

CHAPTER - IV

OXIDATION OF BENZALDEHYDE

- 4.1 Determination of order of the reaction
- 4.2 Effect of temperature and calculation of thermodynamic parameters
- 4.3 Free radical detection and end product analysis
- 4.4 Mechanism

CHAPTER - IV

OXIDATION OF BENZALDEHYDE

RESULTS AND DISCUSSION :

The results on the kinetics of oxidation of benzaldehyde by Mn(III) sulphate in a mixture of 3 M H_2SO_4 and 4M CH_3COOH , are reported here. Experiments were designed to include the following studies.

- 1) Determination of overall order of the reaction and order with respect to the reactants.
- 2) Effect of concentration of sulphuric acid.
- 3) Effect of concentration of Acetic acid.
- 4) Effect of concentration of Mn^{++}
- 5) Effect of concentration of sodium acetate on the velocity constant of the reaction.
- 6) Effect of temperature and evaluation of thermodynamic parameters.
- 7) End product analysis and free radical detection.

4.1 DETERMINATION OF ORDER OF THE REACTION :

Order of the reaction with respect to Mn(III) was determined by isolation method. The concentration of Mn(III) was varied from $5 \times 10^{-3}\text{M}$ to $8 \times 10^{-3}\text{M}$ at constant

concentration of benzaldehyde (0.08M). The reaction was carried out at 40°C. The order with respect to benzaldehyde could not be determined by isolation method because Mn(III) which is absorbing species could not be used in large excess as compared to benzaldehyde. Hence, to determine order of the reaction with respect to benzaldehyde, concentration of Mn(III) was kept constant ($7 \times 10^{-3}M$) while the concentration of benzaldehyde was varied from $2 \times 10^{-2}M$ to $8 \times 10^{-2}M$.

4.1 a EFFECT OF VARIATION OF [Mn(III)] :

The results on the effect of variation of Mn(III) at constant substrate concentration i.e. 0.08 M and constant ionic strength at 40°C are reported here. The observations are recorded in table 4.1. The plots of absorbance A Vs t are shown in figure 4.1. These plots are hyperbolic in nature. The plots of log A Vs t are linear as shown in figure 4.2. Pseudo-first order rate constants obtained are included in the table 4.1. It is seen that these values of k_1 are nearly constant. Hence, order of the reaction with respect to Mn(III) seems to be one. The order with respect to Mn(III) was further confirmed by Van't Hoff differential method. From the plots (figure 4.1), initial rates $(-dc/dt)_0$ were evaluated and were used to calculate order of the reaction as given in the table 4.2. The mean order of the reaction was found to be 0.91 i.e. one.

TABLE 4.1

OXIDATION OF BENZALDEHYDE

VARIATION OF Mn(III) SULPHATE CONCENTRATION

[Benzaldehyde] = 0.08M, [Sulphuric acid] = 3 M

[Acetic Acid] = 4 M, Temperature = 313 °K

[Mn(III) Sulphate]	$5 \times 10^{-3} \text{M}$	$6 \times 10^{-3} \text{M}$	$7 \times 10^{-3} \text{M}$	$8 \times 10^{-3} \text{M}$
Time (minute)	O.D	O.D	O.D	O.D
0	0.66	0.76	0.84	0.90
10	0.54	0.64	0.74	0.83
20	0.50	0.60	0.67	0.79
30	0.46	0.56	0.64	0.73
40	0.42	0.50	0.60	0.70
50	0.37	0.465	0.56	0.65
60	0.35	0.435	0.51	0.57
70	0.33	0.40	0.475	0.52
80	0.29	0.37	0.44	0.50
90	0.27	0.34	0.42	0.46
100	0.25	0.31	0.37	0.43
110		0.29	0.35	0.38
120		0.26	0.34	
k_1 Graphical min^{-1}	0.0069	0.0070	0.0066	0.0066

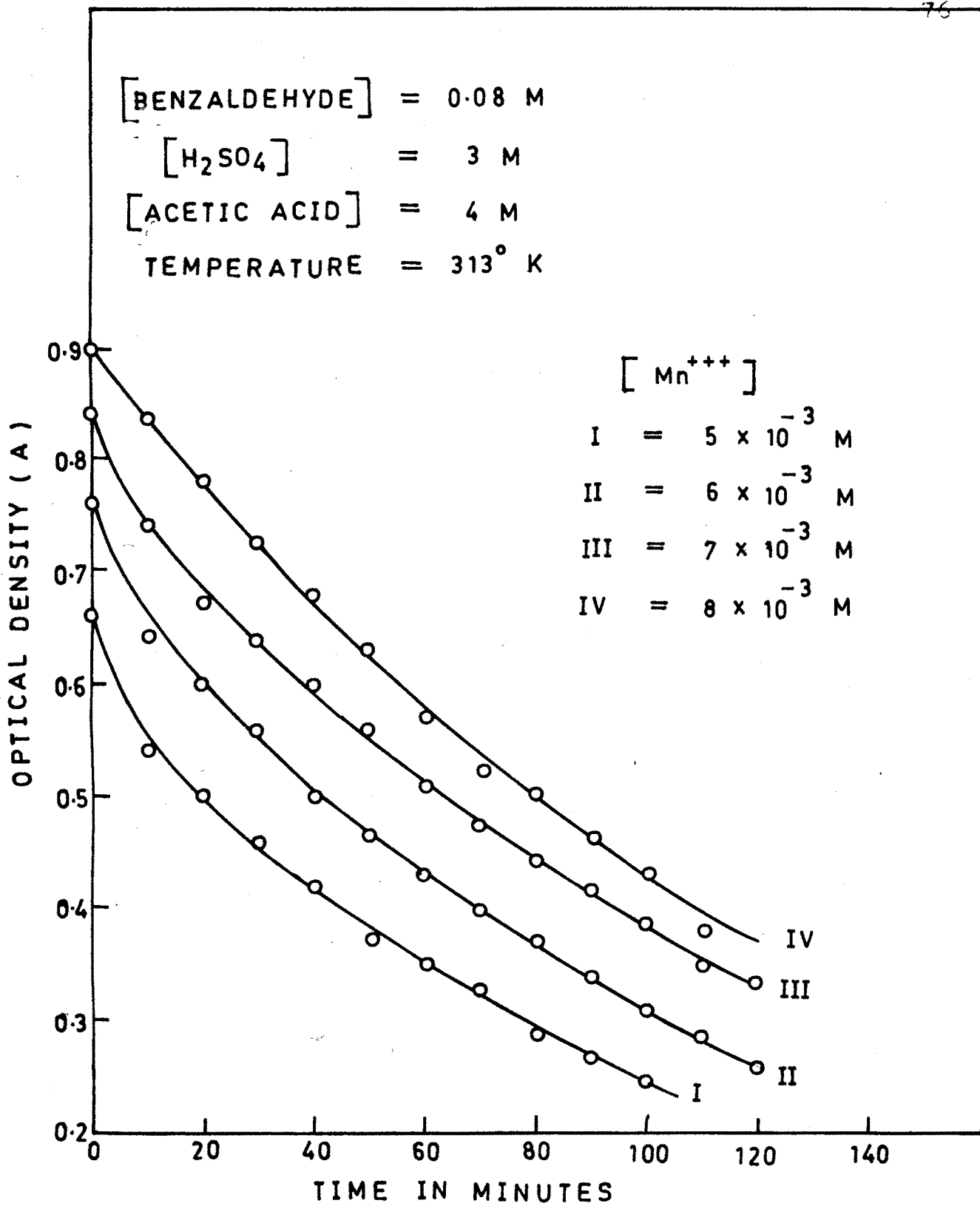


FIG. 4.1 - OXIDATION OF BENZALDEHYDE .
 VARIATION OF [Mn(III) SULPHATE] .

