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CHAPTER - III

RESULTS

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INTRODUCTION

The 3-5 dinitrobenzhydrazide [3-5 DNBH] and p-methoxy benzhydrazide [p-MBH] were oxidised by chloramine-T in aqueous methanol medium in alkaline condition at temperature 40°C. General procedure adopted for study of reactions was as follows.

Known quantity of hydrazide solution was added to a mixture of methanol, water and buffer solution (prepared by mixing equal volumes of sodium carbonate and sodium bi carbonate) in reaction flask. It is kept in thermostate for half an hour to attain constant temperature. Then, after addition of chloramine-T solution, immediately 10 ml of reaction mixture was removed and mixed with acidified potassium iodide solution in iodine flask. After 10 minutes, liberated iodine was titrated against standard sodium thiosulphate solution. Then after definite time intervals 10 ml of reaction mixture was titrated using same method as above.

To study the effect of change in concentration of substrate, concentration of reagent, pH, temperature and addition of salt kinetic runs were carried by making corresponding changes in the reaction conditions. The results obtained are recorded accordingly.

(I) EFFECT OF CHANGE IN CONCENTRATION OF HYDRAZIDES

Effect of change in concentration of hydrazides on the oxidation of hydrazides by chloramine-T

In order to investigate the effect of concentration of hydrazide on the oxidation of hydrazides by chloramine-T, kinetic runs were carried out by changing concentration of hydrazide in the mixture keeping constant the concentration of all other components at temp. 40°C. The changes in the concentrations of 3-5 dinitro benzhydrazide were made from 0.5×10^{-3} M to 2.5×10^{-3} M. Similarly in the case of p-methoxybenzhydrazide changes in the concentration were made from 1×10^{-3} M to 5×10^{-3} M (Table Nos.1,2,3,4). From the kinetic runs first order rate constant (k_1) have been calculated by using formula

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \ldots \qquad (3.1)$$

where a = Initial volume of $Na_2S_2O_3$ (equivalent to chloramine-T)

x = Difference in initial reading and reading at perticular interval (equivalent to amount of chloramine-T consumed).

t = time.

It is observed from the results in the Table No.1 and 3, that the first order rate constants increase with increase in the concentration of hydrazides. Further second order rate constants (k_2) were calculated by using the formula

$$k_2 = \frac{k_1}{[\text{con. of Hydrazide}]} \quad \ldots \quad (3.2)$$

It was found that second order rate constant (k_2) is constant for each hydrozides. These results indicate that the rate of reactions are first order with respect to concentration of hydrazides.

In order to confirm the order of the reactions, different plots were drawn. First order rate constants (k_1) were calculated by using formula

$$k_1 = \left[\frac{-dc}{dt}\right] \times 2.303 \quad \ldots \quad (3.3)$$

where $\left[\frac{-dc}{dt}\right]$ is slope of the plot log (a-x) vs time(t) (fig.1 and 4)

The order (n) with respect to hydrazide concentration was determined by Van't Hoff differential method

$$\text{Order (n)} = \frac{\log\left[\frac{-dc_1}{dt}\right] - \log\left[-\frac{dc_2}{dt}\right]}{\log c_1 - \log c_2} \quad \ldots \quad (3.4)$$

It was also further confirmed by the slope of the plot $\log\left[-\frac{dc}{dt}\right]$ vs log [con.Hydrazide][Fig.3 & 6].

In the case of both hydrazides the order was found to be equal to 1(one). The values of change in substrate concentration, $\left[\frac{-dc}{dt}\right]$ and order (n) calculated are tabulated in the tables 2 and 4.

TABLE NO. 1

EFFECT OF CHANGE IN CONCENTRATIONS ON THE OXIDATION OF 3-5 DINITROBENZHYDRAZIDE BY CHLORAMINE-T

Chloramine-T concentration = 5×10^{-4} M

Temperature = 40°C

pH = 8.88

Medium = Methanol/water (50/50 v/v)

Sr. No.	Concentration of substrate [3-5 DNBH] $\times 10^{3}$ M	$k_1 \times 10^{2}$ min^{-1}	$k_2 \times 10^{2}$ mol^{-1} min^{-1}	Mean k_2
1	0.5	1.506	3.006	
2	1.0	3.052	3.052	
3	1.1	3.350	3.045	
4	1.2	3.598	2.998	
5	1.3	4.106	3.158	$k_2 = 3.027 \times 10^{-2}$ min^{-1}
6	1.4	4.189	2.992	
7	1.5	4.385	2.923	
8	2.0	6.129	3.064	
9	2.5	7.515	3.006	

TABLE NO. 2

EFFECT OF CHANGE IN CONCENTRATION ON THE OXIDATION OF 3-5 DINITROBENZHYDRAZIDE BY CHLORAMINE-T

DATA FOR GRAPHICAL REPRESENTATION

Con. of substrate [3.5 DNBH] x 10^3M	0.5	1.0	1.5	2.0	2.5
$[\frac{-dc}{dt}] \times 10^1$ (Fig.1)	0.6660	1.266	1.860	2.667	3.285
$[\frac{-dc}{dt}] \times 2.303 \times 10^2 = k_1 \times 10^2\ min^{-1}$	1.535	2.917	4.290	6.141	7.567
$\frac{k_1}{[substrate]} = k_2 \times 10^2 min^{-1}$	3.070	2.917	2.860	3.070	3.026
$\log [\frac{-dc}{dt}]$	$\bar{2}.8236$	$\bar{1}.1024$	$\bar{1}.2695$	$\bar{1}.4260$	$\bar{1}.5165$
log C	$\bar{3}.3010$	$\bar{3}.0000$	$\bar{3}.1760$	$\bar{3}.3979$	
n	-	0.95	0.93	1.00	0.98
Slope (fig.3)		1			

TABLE NO. 3

EFFECT OF CHANGE IN CONCENTRATION ON THE OXIDATION OF p-METHOXY BENZHYDRAZIDE BY CHLORAMINE-T

Chloramine-T concentration = 5×10^{-4}

Temperature = $40^{\circ}C$

pH = 8.88

Medium = Methanol/water (50/50 v/v)

Sr. No.	Concentration of substrate [p-MBH] $\times 10^3$ M	$k_1 \times 10^2$ min^{-1}	$K_2 \times 10^2$ mol^{-1} min^{-1}	Mean k_2
1	1.0	0.320	0.320	
2	2.0	0.688	0.344	
3	3.0	0.933	0.311	$k_2 = 0.318 \times 10^{-2}$ min^{-1}
4	4.0	1.239	0.308	
5	5.0	1.536	0.307	

TABLE NO. 4

EFFECT OF CHANGE IN CONCENTRATION ON THE OXIDATION OF p-METHOXY BENZHYDRAZIDE BY CHLORAMINE-T

DATA FOR GRAPHICAL REPRESENTATION

Con. of substrate [P-MBH] x 10^3M	1.0	2.0	3.0	4.0	5.0
$[-\frac{dc}{dt}] \times 10^3$ (Fig. 4)	1.3300	3.0430	4.1070	5.3570	6.9570
$[-\frac{dc}{dt}] \times 2.303 \times 10^2 = k_1 \times 10^2\ min^{-1}$	0.3010	0.7009	0.9458	1.2330	1.6020
$\frac{k_1 \times 10^2}{[substrate]} = k_2 \times 10^2$	0.3010	0.3504	0.3152	0.3082	0.3204
$\log [-\frac{dc}{dt}]$	$\bar{3}.1238$	$\bar{3}.4833$	$\bar{3}.6155$	$\bar{3}.7289$	$\bar{3}.8423$
log c	$\bar{3}.0000$	$\bar{3}.3010$	$\bar{3}.4771$	$\bar{3}.6020$	$\bar{3}.6990$
order (n)	-	0.88	0.97	0.99	0.96
Slope (fig.6)		1			

