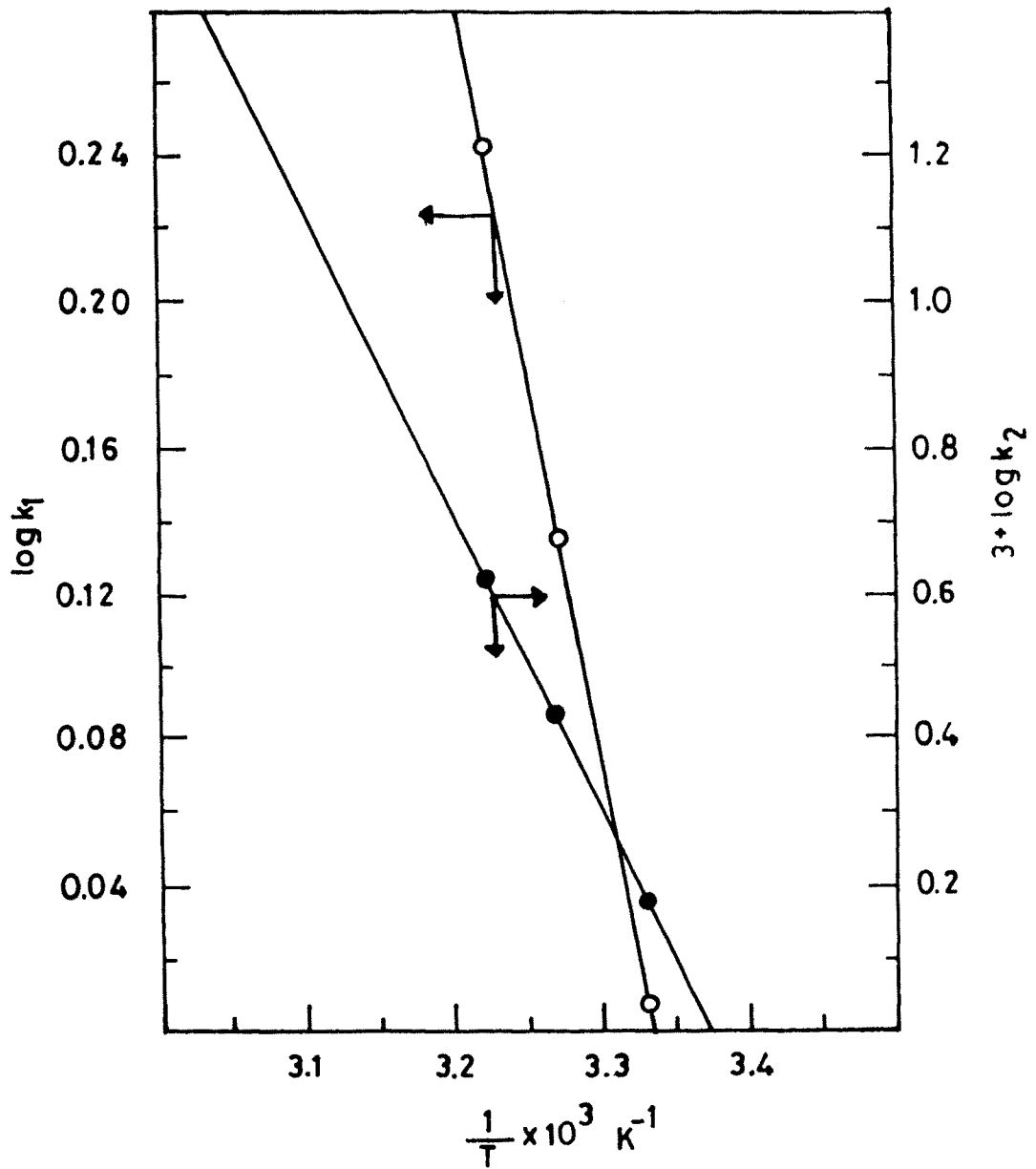


Table II(vii)
 Activation parameters for the oxidation of L-Alanine by
 alkaline permanganate.