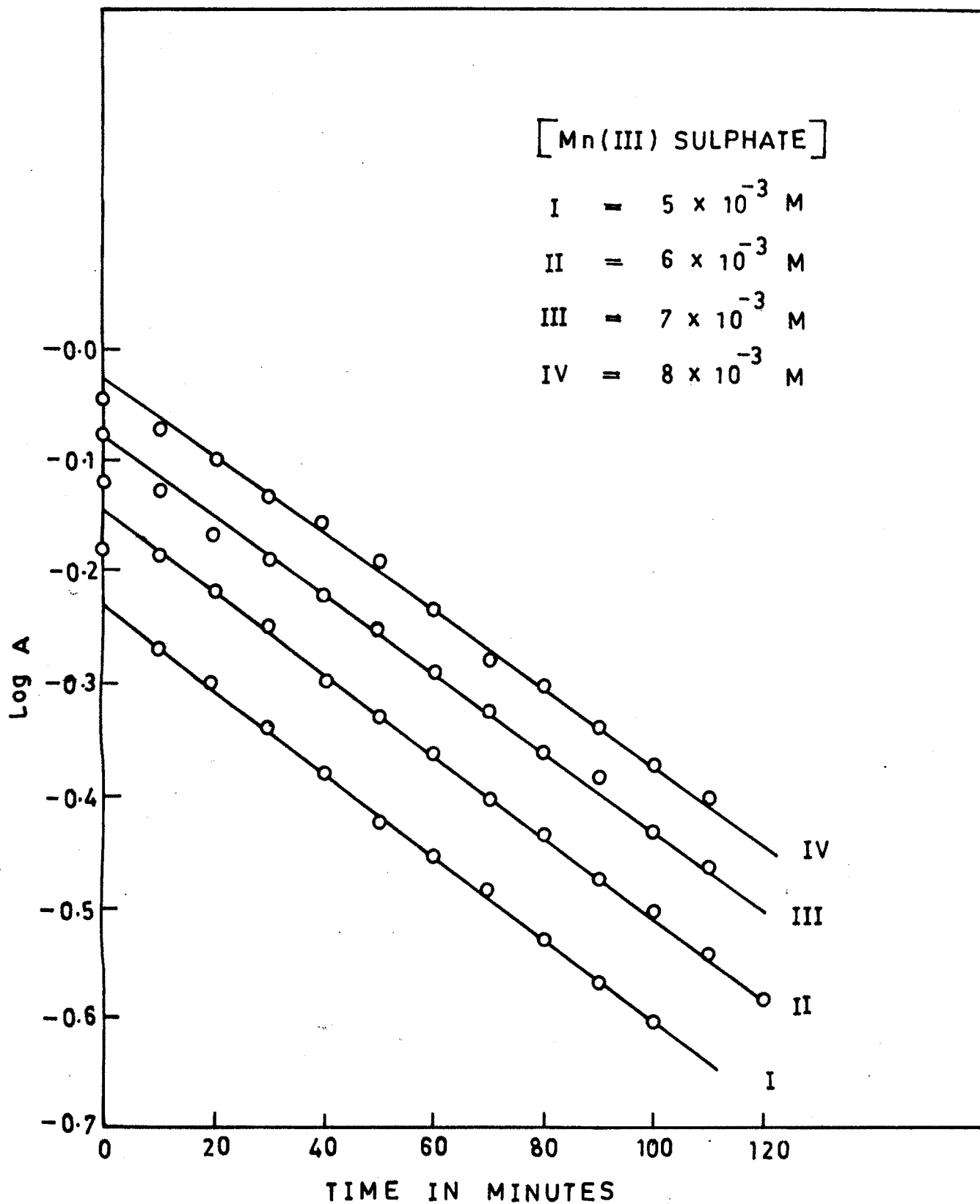


FIG. 4-2 — OXIDATION OF BENZALDEHYDE .

VARIATION OF [Mn(III) SULPHATE] .

TABLE 4.2OXIDATION OF BENZALDEHYDE
ORDER WITH RESPECT TO Mn(III) SULPHATE

[Mn(III) Sulphate]	$(-dc/dt)_0$	Order (n)
$5 \times 10^{-3}M$	0.00875	0.894
$6 \times 10^{-3}M$	0.0090	0.921
$7 \times 10^{-3}M$	0.0112	0.907
$8 \times 10^{-3}M$	0.0117	0.921
	Mean Order	0.910

4.1 b EFFECT OF VARIATION OF BENZALDEHYDE :

The concentration of benzaldehyde was varied from 0.02M to 0.08M keeping concentration of Mn(III) constant (7×10^{-3} M). The observations are recorded in table 4.3. From the plots of log O.D Vs t, it is observed that there is almost no effect on the pseudo-first order rate constant. This shows that the concentration of benzaldehyde has no effect on the rate of reaction. It shows that the order of reaction with respect to benzaldehyde is zero.

4.1 c EFFECT OF ACETIC ACID CONCENTRATION :

The reaction was studied using different concentrations of acetic acid. The concentrations of Mn(III) sulphate (7×10^{-3} M), that of benzaldehyde (0.08M), and that of sulphuric acid (3M) were kept constant. The temperature was kept at 40°C. The observations are recorded in Table 4.4. The plots of log O.D. Vs time are straight lines as shown in figure 4.4. Pseudo-first order rate constants obtained graphically are also included in Table 4.4. It was seen that these values of k_1 are not constant but increase with concentration of acetic acid. The ratio $k_1/[\text{acetic acid}]$ is fairly constant which shows that the reaction is first order with respect to acetic acid. This is also seen from calculation of the order by differential method.

TABLE 4.3

OXIDATION OF BENZALDEHYDE
 VARIATION OF BENZALDEHYDE CONCENTRATION

[Mn(III)Sulphate] = 7×10^{-3} M, [Sulphuric Acid] = 3M

[Acetic acid] = 4 M, Temperature = 313°K

[Benzaldehyde]	2×10^{-2} M	4×10^{-2} M	6×10^{-2} M	8×10^{-2} M
Time (minutes)	O.D	O.D	O.D	O.D
0	0.80	0.81	0.80	0.80
10	0.70	0.71	0.71	0.70
20	0.66	0.67	0.67	0.67
30	0.61	0.61	0.62	0.62
40	0.57	0.58	0.57	0.58
50	0.54	0.55	0.55	0.55
60	0.50	0.50	0.51	0.52
70	0.47	0.48	0.47	0.49
80	0.43	0.44	0.45	0.45
90	0.39	0.39	0.41	0.42
100	0.36	0.37	0.37	0.38
110	0.33	0.33	0.34	0.36
120	0.30	0.31	0.32	0.32
130	0.28	0.29	0.30	0.29
k_1 Graphical min ⁻¹	0.0138	0.0138	0.0138	0.0138

TABLE 4.4

OXIDATION OF BENZALDEHYDE
 VARIATION OF ACETIC ACID CONCENTRATION

[Benzaldehyde] = 8×10^{-2} M, [Mn(III) Sulphate] = 7×10^{-3} M

[Sulphuric Acid] = 3 M

Temperature = 313°K

[Acetic Acid]	3 M	4 M	5 M	6 M
Time (Minutes)	O.D.	O.D.	O.D.	O.D.
0	0.80	0.80	0.80	0.80
10	0.74	0.71	0.69	0.66
20	0.69	0.65	0.62	0.58
30	0.66	0.61	0.58	0.51
40	0.61	0.56	0.53	0.46
50	0.59	0.52	0.48	0.40
60	0.55	0.50	0.43	0.36
70	0.52	0.46	0.40	0.32
80	0.50	0.42	0.36	0.30
90	0.47	0.40	0.33	0.25
100	0.44	0.37	0.31	0.23
110	0.42	0.36	0.28	0.20
120	0.41	0.35	0.27	0.18
k_1 (Graphical) min ⁻¹	0.00518	0.00704	0.00864	0.0106
$k_1 / [\text{CH}_3\text{COOH}]$	0.00173	0.00176	0.00173	0.00177