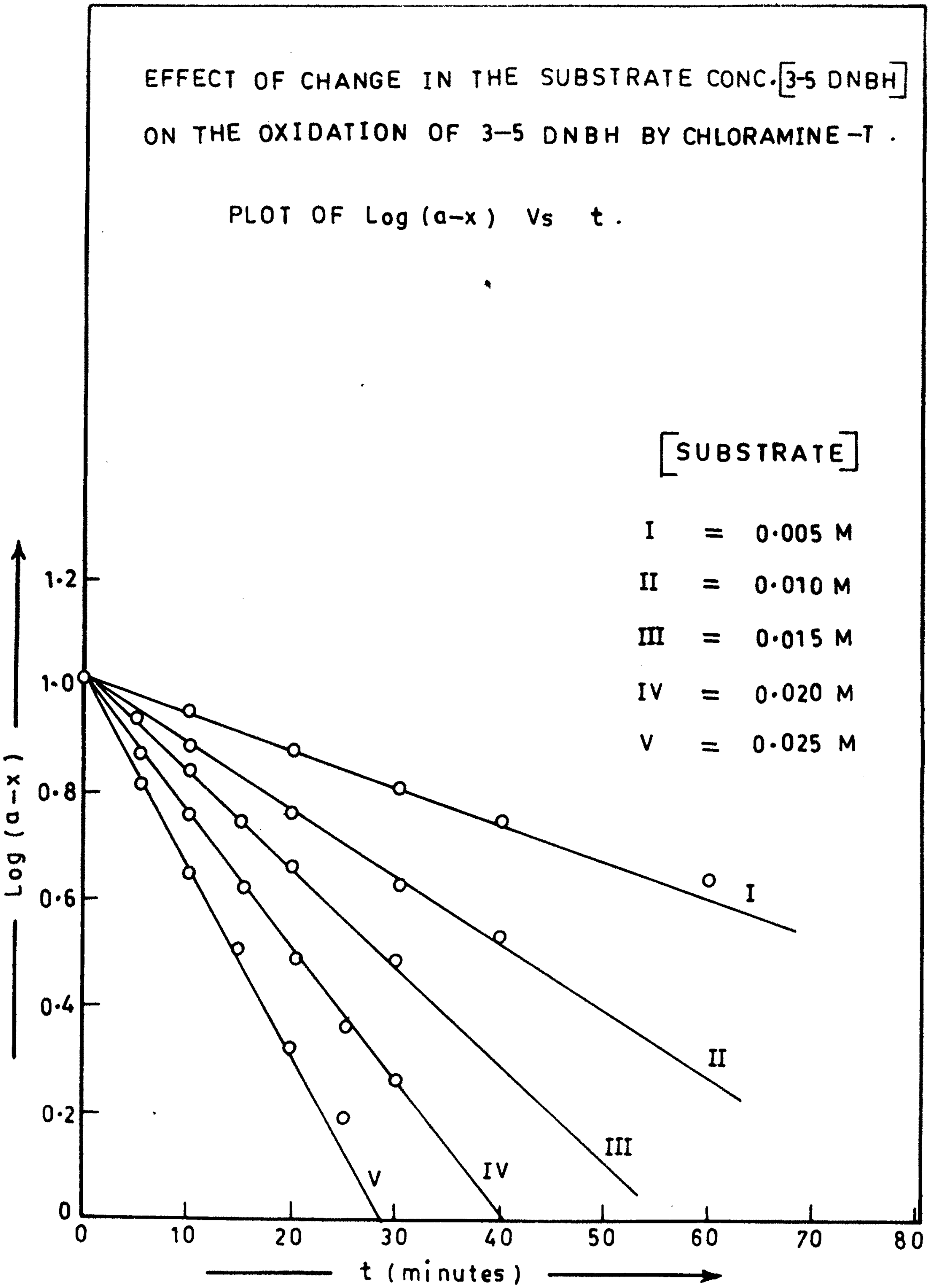

EFFECT OF CHANGE IN THE SUBSTRATE CONC.[3-5 DNBH]
ON THE OXIDATION OF 3-5 DNBH BY CHLORAMINE-T.
PLOT OF Log(a-x) Vs t.
[SUBSTRATE]
I = 0·005 M
II = 0·010 M
III = 0·015 M
IV = 0·020 M
V = 0·025 M
Log (a-x)
1·2
1·0
0·8
0·6
0·4
0·2
0
0
10
20
30
40
50
60
70
80
t (minutes)
I
II
III
IV
V

Fig. 1

EFFECT OF CHANGE IN THE SUBSTRATE CONC. [3-5 DNBH] ON THE OXIDATION OF 3-5 DNBH BY CHLORAMINE-T.

A PLOT OF k Vs 3-5 DNBH CONCENTRATION.