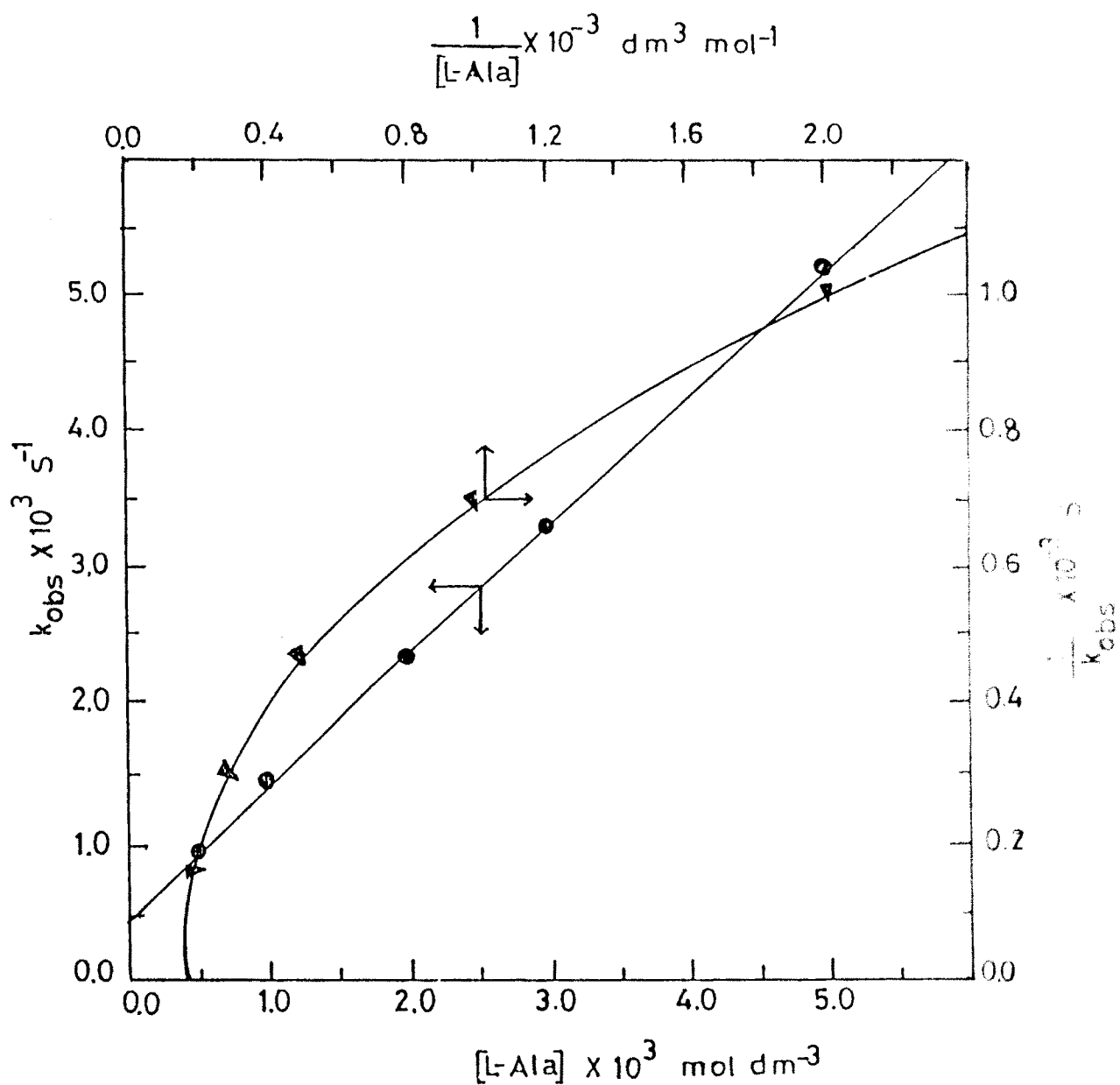
Activation parameters	path I	path II
Ea (kJ mol ⁻¹)	38.3 ± 4	76.6 ± 6
logA	16 ± 1	14 ± 1
ΔS [#] (J K ⁻¹ mol ⁻¹)	-124.24 ± 6	-51.93 ± 2
ΔH [#] (kJ mol ⁻¹)	36.08 ± 2	74.05 ± 4
ΔG [#] (kJ mol ⁻¹)	73.98 ± 4	89.88 ± 4