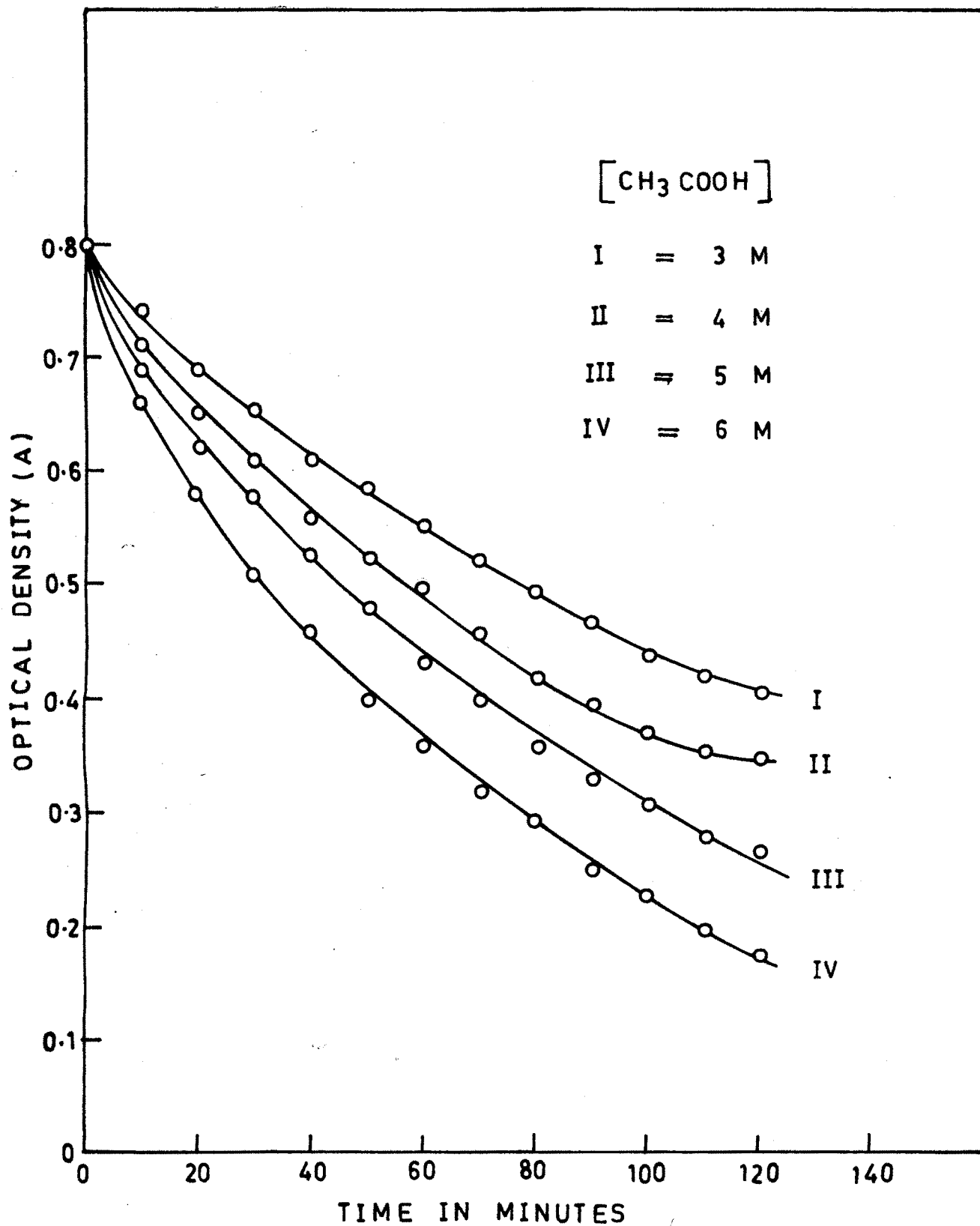


FIG. 4-3 — OXIDATION OF BENZALDEHYDE .
VARIATION OF [ACETIC ACID] .

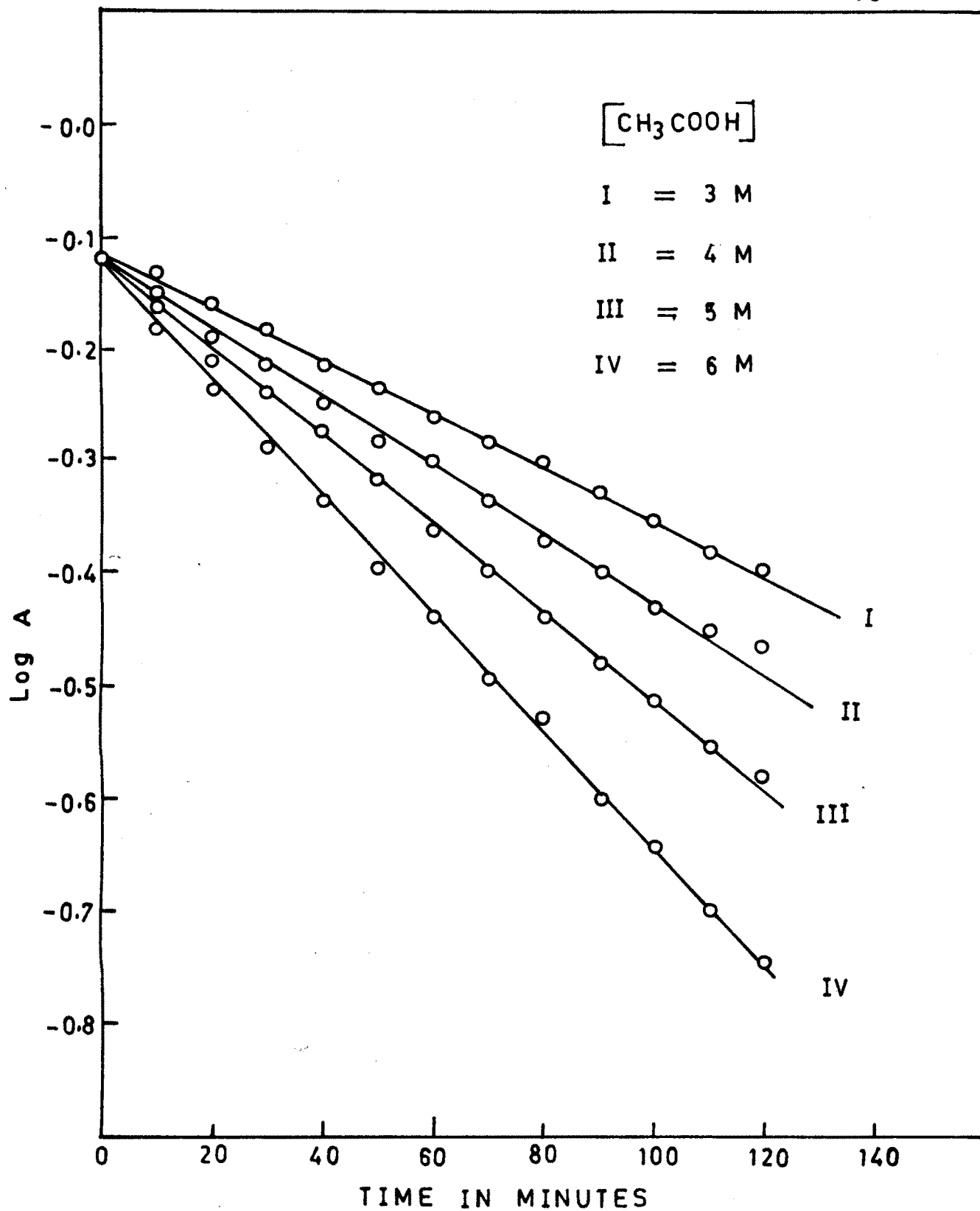


FIG. 4.4 - OXIDATION OF BENZALDEHYDE.
VARIATION OF $[\text{ACETIC ACID}]$.

The values of $(-dc/dt)_0$ at different initial concentrations of acetic acid (C_0) are given in Table 4.5 and the plot of $\log (-dc/dt)_0$ Vs $\log C_0$ is given in figure 4.5. It is seen from the figure that the plot is linear with slope = 0.96 which shows that the order with respect to acetic acid should be 1. Similarly the values of $\log k_1$ and $\log C_0$ values are recorded in table 4.6. The plot of $\log k_1$ Vs $\log C_0$ is straight line (figure 4.6) with slope = 1. This confirms that order with respect to acetic acid should be 1.

4.1 d EFFECT OF VARIATION OF SULPHURIC ACID :

The reaction was studied in presence of different concentrations of sulphuric acid i.e. 2 M, 3M, 4M and 5M. The concentration of Mn(III) ($7 \times 10^{-3} M$), benzaldehyde ($8 \times 10^{-2} M$) and acetic acid (4M) were kept constant. The observations are recorded in table 4.7.

From the observations it is seen that there is almost no effect on the pseudo-first order rate constant. This shows that the concentration of sulphuric acid has no effect on the reaction.

4.1 e EFFECT OF VARIATION OF SODIUM ACETATE :

A solution containing 4M acetic acid and 3M H_2SO_4 was used as a medium for the reaction. The effect of sodium acetate on the reaction rate was studied by using different concentrations (0.05 M, 0.10M, 0.15M, 0.20M). The

TABLE 4.5

OXIDATION OF BENZALDEHYDE
ORDER WITH RESPECT TO ACETIC ACID

[Acetic acid]	$(-dc/dt)_0$	$\log(-dc/dt)_0$	$\log C_0$
3 M	0.0075	- 2.1249	0.4771
4 M	0.00875	- 2.0603	0.6021
5 M	0.0125	- 1.9031	0.6990
6 M	0.0140	- 1.8539	0.7782