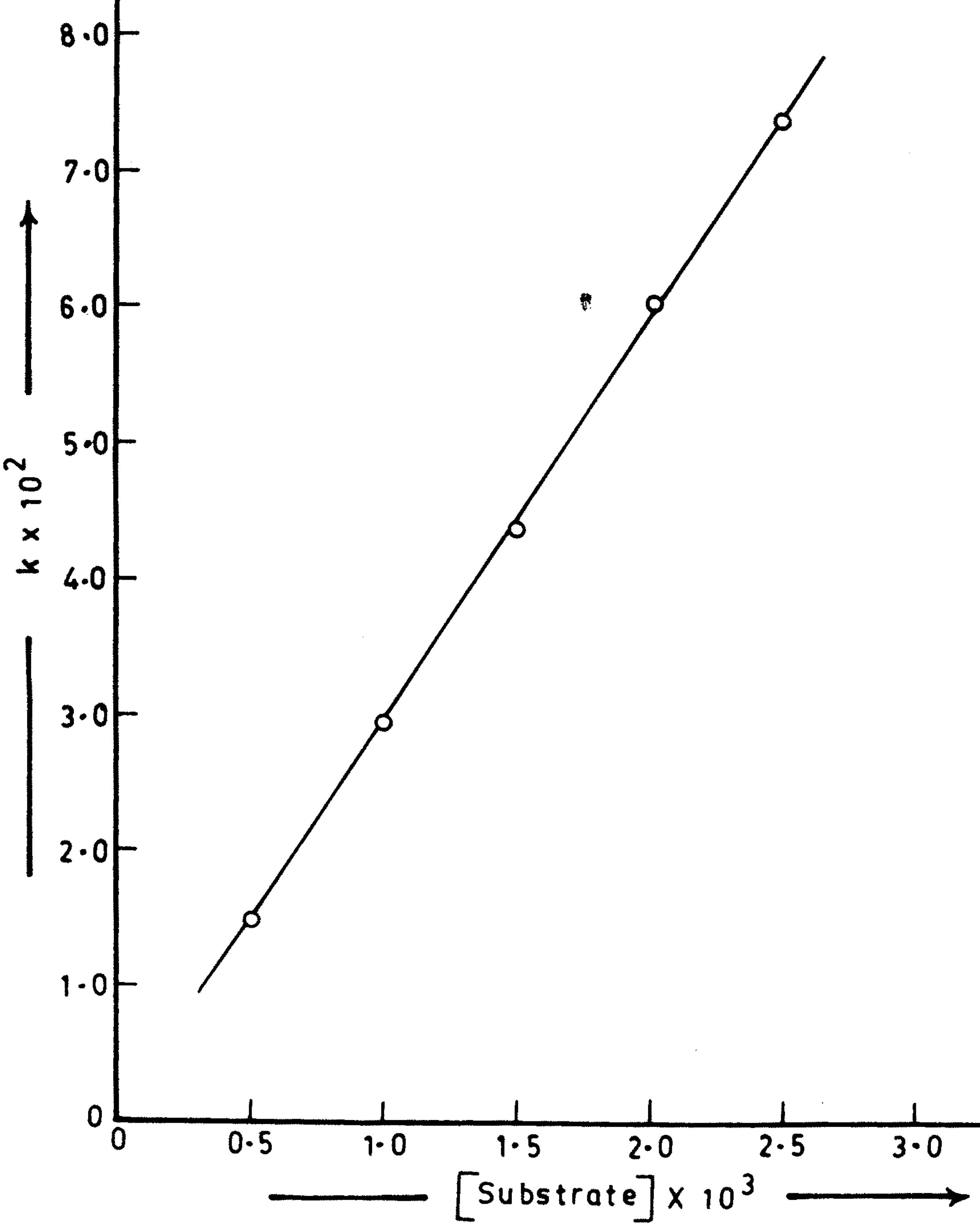


Fig. 2

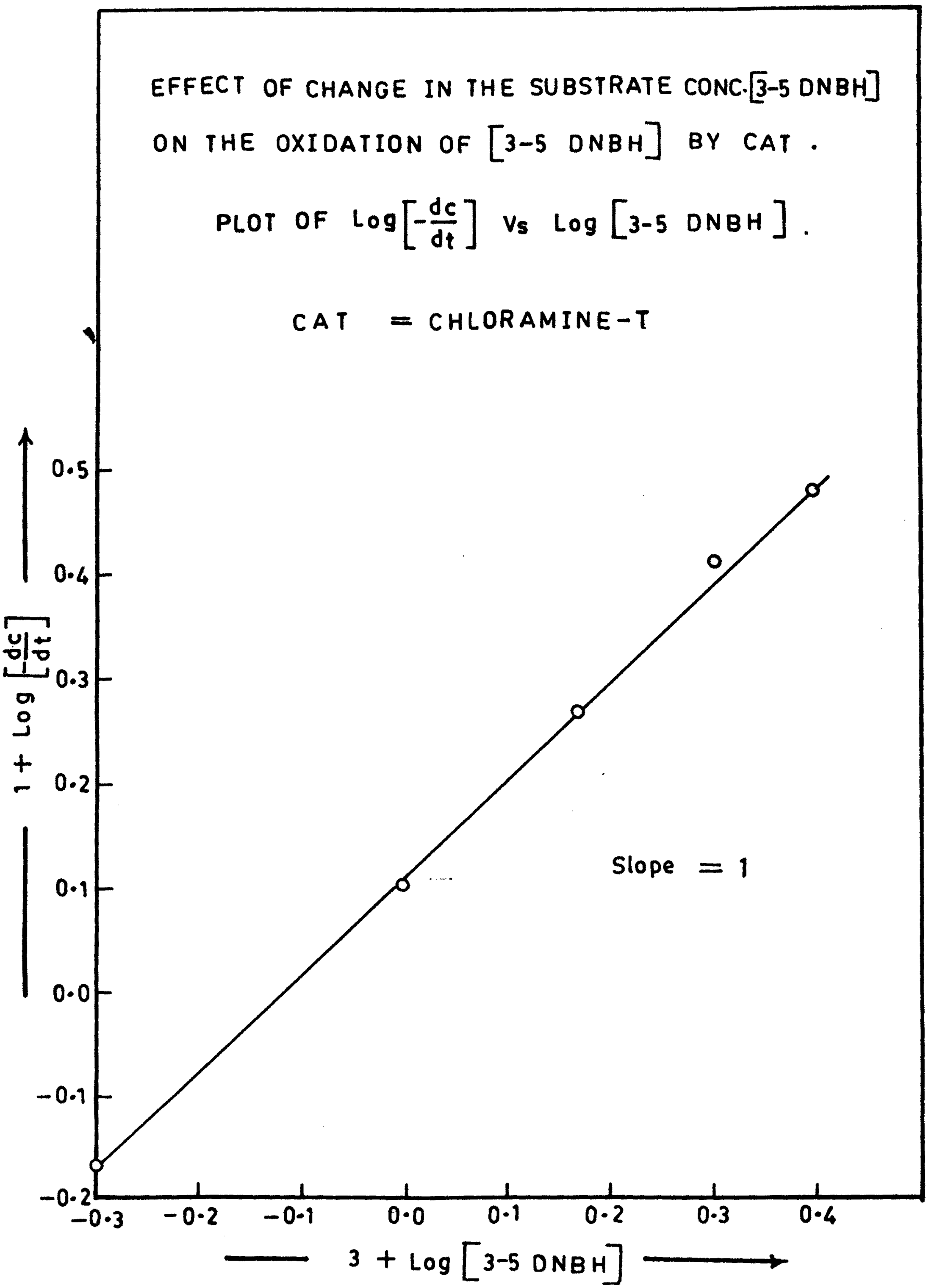

EFFECT OF CHANGE IN THE SUBSTRATE CONC.[3-5 DNBH]
ON THE OXIDATION OF [3-5 DNBH] BY CAT .
PLOT OF Log[-dc/dt] Vs Log [3-5 DNBH] .
CAT = CHLORAMINE-T
Slope = 1
0·5
0·4
0·3
0·2
0·1
0·0
−0·1
−0·2
−0·3
−0·2
−0·1
0·0
0·1
0·2
0·3
0·4
1 + Log [-dc/dt]
3 + Log [3-5 DNBH]