Error ± 5%

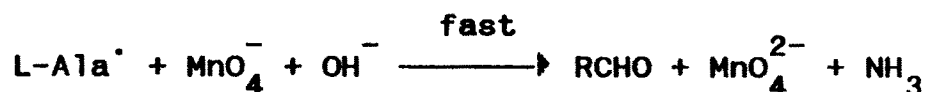
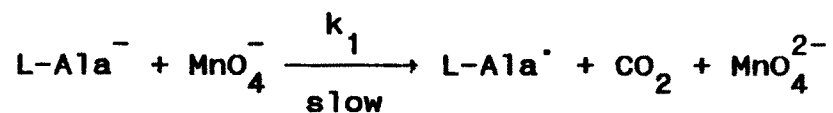
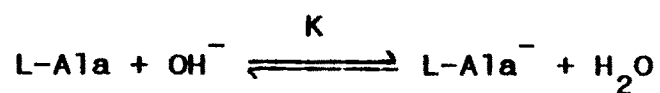
Figure II(vi)

Plots of $k_{(obs)}$ versus [L-Alanine] and $1/k_{(obs)}$ versus $1/[L-Alanine]$ of oxidation of L-Alanine by alkaline permanganate

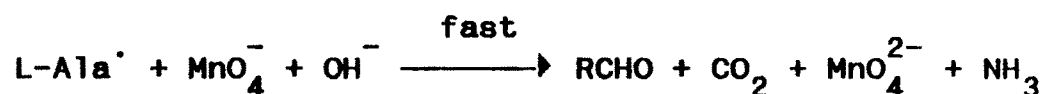
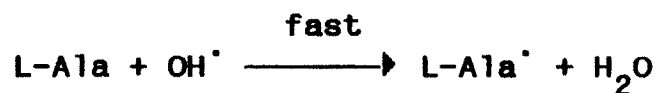
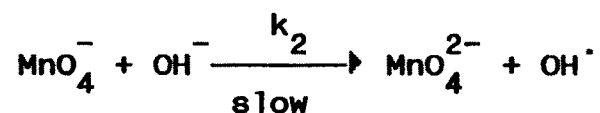
(Conditions as in Table II(iii) p. 90)



Path I



Path II



The observed fractional order in alkali concentration may be due to the substantial existence of L-Alanine as an anionic form in alkaline medium¹³. This anionic form of L-Alanine will react with the active species of permanganate ion, MnO_4^- , in the slow step giving radical of L-Alanine with decarboxylation, which reacts further by another molecule of permanganate species in a fast step to give the products.

Since permanganate species is a one electron oxidant in alkaline medium, the reaction between the substrate and oxidant would afford a radical intervention. Free radical scavenging experiment revealed such a possibility. This type of radical intervention has also been observed in earlier works⁹ with amino acids.

Rate for path I,

$$\text{Rate} = k_1 [\text{L-Ala}] [\text{Mn(VII)}]$$

Rate for path II,

$$\text{Rate} = k_2 [\text{OH}^-] [\text{Mn(VII)}]$$

$$K = \frac{[\text{L-Ala}^-] [\text{H}_2\text{O}]}{[\text{L-Ala}] [\text{OH}^-]}$$

$$[\text{L-Ala}] = \frac{K [\text{L-Ala}] [\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Therefore rate for path I is

$$\text{Rate} = \frac{k_1 K [\text{L-Ala}] [\text{OH}^-] [\text{Mn(VII)}]}{[\text{H}_2\text{O}]} \quad (1)$$