Order with respect to acetic acid from graph = 0.96

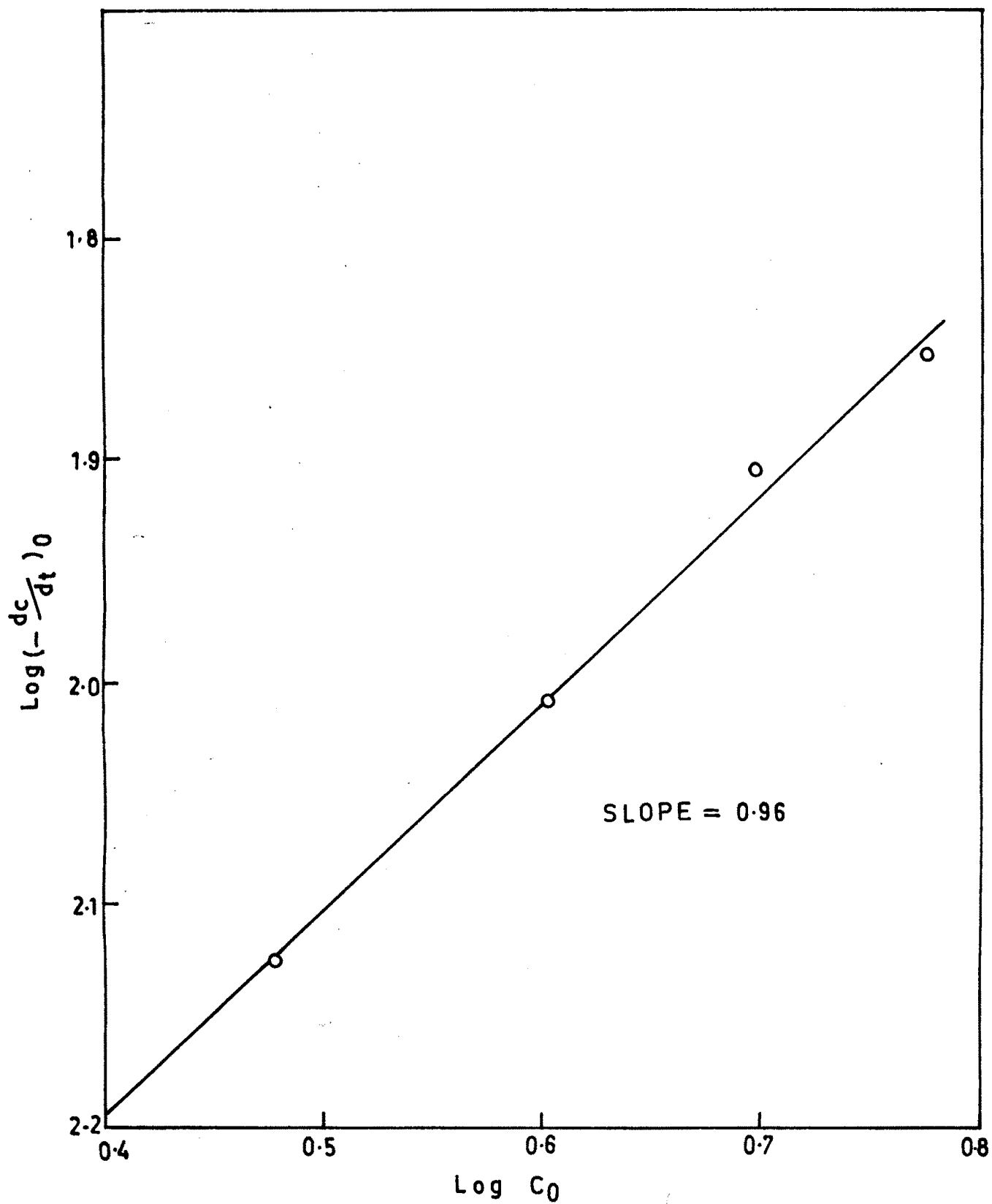


FIG. 4.5 — OXIDATION OF BENZALDEHYDE .
DETERMINATION OF ORDER w.r.t. CH_3COOH .

TABLE 4.6OXIDATION OF BENZALDEHYDE
ORDER WITH RESPECT TO ACETIC ACID

[Acetic acid]	$k_1 \text{ min}^{-1}$	$\log k_1$	$\log C_0$
3 M	0.00518	- 2.2857	0.4771
4 M	0.00704	- 2.1524	0.6021
5 M	0.00864	- 2.0635	0.6990
6 M	0.0106	- 1.9747	0.7782

Order with respect to
Acetic acid from graph = 1.00

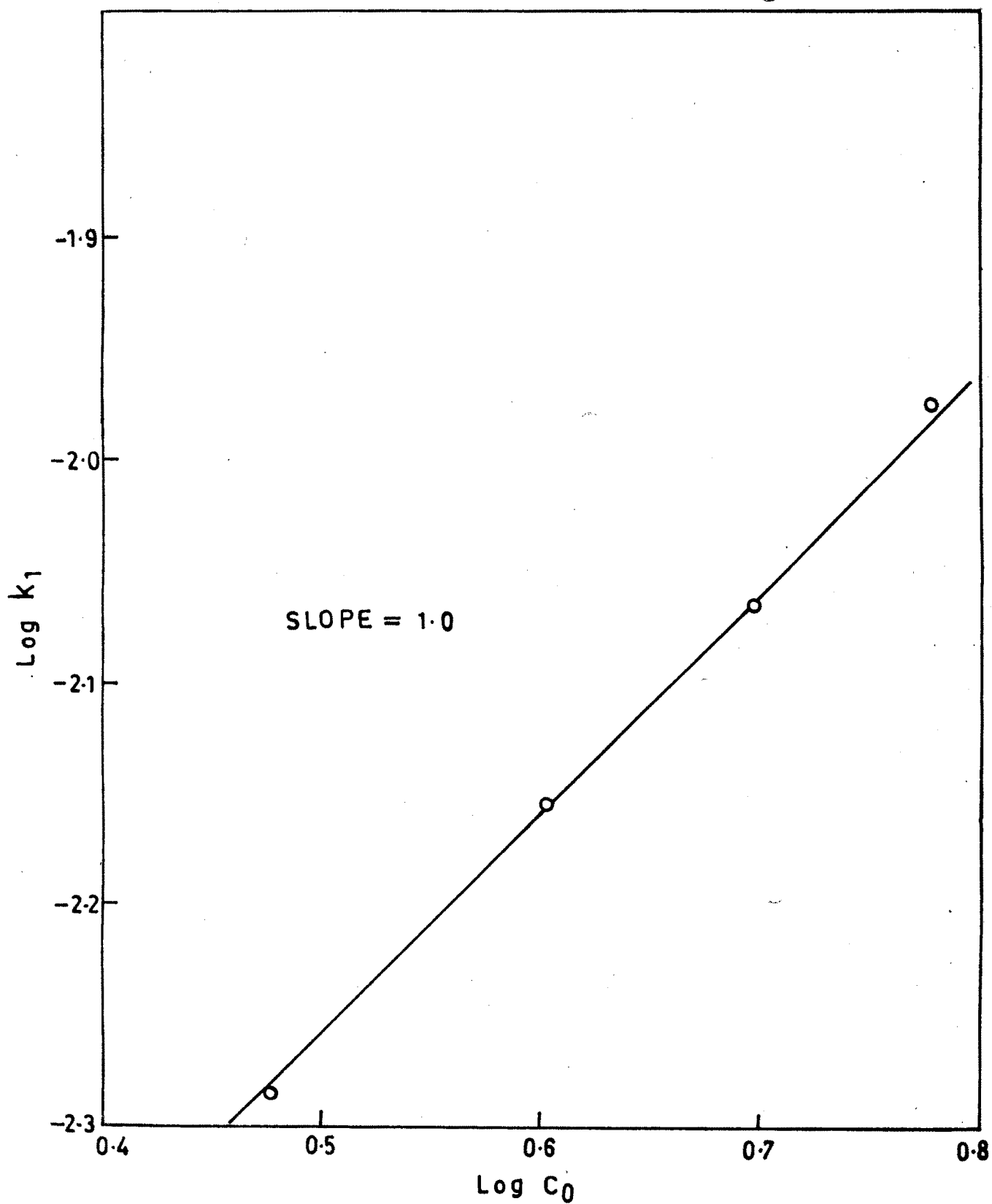


FIG. 4.6 - OXIDATION OF BENZALDEHYDE .

DETERMINATION OF ORDER w.r.t. CH_3COOH .

TABLE 4.7

OXIDATION OF BENZALDEHYDE

VARIATION OF SULPHURIC ACID CONCENTRATION

[Benzaldehyde] = 8×10^{-2} M, [Mn(III) Sulphate] = 7×10^{-3} M[Acetic Acid] = 4 M, Temperature = 313° K

[H ₂ SO ₄]	2 M	3 M	4 M	5 M
Time (minute)	O.D.	O.D.	O.D.	O.D.
0	0.81	0.81	0.81	0.81
10	0.75	0.76	0.75	0.75
20	0.71	0.72	0.71	0.70
30	0.68	0.69	0.68	0.67
40	0.66	0.67	0.66	0.65
50	0.64	0.65	0.64	0.63
60	0.62	0.63	0.62	0.61
70	0.59	0.60	0.60	0.58
80	0.55	0.56	0.55	0.54
90	0.52	0.53	0.51	0.51
100	0.52	0.51	0.49	0.48
110	0.50	0.49	0.47	0.46
120	0.48	0.47	0.45	0.44
130	0.46	0.45	0.43	0.42
k_1 graphical min ⁻¹	0.00202	0.00202	0.00202	0.00202

TABLE 4.8

OXIDATION OF BEZALDEHYDE

VARIATION OF SODIUM ACETATE CONCENTRATION

[Benzaldehyde] = 8×10^{-2} M, [Mn(III) Sulphate] = 7×10^{-3} M

[Sulphuric Acid] = 3 M, [Acetic Acid] = 4 M

Temp = 313° K

[CH ₃ COONa]	0.05 M	0.1 M	0.15 M	0.2 M
Time (minutes)	O.D.	O.D.	O.D.	O.D.
0	0.80	0.80	0.80	0.81
10	0.72	0.72	0.71	0.71
20	0.67	0.68	0.66	0.67
30	0.64	0.63	0.62	0.62
40	0.61	0.61	0.60	0.59
50	0.59	0.59	0.58	0.57
60	0.57	0.57	0.56	0.54
70	0.55	0.55	0.53	0.52
80	0.53	0.53	0.51	0.51
90	0.51	0.51	0.49	0.48
100	0.49	0.49	0.47	0.46
110	0.47	0.47	0.45	0.44
120	0.45	0.45	0.43	0.42
130	0.43	0.44	0.41	0.40
k_1 Graphical min ⁻¹	0.0019	0.0019	0.0019	0.0019

concentrations of Mn(III) ($7 \times 10^{-3} \text{M}$) and benzaldehyde ($8 \times 10^{-2} \text{M}$) were kept constant. The observations are recorded in table 4.8. From the observations it is seen that there is no any effect of sodium acetate on the rate of the reaction. Pseudo-first order rate constant almost remains constant.