Fig. 3

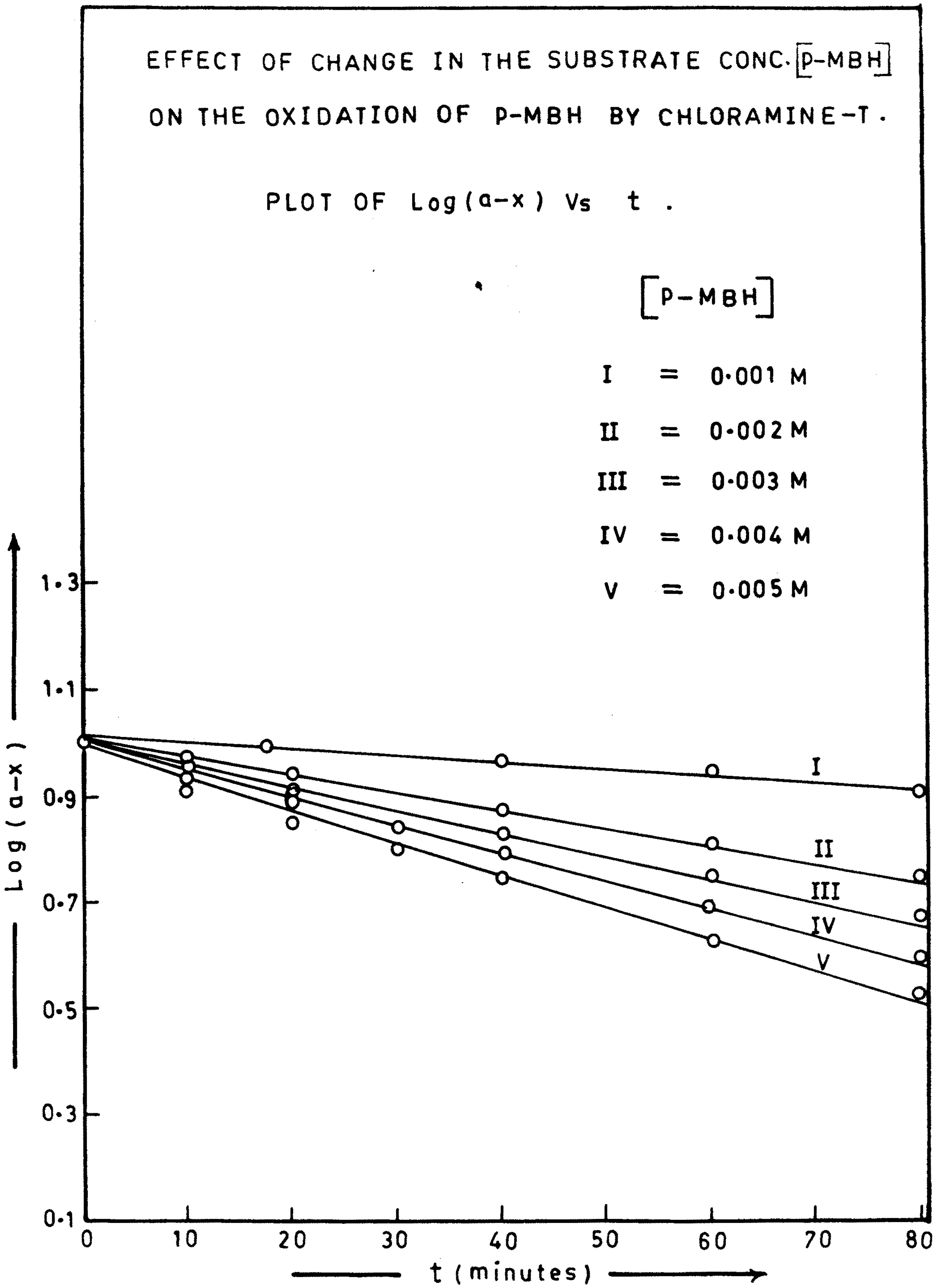

EFFECT OF CHANGE IN THE SUBSTRATE CONC. [P-MBH]
ON THE OXIDATION OF P-MBH BY CHLORAMINE-T.
PLOT OF Log(a-x) Vs t.
[P-MBH]
I = 0·001 M
II = 0·002 M
III = 0·003 M
IV = 0·004 M
V = 0·005 M
Log (a-x)
1·3
1·1
0·9
0·7
0·5
0·3
0·1
0
10
20
30
40
50
60
70
80
I
II
III
IV
V
t (minutes)

Fig. 4

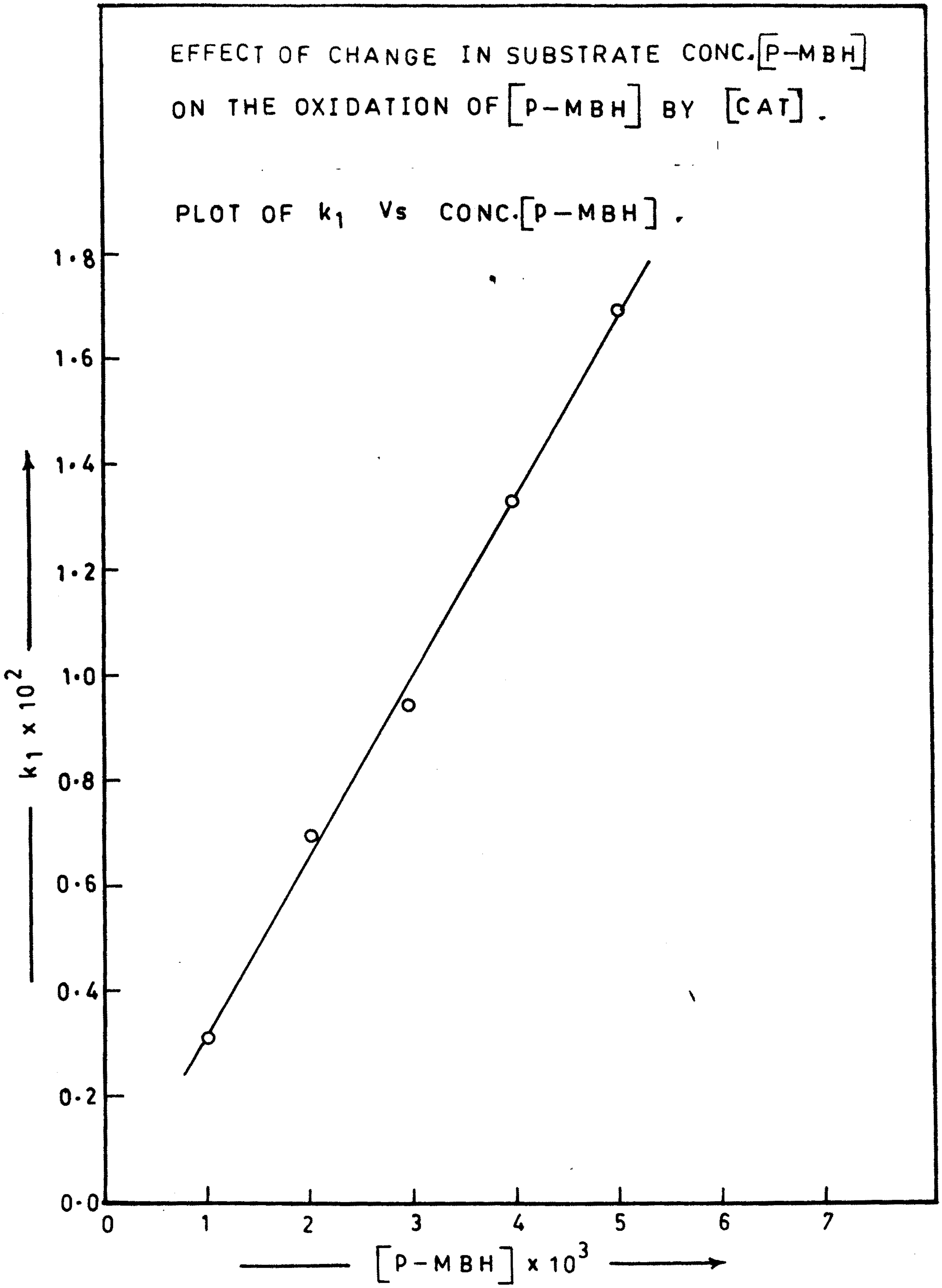

EFFECT OF CHANGE IN SUBSTRATE CONC.[P-MBH]
ON THE OXIDATION OF [P-MBH] BY [CAT].
PLOT OF k1 Vs CONC.[P-MBH].
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·0
0
1
2
3
4
5
6
7
k1 x 10^2
[P-MBH] x 10^3