Therefore combined rate law

$$\text{Rate} = k_2 [\text{Mn(VII)}] [\text{OH}^-] + \frac{K k_1 [\text{L-Ala}] [\text{OH}^-] [\text{Mn(VII)}]}{[\text{H}_2\text{O}]} \quad (2)$$

$$\frac{\text{Rate}}{[\text{Mn(VII)}]} = k_{(\text{obs})} = k_2 [\text{OH}^-] + \frac{K k_1 [\text{L-Ala}] [\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (3)$$

Now

$$[\text{L-Ala}]_T = [\text{L-Ala}]_f + [\text{L-Ala}^-] \quad (4)$$

$$[\text{L-Ala}]_T = [\text{L-Ala}]_f + \frac{K [\text{L-Ala}]_f [\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (5)$$

$$[\text{L-Ala}]_T = [\text{L-Ala}]_f \left\{ 1 + \frac{K [\text{OH}^-]}{[\text{H}_2\text{O}]} \right\} \quad (6)$$

$$[\text{L-Ala}]_f = \frac{[\text{L-Ala}]_T [\text{H}_2\text{O}]}{(1 + K [\text{OH}^-]) [\text{H}_2\text{O}]} \quad (7)$$

substituting the equation (7) in equation (3), we have

$$k_{(\text{obs})} = k_2 [\text{OH}^-] + \frac{K k_1 [\text{L-A1a}] [\text{H}_2\text{O}] [\text{OH}^-]}{(1 + K [\text{OH}^-]) [\text{H}_2\text{O}]} \quad (8)$$

$$\text{or} \quad k_{(\text{obs})} = k_2 [\text{OH}^-] + \frac{K k_1 [\text{L-A1a}] [\text{OH}^-]}{(1 + K [\text{OH}^-])} \quad (9)$$

on rearrangement of equation (9), we obtain

$$k_{(\text{obs})} - k_2 [\text{OH}^-] = \frac{K k_1 [\text{L-A1a}] [\text{OH}^-]}{(1 + K [\text{OH}^-])} \quad (10)$$

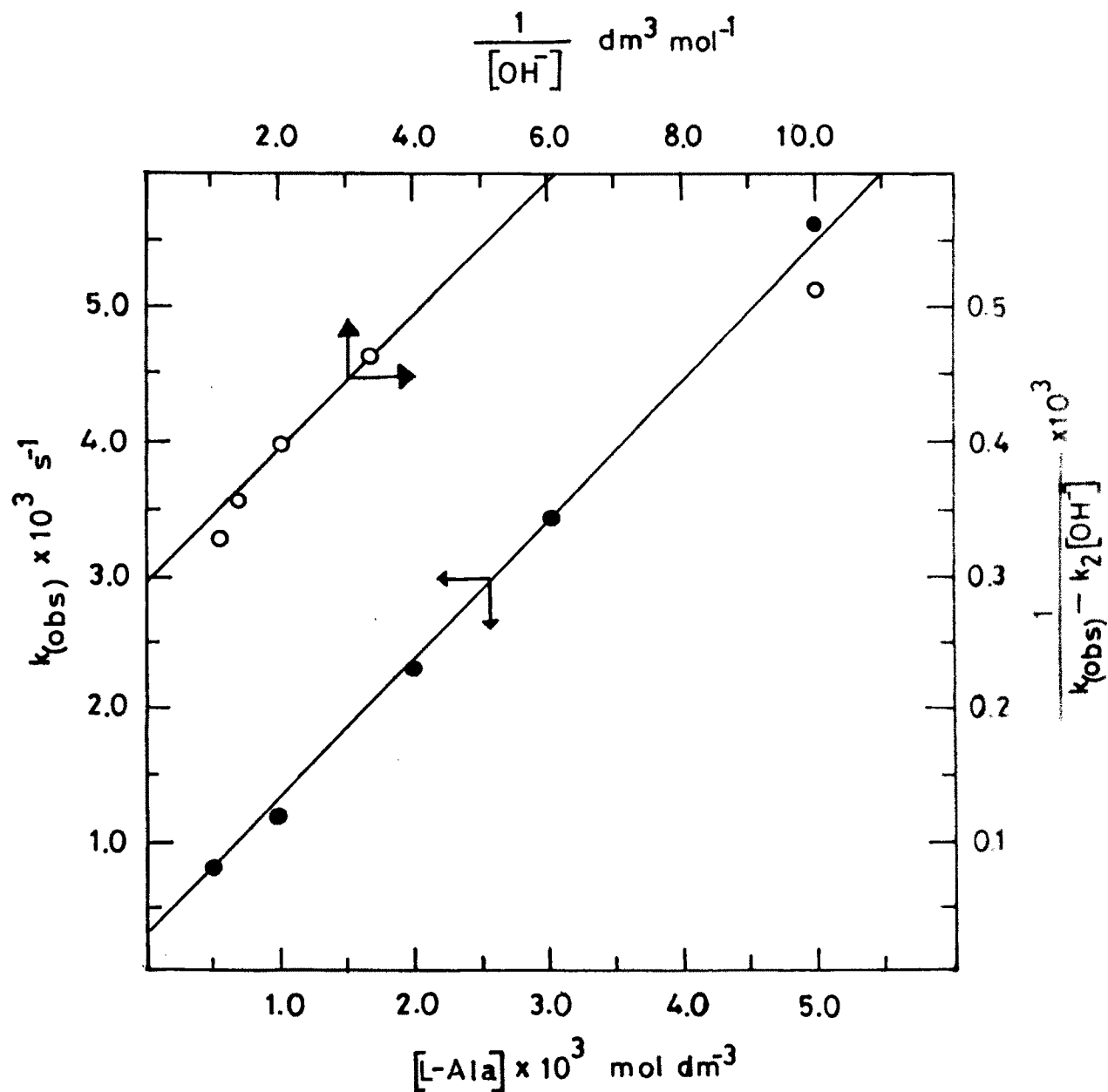
This above equation (10) may be rearranged to (11) which is suitable for verification