4.1 f EFFECT OF VARIATION OF Mn(II) SULPHATE :

In course of the reaction, Mn(III) is reduced to Mn(II). The effect of Mn(II) was studied by using different concentrations of Mn(II) sulphate ($5 \times 10^{-3} \text{M}$, $7 \times 10^{-3} \text{M}$, $9 \times 10^{-3} \text{M}$, $11 \times 10^{-3} \text{M}$). The observations are recorded in table 4.9. The observations show that there is almost no effect of Mn(II) on the rate of the reaction. Pseudo-first order rate constant remains almost constant.

4.2 EFFECT OF TEMPERATURE AND CALCULATION OF THERMODYNAMIC PARAMETERS

The reaction was studied at four different temperatures i.e. 30°C , 35°C , 40°C and 45°C . Concentrations of benzaldehyde ($8 \times 10^{-2} \text{M}$) and Mn(III) ($7 \times 10^{-3} \text{M}$) were kept constant. A mixture of 3M sulphuric acid and 4M acetic acid was used as a medium for the reaction. The observations are recorded in table 4.10. Plots of log O.D Vs time are shown in figure 4.7. The specific reaction rate constant (k_1) are calculated at different temperatures which are shown in table 4.10. The temperature coefficient of the reaction is 2.15. Table 4.11 was ^{used} to plot log k_1 Vs $1/T$. It was a straight line. E_a was

TABLE 4.9

OXIDATION OF BENZALDEHYDE

VARIATION OF Mn(II) SULPHATE CONCENTRATION

[Benzaldehyde] = $8 \times 10^{-2} \text{M}$, [Mn(III) Sulphate] = $7 \times 10^{-3} \text{M}$ [Sulphuric Acid] = 3M, [Acetic Acid] = 4 M, Temp = 313°K

[Mn(II)]	$5 \times 10^{-3} \text{M}$	$7 \times 10^{-3} \text{M}$	$9 \times 10^{-3} \text{M}$	$11 \times 10^{-3} \text{M}$
Time(minutes)	O.D.	O.D.	O.D.	O.D.
0	0.82	0.83	0.83	0.83
10	0.65	0.66	0.66	0.65
20	0.55	0.56	0.56	0.55
30	0.51	0.52	0.52	0.51
40	0.48	0.49	0.50	0.49
50	0.44	0.45	0.46	0.45
60	0.40	0.41	0.42	0.41
70	0.37	0.38	0.39	0.38
80	0.32	0.32	0.33	0.33
90	0.30	0.29	0.30	0.31
100	0.27	0.26	0.27	0.28
110	0.24	0.23	0.24	0.25
120	0.22	0.21	0.21	0.22
k_1 Graphical min^{-1}	0.00428	0.00428	0.00428	0.00428

TABLE 4.10

 OXIDATION OF BENZALDEHYDE
 VARIATION OF TEMPERATURE

 $[\text{Benzaldehyde}] = 8 \times 10^{-2} \text{M}$, $[\text{Mn(III) Sulphate}] = 7 \times 10^{-2} \text{M}$
 $[\text{Sulphuric Acid}] = 3 \text{M}$, $[\text{Acetic Acid}] = 4 \text{M}$

Temp. °K	313	318	323	328
Time(minutes)	O.D	O.D	O.D	O.D
0	0.82	0.82	0.82	0.82
10	0.70	0.66	0.59	0.56
20	0.64	0.62	0.53	0.48
30	0.60	0.54	0.46	0.41
40	0.56	0.49	0.42	0.34
50	0.51	0.44	0.37	0.29
60	0.46	0.41	0.33	
70	0.43	0.37	0.29	
80	0.41	0.34		
90	0.39	0.31		
100	0.37			
110	0.35			
120	0.34			
k_1 Graphical min^{-1}	0.00648	0.00848	0.0138	0.0184
k_1 sec^{-1}	1.079×10^{-4}	1.413×10^{-4}	2.3×10^{-4}	3.07×10^{-4}

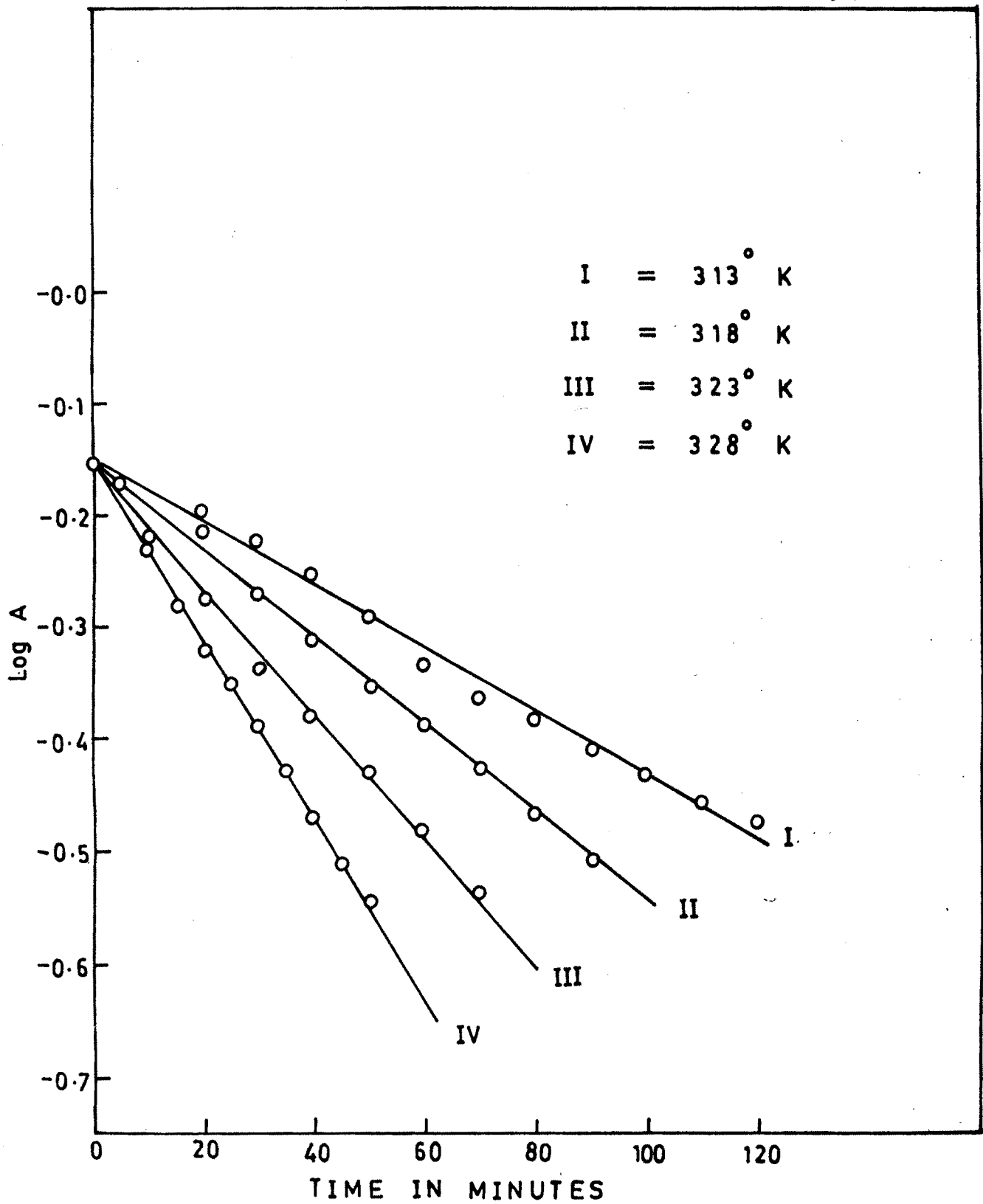


FIG. 4.7 - OXIDATION OF BENZALDEHYDE .
VARIATION OF TEMPERATURE .

found to be 15.35 K cal/mole (figure 4.8). E_a was also calculated by direct substitution of k_1 and k_2 at temperatures T_1 and T_2 in the following equation.

$$E_a = \frac{2.303 \log (k_2/k_1) R T_1 T_2}{(T_2 - T_1)} \quad \dots (4.1)$$

The mean value of E_a obtained was 15.729 k cal/mole. It is very close to the graphical value of E_a (15.35 k cal/mole).