Fig. 5

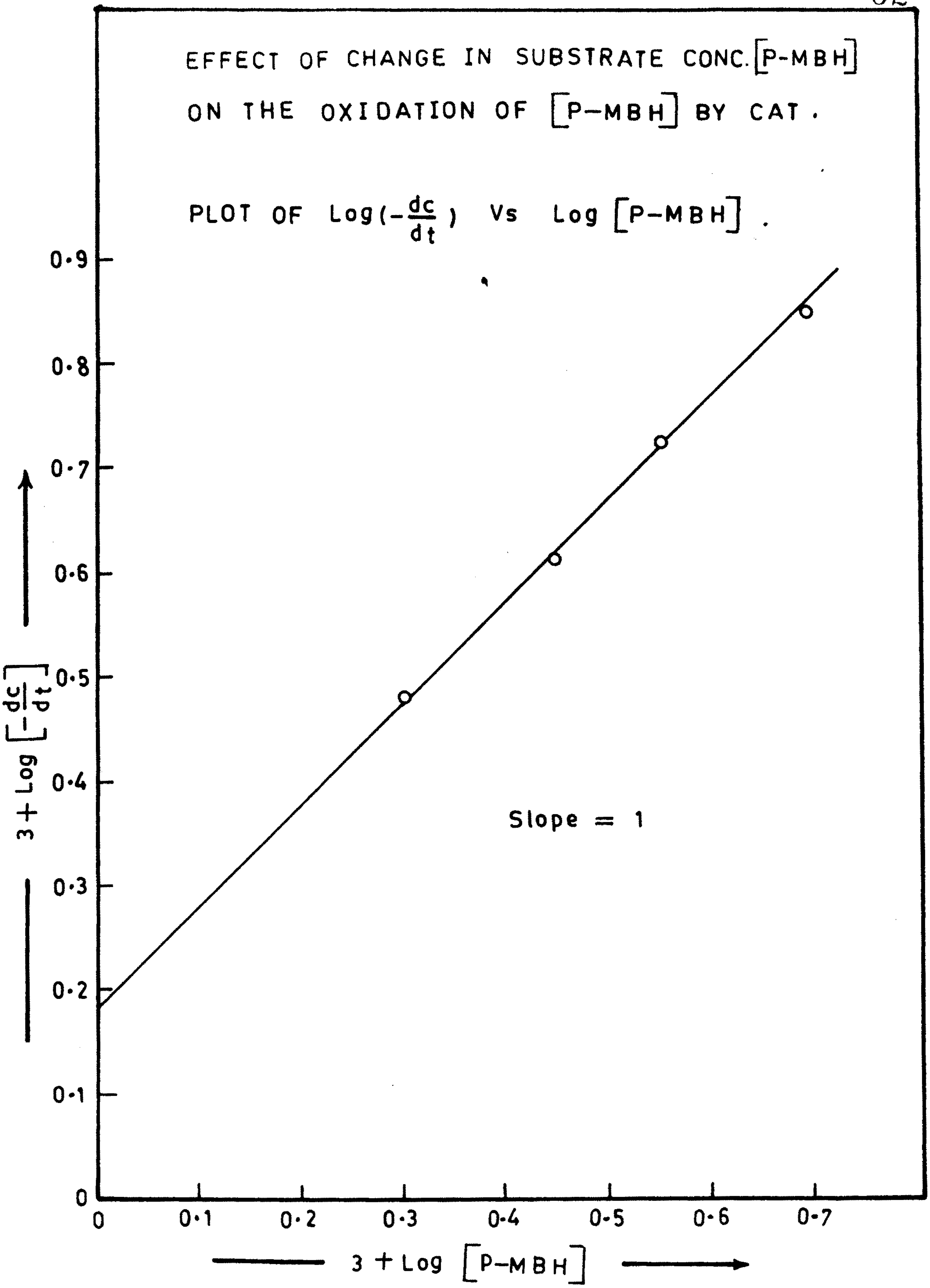

EFFECT OF CHANGE IN SUBSTRATE CONC. [P-MBH]
ON THE OXIDATION OF [P-MBH] BY CAT.
PLOT OF Log(-dc/dt) Vs Log [P-MBH].
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
3 + Log [-dc/dt]
Slope = 1
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
3 + Log [P-MBH]

Fig. 6

(II) EFFECT OF TEMPERATURE ON THE OXIDATION OF THE HYDRAZIDES BY CHLORAMINE-T

In order to investigate the effect of temperature on oxidation of hydrazides by charamine-T, the reactions were studied at five different temperatures from 30 to 50^{o}C. The results obtained were tabulated in tables No.5 and 6. It is observed that first order rate constant (k_1) increases with increase in the temperature. The mean values of temperature coefficients for increase of first order rate constants (k_1) per 10^{o}C were found to be 1.73 and 1.94 for 3.5 dinitrobenzhydrazide and p-methoxy benzhydrazide respectively.

From the observed values cf first order rate constants (k_1) with respect to temperature, different thermodynamic parameters were computed. To evaluate different values of thermodynamic parameters, the equations used were as follows.

1) Energy of Activation (Ea)

$$Ea = \log \frac{k_2}{k_1} \left[\frac{T_2 \times T_1}{T_2 - T_1} \right] \times 4.576 \quad \ldots \quad (3.5)$$

2) Frequency factor (A)

$$k = Ae^{-Ea/RT} \quad \ldots \quad (3.6)$$

$$\text{i.e.} \quad \log A = k + \frac{Ea}{RT} \log 2.7183 \quad \ldots \quad (3.7)$$

3) Entropy of activation ΔS^*

$$\log k = \log e + \log \frac{KT}{h} + \left[\frac{\Delta S}{R} - \frac{Ea}{RT} \right] \log e \quad \ldots (3.8)$$

Introducing values of constants k, h, e, R the equation (3.8) becomes

$$\Delta S^* = 4.576 \left[\log k + 10.576 - \log T + \frac{Ea}{4.576 \times T} \right. \quad \ldots (3.9)$$

4) Enthalpy ΔH^*

$$\Delta H^* = Ea - RT \quad \ldots (3.10)$$

5) Free energy ΔG^*

$$\Delta G^* = \Delta H^* - T\Delta S \quad \ldots (3.11)$$

All above values for these reactions of different hydrazides were tabulated in table No.7.

These parameters were also calculated graphically. The plot of log k vs $\frac{1}{T}$ (Fig.7 and 9) gave straight line. From the slope of the straight line energy of activation (Ea) was calculated by using the equation

$$Ea = \text{Slope} \times 2.303 \times R \quad \ldots (3.12)$$

Similarly a plot of log $\left[\frac{k}{T} \right]$ vs $\frac{1}{T}$ also gives linear plot (Fig.Nos. 8 and 10). From the slope of this linear plot enthalpy of the reaction (ΔH) was calculated by using the formula

$$\Delta H^{*} = \text{slope} \times 2.303 \times R \qquad \ldots \qquad (3.13)$$

Graphically depicted values of enthalpy and energy of activation were found to be in accordance with the calculated values.

A large negative values of entropy of activation (ΔS^{*}) and smaller values of frequency factor are indicative of the formation of an activated complex involving two oppositely charged species or a neutral molecules.

TABLE NO. 5

EFFECT OF THE TEMPERATURE ON THE OXIDATION OF 3-5 DINITROBENZHYDRAZIDE BY CHLORAMINE-T

Substrate concentration = [3.5 DNBH] = 1×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

pH = 8.88

Medium = Methanol/water (50/50 v/v)

Temp.	$k \times 10^{2}$	$\frac{10^{3}}{T}$	log k	log $\frac{k}{T}$
303	1.883	3.3000	$\bar{2}.2748$	- 4.2065
308	2.259	3.2460	$\bar{2}.3539$	- 4.0752
313	3.052	3.1948	$\bar{2}.4845$	- 4.0109
318	4.152	3.1446	$\bar{2}.6182$	- 3.8840
323	5.294	3.0959	$\bar{2}.7237$	- 3.7851

TABLE NO. 6

EFFECT OF TEMPERATURE ON THE OXIDATION OF P-METHYL BENZHYDRAZIDE BY CHLORAMINE-T

Substrate concentration = [P.MBH] = 4×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

pH = 8.88

Medium = Methanol/water (50/50 v/v)

Temp.	$k_1 \times 10^2$	$\frac{10^3}{T}$	log k	log $\frac{k}{T}$
303	0.515	3.3000	$\bar{3}.7118$	- 4.7696
308	0.793	3.2460	$\bar{3}.8993$	- 4.5892
313	1.239	3.1948	$\bar{2}.09307$	- 4.4024
318	1.416	3.1446	$\bar{2}.1510$	- 4.3513
323	2.004	3.0959	$\bar{2}.3018$	- 4.2073

TABLE NO. 7

ACTIVATION PARAMETER VALUES FOR THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