$$\frac{1}{k_{(\text{obs})} - k_2 [\text{OH}^-]} = \frac{1}{K k_1 [\text{L-A1a}] [\text{OH}^-]} + \frac{1}{k_1 [\text{L-A1a}]} \quad (11)$$

According to above equations (10) and (11) the plots of $k_{(\text{obs})}$ versus $[\text{L-A1a}]$ and $1/k_{(\text{obs})} - k_2 [\text{OH}^-]$ versus $1/[\text{OH}^-]$ are expected to be linear which are verified in Fig.II(vii) (p. 107). The slopes and intercepts of such plots led to the values of k_1 , k_2 and K at 27.0°C as $1.66 \pm 0.08 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $1.0 \times 10^{-3} \pm 0.05 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $6.02 \pm 0.3 \text{ dm}^3 \text{ mol}^{-1}$

Figure II(vii)

Verification of rate equation (11): on oxidation of L-Alanine
 by alkaline permanganate
 (Conditions as in Table II(iii) p. 90)



respectively. These constants were used to calculate the rate constants under various experimental conditions. There is a reasonable agreement between the calculated and observed rate constants as shown in Table II(iii) (p. 90).

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, 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 rate¹⁴. The values of ΔH^\ddagger and ΔS^\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 ΔS^\ddagger within the range for radical reactions have been ascribed¹⁵ 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 yellow turbidity slowly. Thus it becomes apparent that in this reaction the role of pH is crucial.

Findings

The stoichiometry of the title reaction is found to be 2:1 (oxidant:reductant). The order in both L-Alanine and alkali is fractional. Added products have negligible effect on the reaction rate. However increase in ionic strength and percentage of t-butanol enhances the reaction rate.

Importance of the results of Chapter II

It is clear that alkaline permanganate reactions should be carried at pH not less than 12 and if the pH is less than 12 the formation of colloidal takes place and reaction system gets disturbed and then the reaction will proceed further to yield the reduced product of permanganate as Mn(IV) which turns to tobacco coloured turbidity on long standing. Thus it is evident that the role of pH in this reaction is crucial.

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