DETERMINATION OF ΔH^*

We have the equation

$$k_1 = \frac{kT}{h} e^{-\Delta S^*/R} e^{-\Delta H^*/RT}$$

$$\therefore \log k_1 = \log \frac{kT}{h} + \frac{\Delta S^*}{2.303 R} - \frac{\Delta H^*}{2.303 RT}$$

$$\text{i.e. } \log (k_1/T) = \log (k/h) + \frac{\Delta S^*}{2.303 R} - \frac{\Delta H^*}{2.303 RT} \quad \dots (4.2)$$

ΔH^* can be found from the slope of the linear plot of $\log k_1/T$ against $1/T$.

$$-\Delta H^* = \text{slope} \times 2.303 R.$$

$$\text{i.e. } \Delta H^* = -2.303 R \times \text{slope} \quad \dots (4.3)$$

TABLE 4.11

OXIDATION OF BENZALDEHYDE
DETERMINATION OF E_a

$k_1 \text{ sec}^{-1}$	$T \text{ }^\circ\text{K}$	$\text{Log } k_1$	$1/T \times 10^{-3}$	$E_a \text{ K cal/mole}$
1.079×10^{-4}	313	- 3.9669	3.195	15.292
1.413×10^{-4}	318	- 3.8499	3.145	16.166
2.3×10^{-4}	323	- 3.6383	3.096	
3.07×10^{-4}	328	- 3.5129	3.049	

Energy of activation (E_a)
from graph = 15.353 K cal/mole

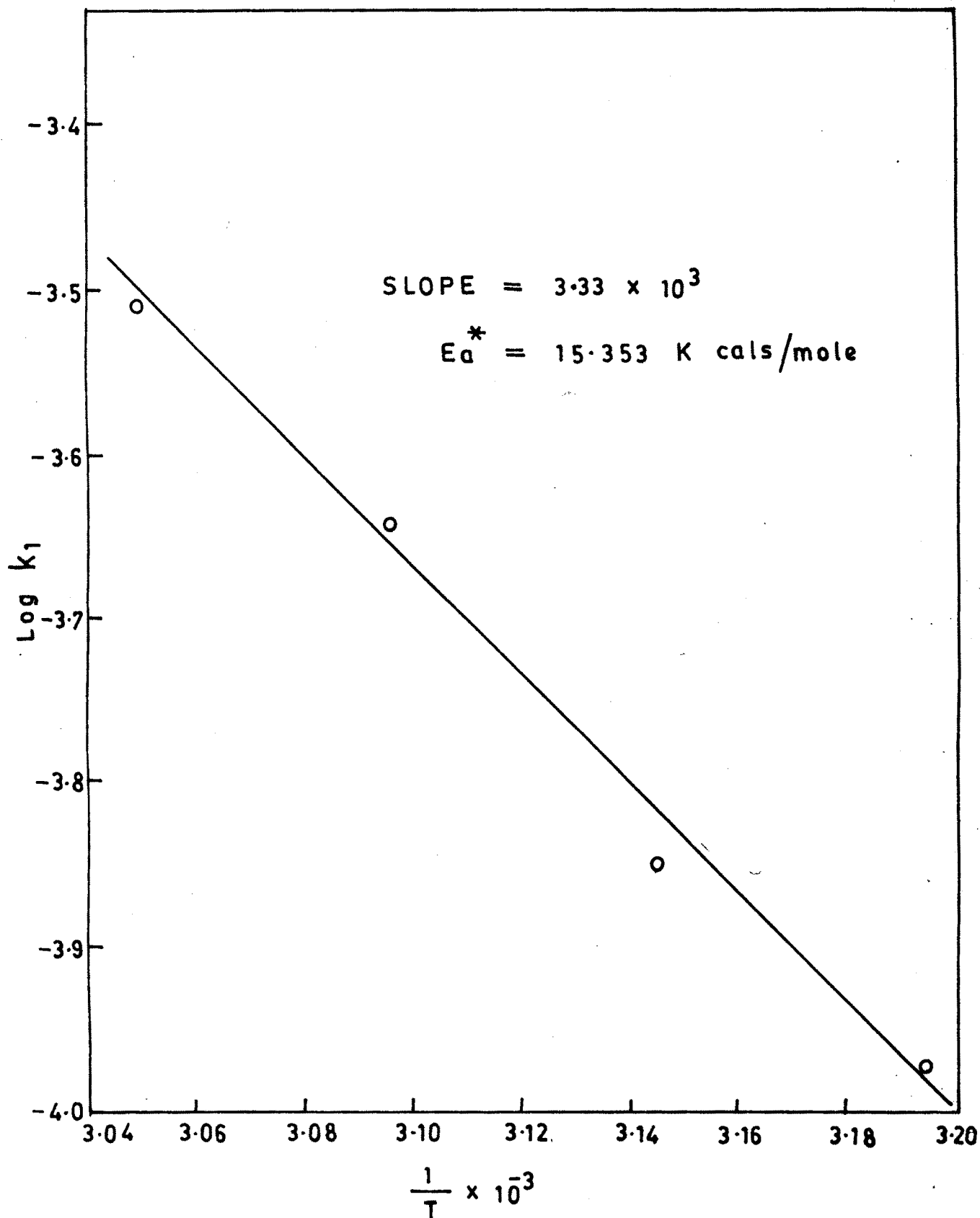


FIG. 4.8 — OXIDATION OF BENZALDEHYDE.
DETERMINATION OF E_a^* .

TABLE 4.12

OXIDATION OF BENZALDEHYDE

DETERMINATION OF ΔH^*

$k_1 \text{ sec}^{-1}$	T °K	k_1/T	Log k_1/T	$1/T \times 10^{-3}$
1.079×10^{-4}	313	3.447	- 6.4625	3.195
1.413×10^{-4}	318	4.443	- 6.3523	3.145
2.3×10^{-4}	323	7.121	- 6.1474	3.096
3.07×10^{-4}	328	9.36	- 6.0287	3.049

ΔH^* By graph = 13.434 K cal/mole

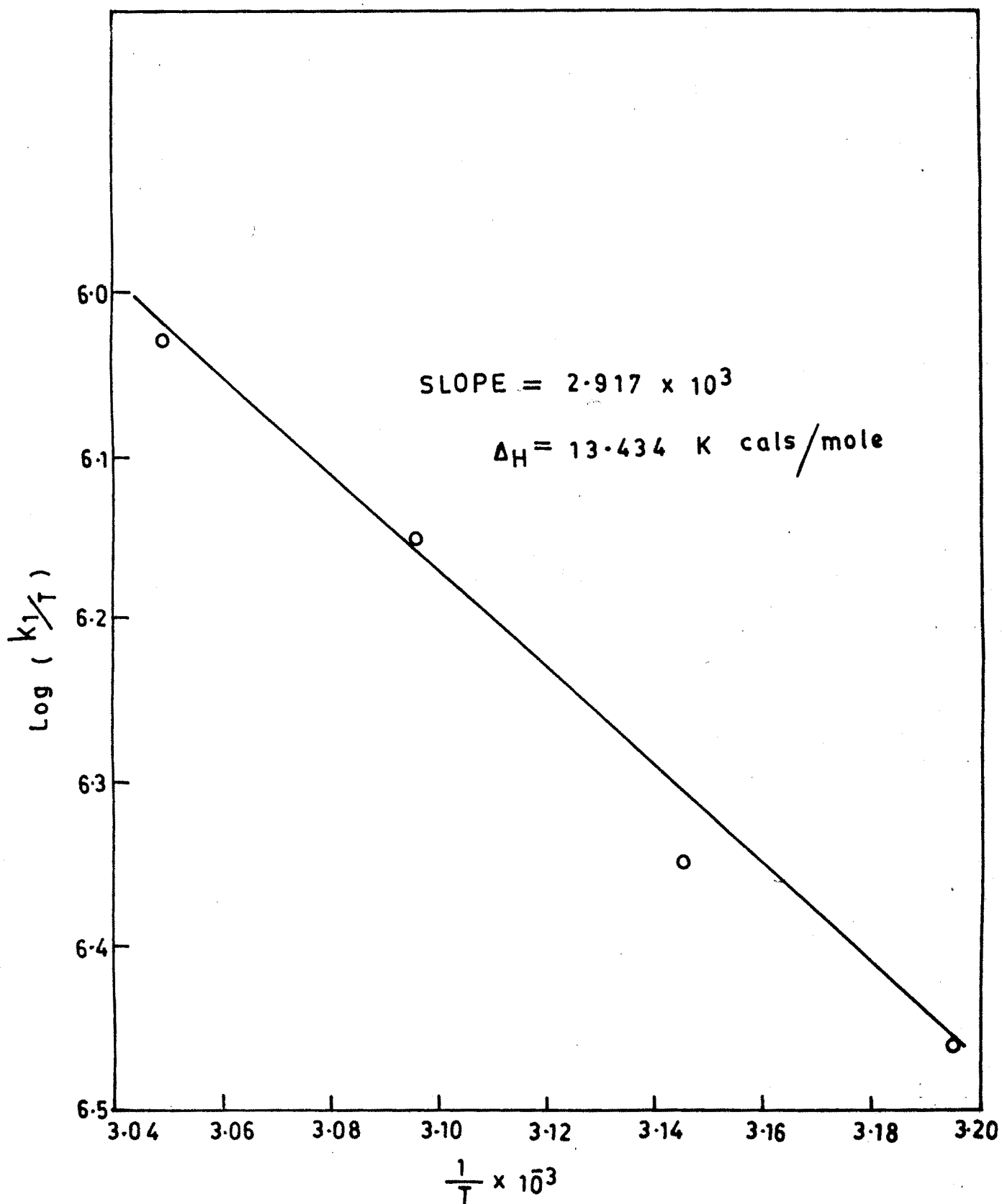


FIG. 4.9 — OXIDATION OF BENZALDEHYDE
DETERMINATION OF Δ_H^* .