Parameters		Values for [3.5 DNBH]	Values for [P. MBH]
	I - Calculated		
Energy of Activation E_{act}		11.36 K cal/mol	15.76 K cal $mole^{-1}$
Frequency factor (A)		4.266×10^{4} sec^{-1}	1.852×10^{7} sec^{-1}
Entropy (ΔS)		- 30.40 e.u.	- 18.44 e.u.
Enthalpy (ΔH)		10.94 K cal $mole^{-1}$	15.14 K cal $mole^{-1}$
Free Energy (ΔG)		20.48 K cal $mole^{-1}$	20.91 K cal $mole^{-1}$
	II - Graphical		
Energy of Activation (E_{act})		10.98 K cal $mole^{-1}$	14.76 K cal $mole^{-1}$
Enthalpy (ΔH)		10.07 K cal $mole^{-1}$	14.70 K cal $mole^{-1}$

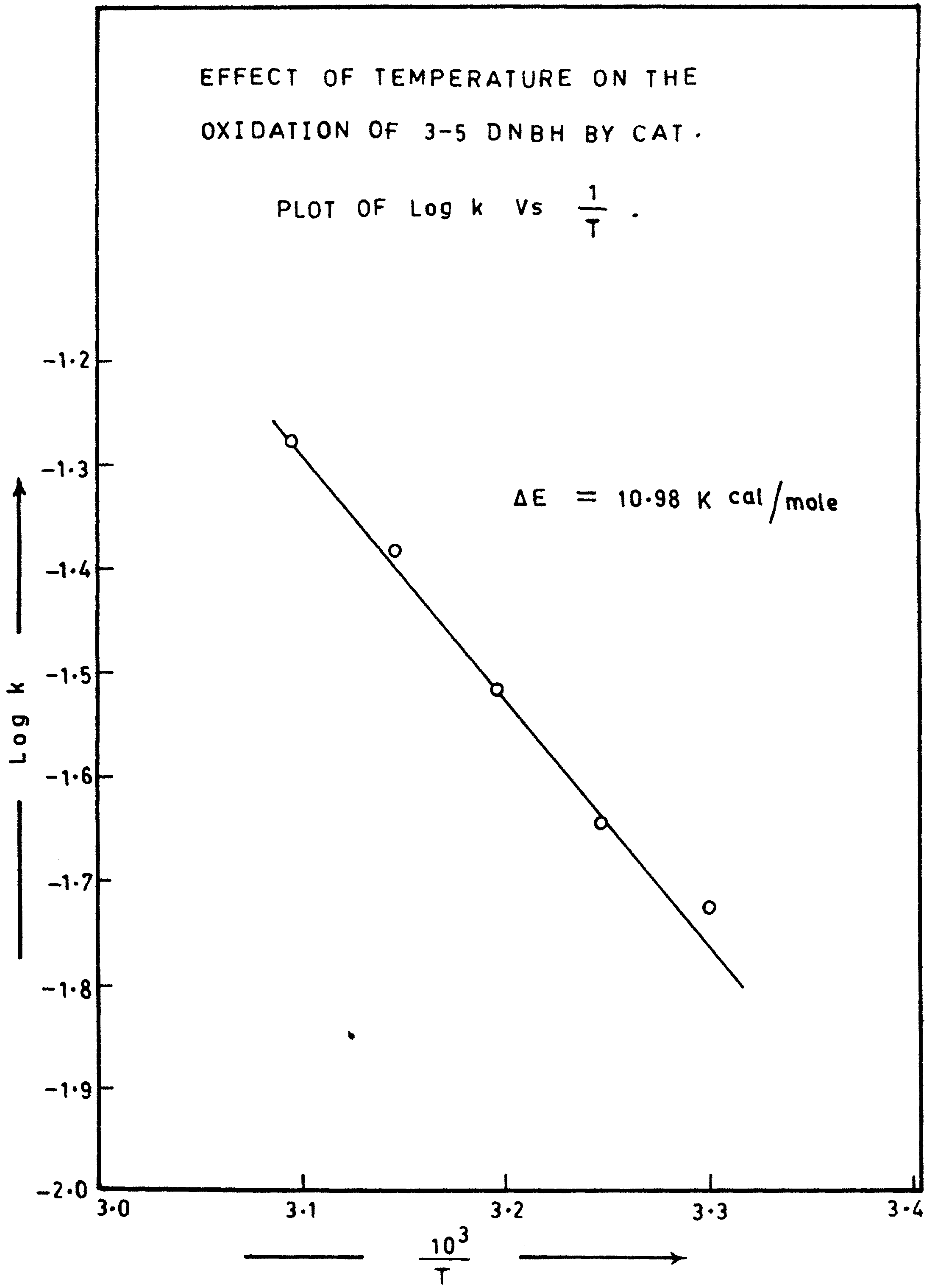

EFFECT OF TEMPERATURE ON THE
OXIDATION OF 3-5 DNBH BY CAT.
PLOT OF Log k Vs 1/T.
ΔE = 10·98 K cal/mole
Log k
10^3/T
-1·2
-1·3
-1·4
-1·5
-1·6
-1·7
-1·8
-1·9
-2·0
3·0
3·1
3·2
3·3
3·4

Fig 7

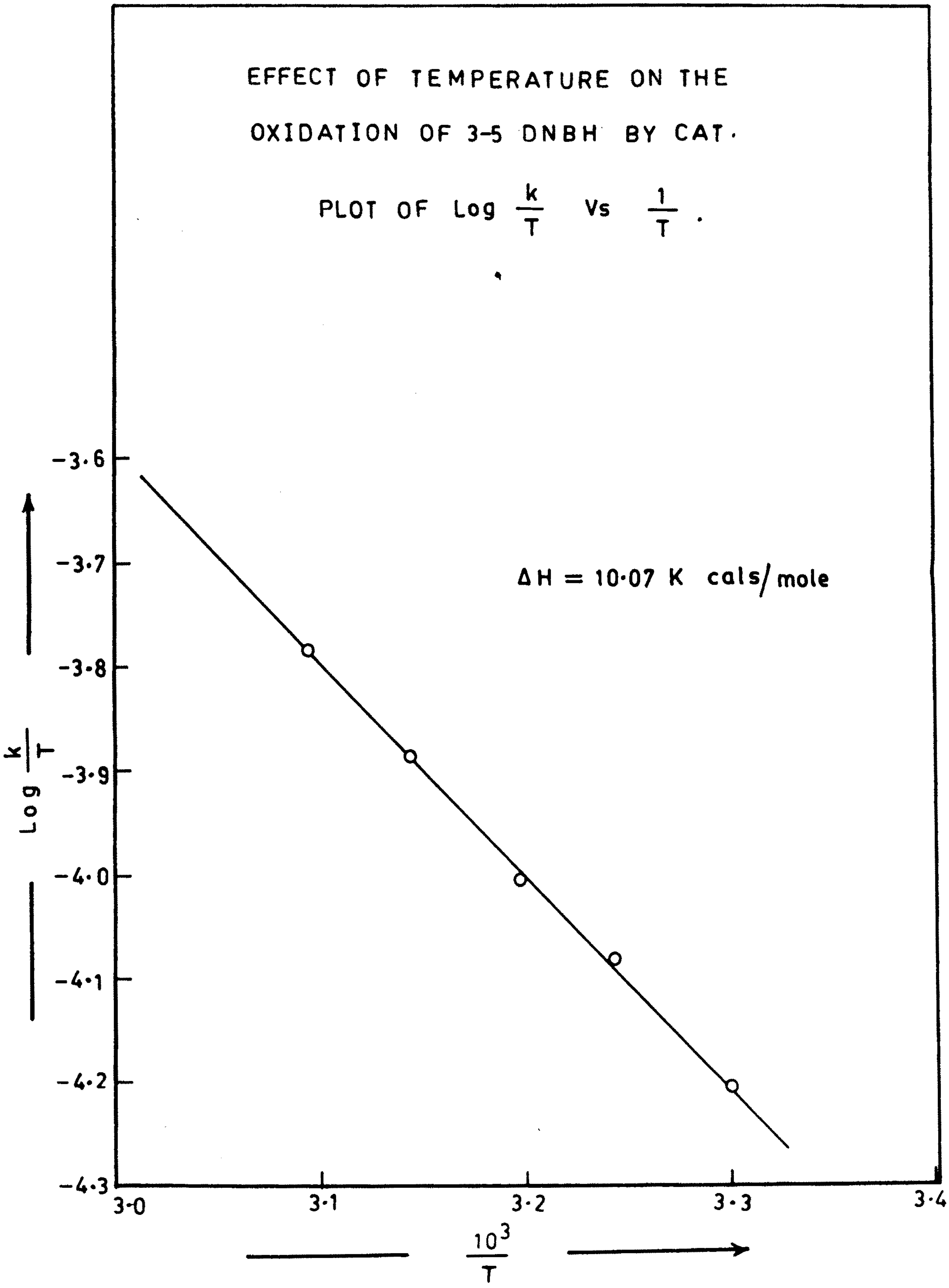

EFFECT OF TEMPERATURE ON THE
OXIDATION OF 3-5 DNBH BY CAT.
PLOT OF Log k/T Vs 1/T.
ΔH = 10·07 K cals/mole
Log k/T
-3·6
-3·7
-3·8
-3·9
-4·0
-4·1
-4·2
-4·3
3·0
3·1
3·2
3·3
3·4
10^3/T

Fig. 8

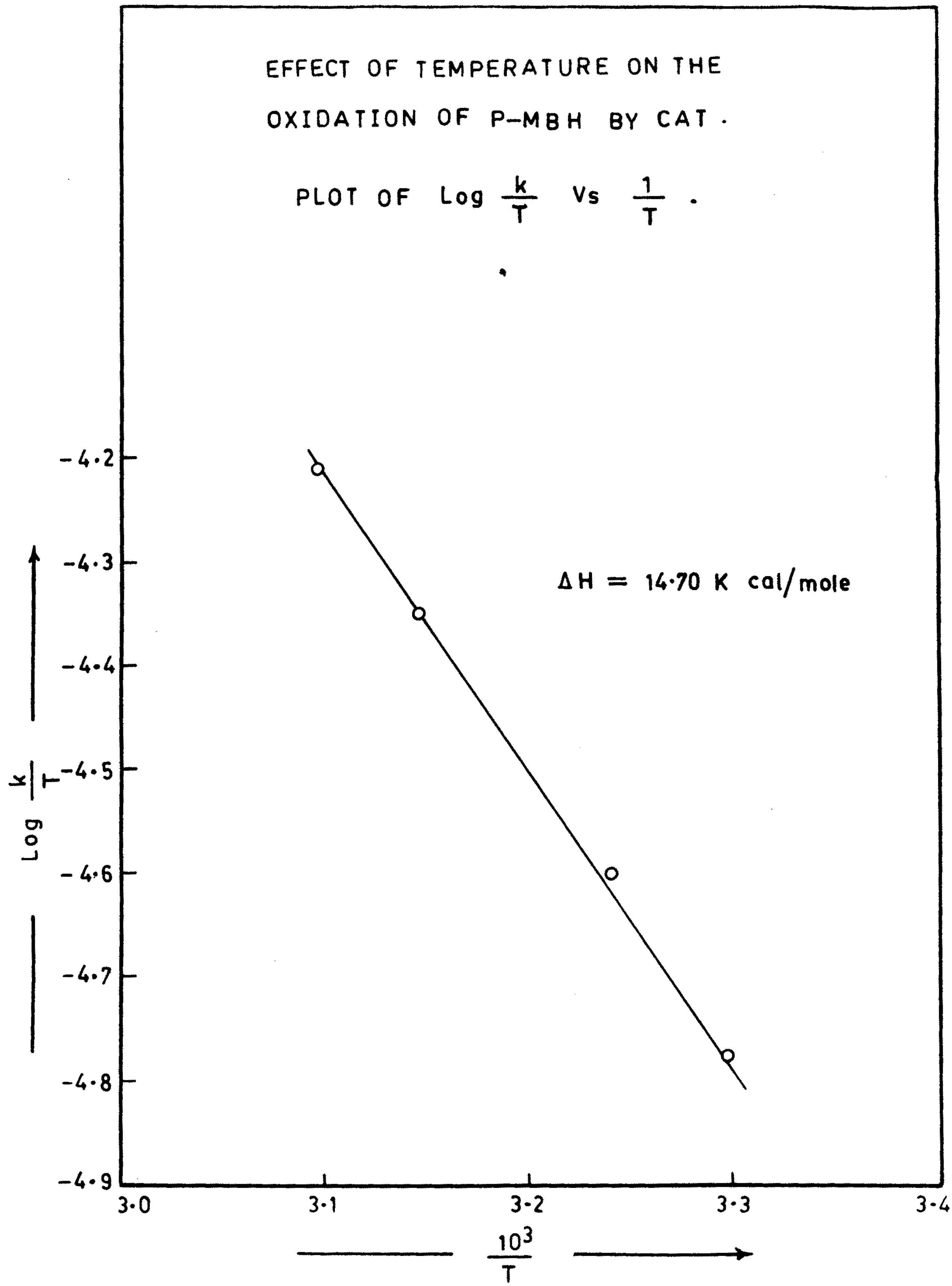
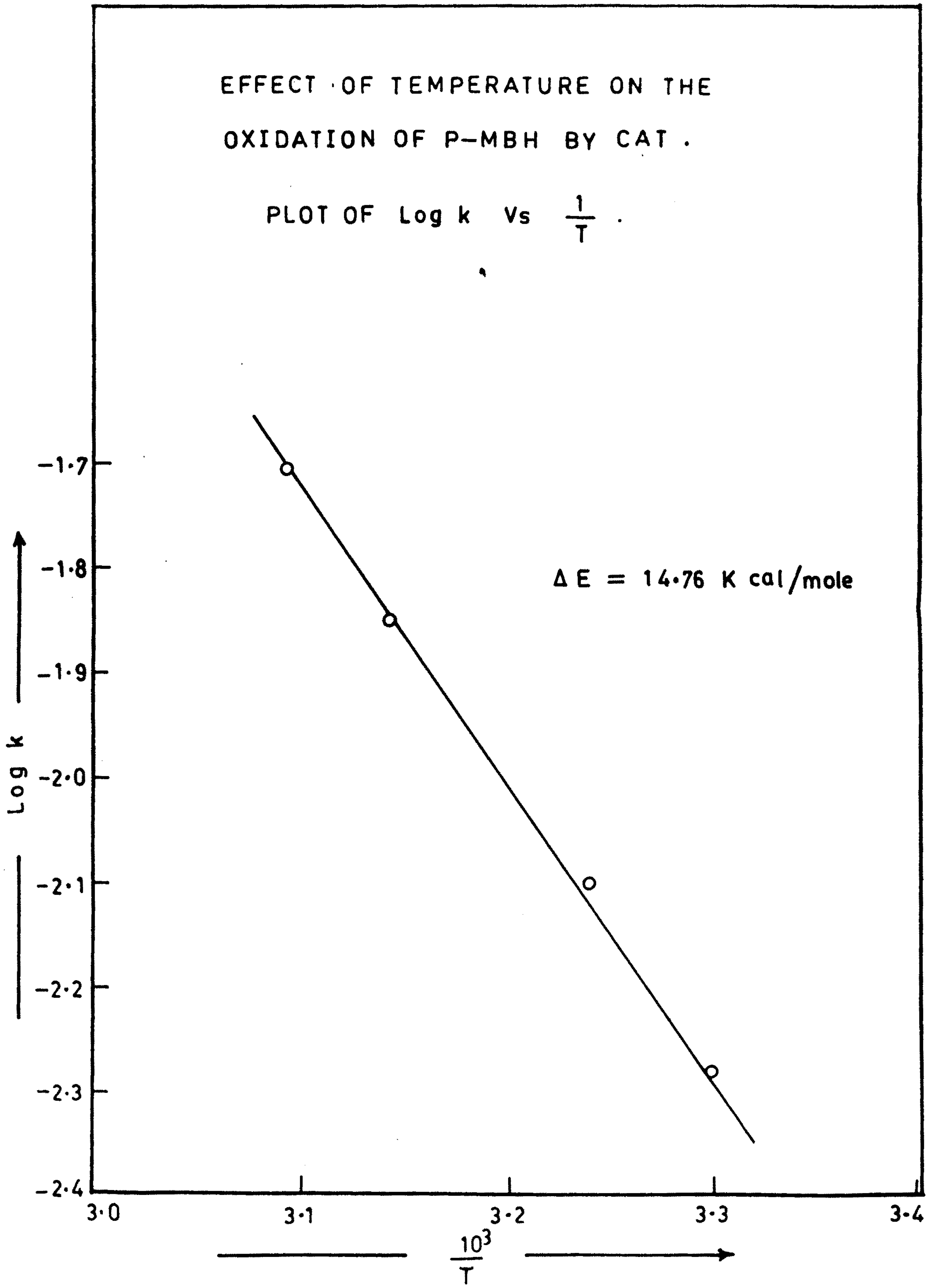