TABLE 4.13

THERMODYNAMIC PARAMETERS FOR OXIDATION OF BENZALDEHYDE

Temperature °K	k_1 Sec ⁻¹	Temp Coeffi- cient	E_a K cal/mole By graph	By calcula- tion	ΔH^* K cal/mole	Frequency Factor A sec ⁻¹	ΔS^* e.u.	ΔG^* K cal/mole
313	1.079×10^{-4}	2.13	15.292	15.292	13.434	4.814×10^6	-115.272	49.514
318	1.413×10^{-4}	2.17	15.353	16.166	13.434	4.285×10^6	-116.075	50.346
323	2.3×10^{-4}					4.801×10^6	-116.855	51.178
328	3.07×10^{-4}					4.462×10^6	-117.609	52.010
Mean			15.353	15.729	13.434		-116.453	50.762

A graph of $\log (k_1/T)$ Vs $\frac{1}{T}$ was a straight line (figure 4.9). The value of ΔH^* was found to be 13.43 K cal/mole. Table 4.12 was used to calculate frequency factor, ΔS^* and ΔG^* . The following relations were used for above calculations.

$$\Delta S^* = 2.303 R \log \frac{Ah}{k_1 T} \quad \dots (4.4)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad \dots (4.5)$$

$$\log A = \log k_1 + \frac{E_a}{2.303 RT} \quad \dots (4.6)$$

The values of energy of activation E_a , frequency factor A, enthalpy change ΔH^* , entropy change ΔS^* and free energy change ΔG^* obtained are given in table 4.13.

4.3 FREE RADICAL DETECTION AND END PRODUCT ANALYSIS :

Existence of free radical during the course of the reaction was shown by acrylonitrile polymerisation test. When acrylonitrile (1 ml) was added to the reaction mixture (5 ml) containing both Mn(III) and benzaldehyde, white ppt. was formed. However, such ppt. was not obtained when Mn(III) or benzaldehyde alone was present in the solution. This clearly indicates that reaction proceeds via free radical formation. The end product was identified to be benzoic acid. It was separated by filtration, purified by recrystallisation, dried and M.P. was measured.

4.4 MECHANISM

From this work, the following results were obtained :

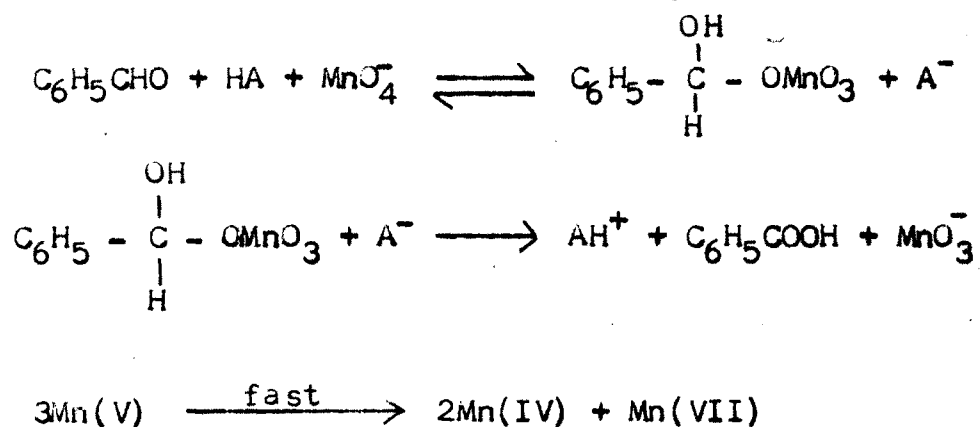
- 1) The order of reaction with respect to Mn(III) is one.
- 2) Benzaldehyde has no effect on the rate of reaction.
- 3) The order of reaction with respect to acetic acid is one.
- 4) Sulphuric acid, sodium acetate, and Mn(II) have no effect on the rate of reaction.
- 5) The temperature coefficient is 2.15.
- 6) The energy of activation is 15.730 K cal/mole.
- 7) The values of ΔH^* , ΔS^* and ΔG^* are 13.43 k cal/mole, -116.45 e.u. and 50.762 Kcal/mole respectively.
- 8) Free radical exists and the end product is benzoic acid.

Before going to decide the mechanism of the reaction in the present study, it is worthwhile to summarize the various mechanisms suggested for the oxidation of benzaldehyde.

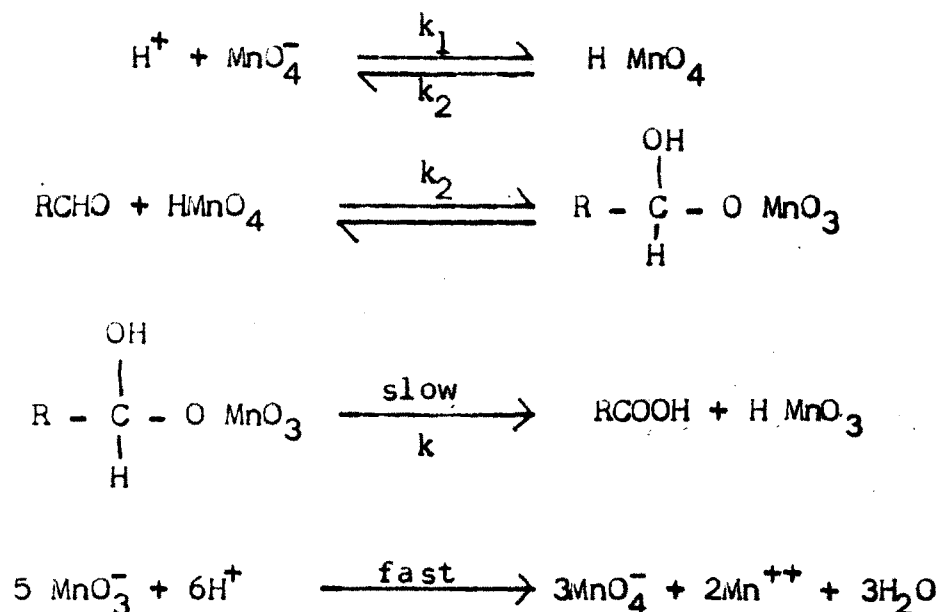
Kinetics and mechanism of oxidation of benzaldehyde by various oxidants has been reported.

Permanganate oxidation of benzaldehyde in water-acetic acid mixtures has been studied. The initial amounts of benzaldehyde and KMnO_4 were taken in equivalent proportions and rate constants were calculated treating the reaction to be of second order. The bimolecular rate constant increases with increasing proportion of acetic acid in the solvent mixture.

Wiberg and Stewart⁷⁷ studied the rate of oxidation of aldehydes and found that the reactions are catalysed specifically by the hydroxyl ions and generally by the acids. The C-H bond is broken in the rate controlling step. To accommodate these facts the following mechanism involving manganese ester intermediate was proposed by them.



The oxidation of benzaldehyde by permanganate in acetic acid-sulphuric acid mixture has been studied. The reaction is first order each in substrate and oxidant. Following mechanism was proposed.



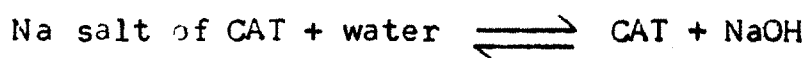
The rate of disappearance of permanganate is given by the rate expression

$$\frac{-d[\text{MnO}_4^-]}{dt} = k \cdot K_1 K_2 [\text{RCHO}] [\text{H}^+] [\text{MnO}_4^-]$$

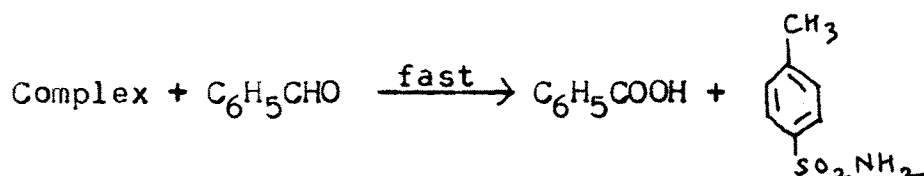
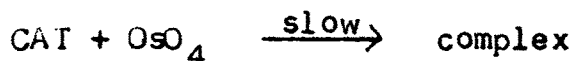
From this expression it can be seen that the order with respect to aldehyde, permanganate and hydrogen ion must be unity.

Kinetics of Os(VIII) catalysed oxidation of benzaldehyde by Chloramine-T has been reported. The order of reaction was found one each in [CAT] and [OsO₄]. It has inverse first

order dependence on $[\text{OH}^-]$. The reactions are zero order in substrate. The inverse dependence on alkali shows that it is not the sodium salt of CAT but CAT itself that takes part in the reaction.

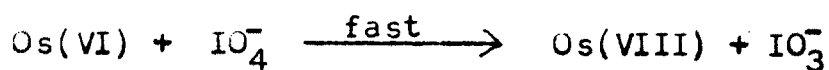
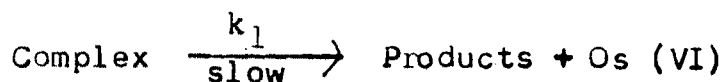
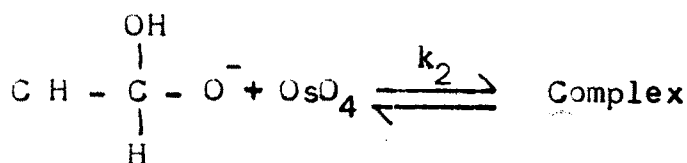
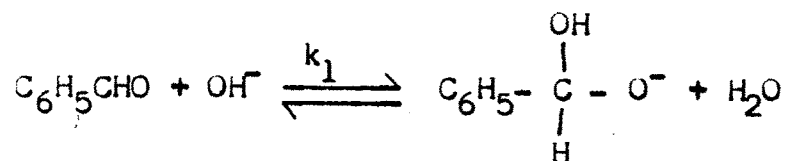


OsO_4 molecules probably are able to form complex with CAT acquiring octahedral geometry whereas the species like $[\text{OsO}_4(\text{OH}_2)]^{--}$ may not be able to form complex effectively with CAT. Perhaps it is more realistic to postulate OsO_4 as the active species.

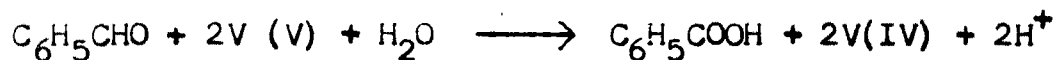


Kinetics and mechanism of Os(VIII) catalysed

oxidation of benzaldehyde by sodium periodate has been reported. The reaction exhibits zero order dependence on $[\text{IO}_4^-]$, and first order dependence each on $[\text{aldehyde}]$ and $[\text{OsO}_4]$. The data suggest that the oxidation proceeds via the rapid formation of the complex between the aldehyde hydrate mono-anion and Os(VIII) which decomposes slowly with H^+ loss followed by a fast reaction between the reduced Os(VI) species and periodate. The mechanism of the reaction at $[\text{OH}^-] > 1.25 \times 10^{-2} \text{M}$ may be proposed as follow

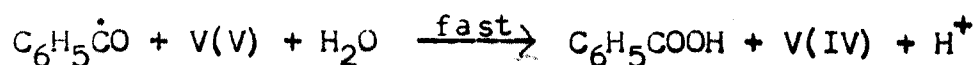
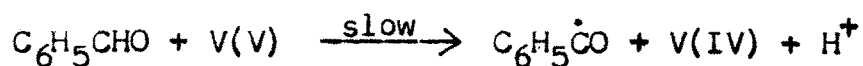


The complex breaks in rate determining step. It has not been possible to detect the complex probably because it has low stability constant. The reaction between benzaldehyde and Vanadium (V) in sulphuric acid-acetic acid mixtures in nitrogen atmosphere is found to obey a second order rate law. There is no evidence for complex formation between benzaldehyde and Vanadium(V). The stoichiometry was calculated to be two moles of Vanadium for one mole of benzaldehyde

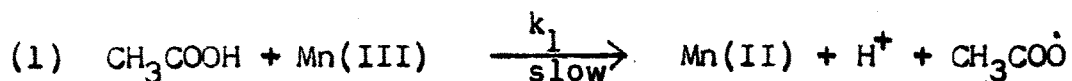


Under the conditions of $[\text{aldehyde}] \gg \text{V(V)}$, The reaction was first order with respect to $[\text{benzaldehyde}]$. The rate is

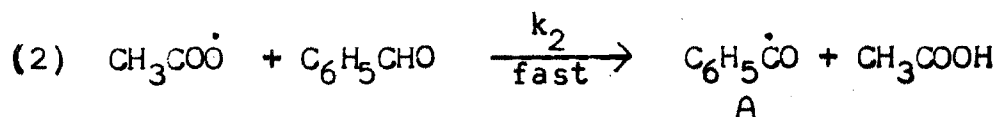
increased with increasing percentage of acetic acid. The oxidation may be represented as follow.



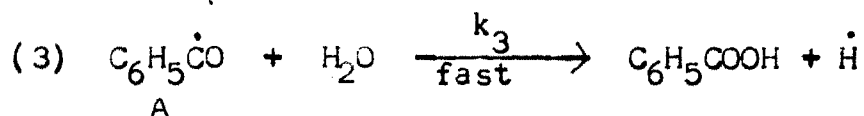
As reported in previous chapter, the oxidation of formaldehyde follows first order with respect to [substrate] but in case of benzaldehyde, the oxidation is found to have zero order with respect to [benzaldehyde]. Also the reaction is zero order with respect to $[\text{H}_2\text{SO}_4]$ i.e. $[\text{H}^+]$, $[\text{Mn(II)}]$, and $[\text{CH}_3\text{COONa}]$. It is found to be first order with respect to $[\text{Mn(III)}]$ and $[\text{CH}_3\text{COOH}]$. These observations show that the rate determining step involves Mn(III) and acetic acid. In highly acidic medium, dissociation of acetic acid is completely suppressed and it is most probably as a 'molecule' involved. Thus we may suggest the rate determining step as



This acetate free radical formed then reacts with benzaldehyde to form a free radical A.



This free radical A then reacts with water to produce benzoic acid and $\dot{\text{H}}$



The mechanism given above suggests that the rate expression for the reaction should be of the form

$$\frac{-dc}{dt} = K_1 [\text{CH}_3\text{COOH}] [\text{Mn(III)}] \quad \dots (4.7)$$

The above mechanism suggested by us requires that the mole ratio of oxidant : substrate should be 2:1. However, this could not be confirmed experimentally as Mn(III) is the absorbing species and could not be used in large excess over benzaldehyde. The mechanisms of oxidation of benzaldehyde suggested by Manjrekar and Soman⁵⁷, Radhakrishnamurthi and Sahu⁶⁰ involve oxygen transfer oxidations but Mn(III) is one electron-oxidant and, therefore, the mechanisms suggested by them may not be applicable here.

The mechanism of oxidation of benzaldehyde by Vanadium(V) has been reported by Sethuram and Navaneeth Rao.⁵⁸ V(V) is also one electron oxidant and hence mechanism

suggested by them seems to be applicable for the Mn(III) oxidation of benzaldehyde. Since, Oxygen atom is more electronegative than carbon atom, it is more likely that Mn(III) abstracts electron from Oxygen atom of OH group with elimination of a proton rather than the extraction of electron from C - H bond of -CHO group to eliminate H⁺ ion. Hence, we have suggested the formation of CH₃CO \dot{O} radical as an intermediate. The fact that the order of reaction w.r. to [CH₃COOH] is one also supports this view. They have suggested the free radical C₆H₅ \dot{O} which also seems to be formed in the present mechanism.

The mechanism suggested above is in accordance with our observations namely,

- (1) Order with respect to [Mn(III)] and [CH₃COOH] is one.
- (2) The reaction rate is independent of [H₂SO₄], [benzaldehyde], [Mn(II)] and [CH₃COONa]
- (3) End product of the reaction is Benzoic acid as has been suggested by many other oxidation reactions of benzaldehyde.
- (4) Since the rate determining step involves an ion and a neutral molecule, it should not exhibit any ionic strength effect as is observed in the present study.
- (5) The reaction proceeds via free radical formation as it is observed in the present study.

The values of E_a and ΔH^* obtained by us are 15.73 K cal/mole and 13.43 K cal/mole respectively. These values are slightly higher than the values of E_a and ΔH^* (11.00 K cal/mole and 10.47 K cal/mole) reported by Manjrekar and Soman⁵⁷ for the oxidation of benzaldehyde by permanganate in water-acetic acid mixtures. This difference may be probably due to the fact that Mn(III) exists as a complex in sulphuric acid medium.⁴

The oxidation of formaldehyde and benzaldehyde may be compared by considering the respective rate determining steps. The reaction is first order with respect to formaldehyde but for the oxidation of benzaldehyde it shows zero order dependence on the substrate. Formaldehyde is involved in rate determining step while benzaldehyde is not involved. Both the mechanisms proceed via free radical formation. E_a and ΔH^* values for the oxidation of benzaldehyde are slightly less than that of formaldehyde. This may be probably due to the fact that the proton is easily abstracted from -OH group of acetic acid rather than from C-H bond in formaldehyde.