EFFECT OF TEMPERATURE ON THE
OXIDATION OF P-MBH BY CAT.
PLOT OF Log k/T Vs 1/T.
ΔH = 14·70 K cal/mole
Log k/T
-4·2
-4·3
-4·4
-4·5
-4·6
-4·7
-4·8
-4·9
3·0
3·1
3·2
3·3
3·4
10^3/T

Fig. 9



EFFECT OF TEMPERATURE ON THE OXIDATION OF P-MBH BY CAT.
PLOT OF Log k Vs 1/T.
ΔE = 14·76 K cal/mole
Log k
-1·7
-1·8
-1·9
-2·0
-2·1
-2·2
-2·3
-2·4
3·0
3·1
3·2
3·3
3·4
10^3/T

Fig. 10

(III) EFFECT OF THE CHANGE IN THE CONCENTRATION CF CHLORAMINE-T ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

To investigate the effect of concentration of chloramine-T, on the reaction, the reactions were studied with different concentrations of chloramine-T with keeping constant the concentration of different reactants mixed in the reaction at temperature 50^{o}C. Kinetic runs were carried out with varying concentrations of chloramine-T from 5 x 10^{-4} M to 15 x 10^{-4} M. The results were tabulated in tables 8A and 8B. From the results in tables 8A and 8B, it is clear that rate constants (k) are almost constant. Plots of log (a-x) against time are linear. These lines are parallel with change in the initial concentration [Fig.11, 12].

TABLE NO. 8A

EFFECT OF THE CHANGE IN THE CONCENTRATION OF CHLORAMINE-T ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

Substrate concentration = [3.5 DNBH] = 1×10^{-3} M
Temperature = 40^{o} C
pH = 8.88
Medium = Methanol/water (50/50 v/v)

Concentration of chloramine-T [CAT] $\times 10^{4}$ M	5.0	8.0	10.0	12.0	15.0
$k_1 \times 10^{2}$ min^{-1}	3.052	3.164	3.161	3.128	2.842

===

TABLE NO. 8B

EFFECT OF THE CHANGE IN THE CONCENTRATION OF CHLORAMINE-T ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

Substrate concentration = [PMBH] = 4×10^{-3} M
Temperature = 40^{o}C
pH = 8.88
Medium = Methanol/water (50/50 v/v)

Concentration of chloramine-T [CAT] $\times 10^{4}$ M	5.0	8.0	10.0	12.0	15.0
$k_1 \times 10^{2}$ min^{-1}	1.239	1.119	1.177	1.031	1.107

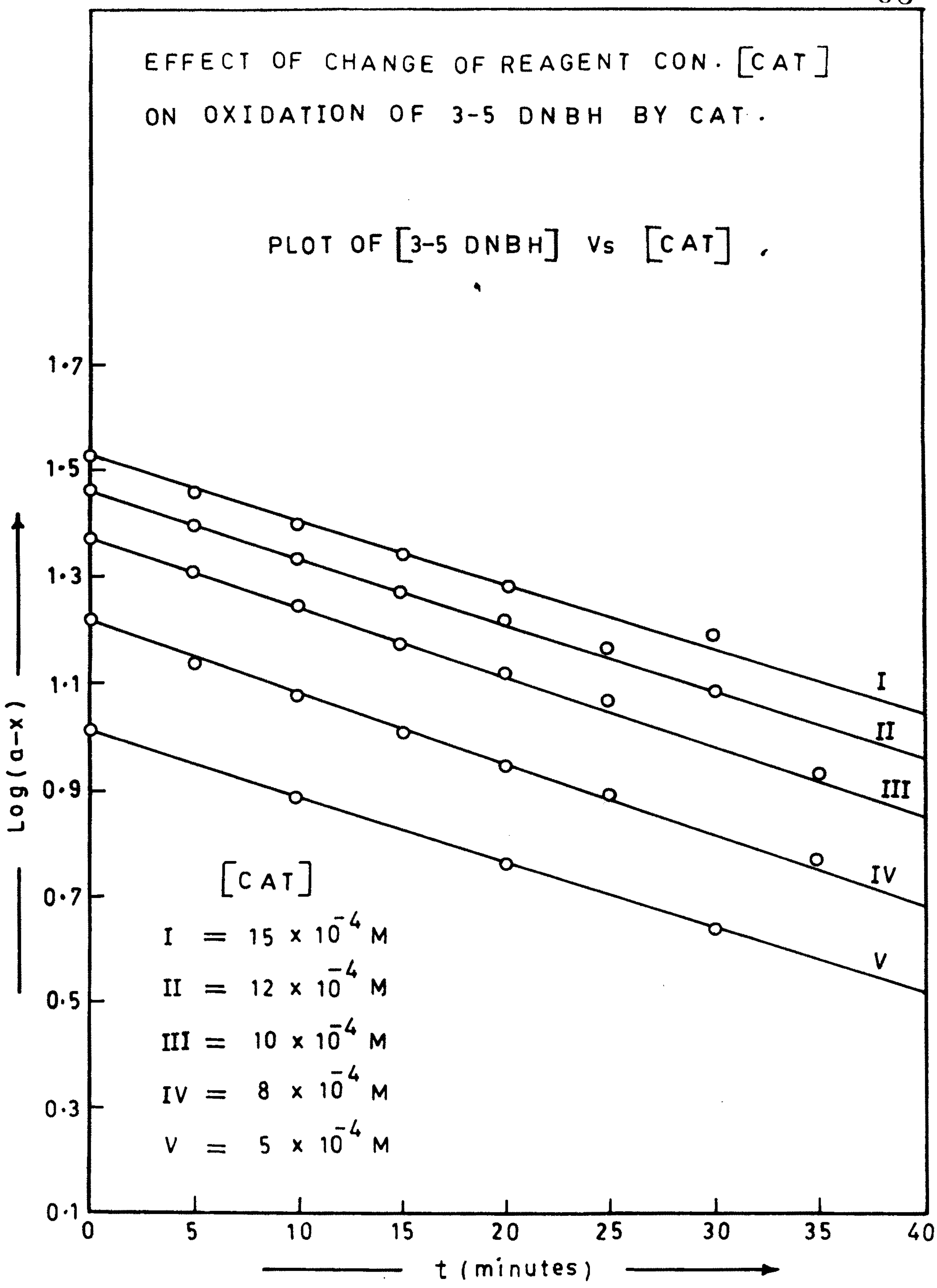
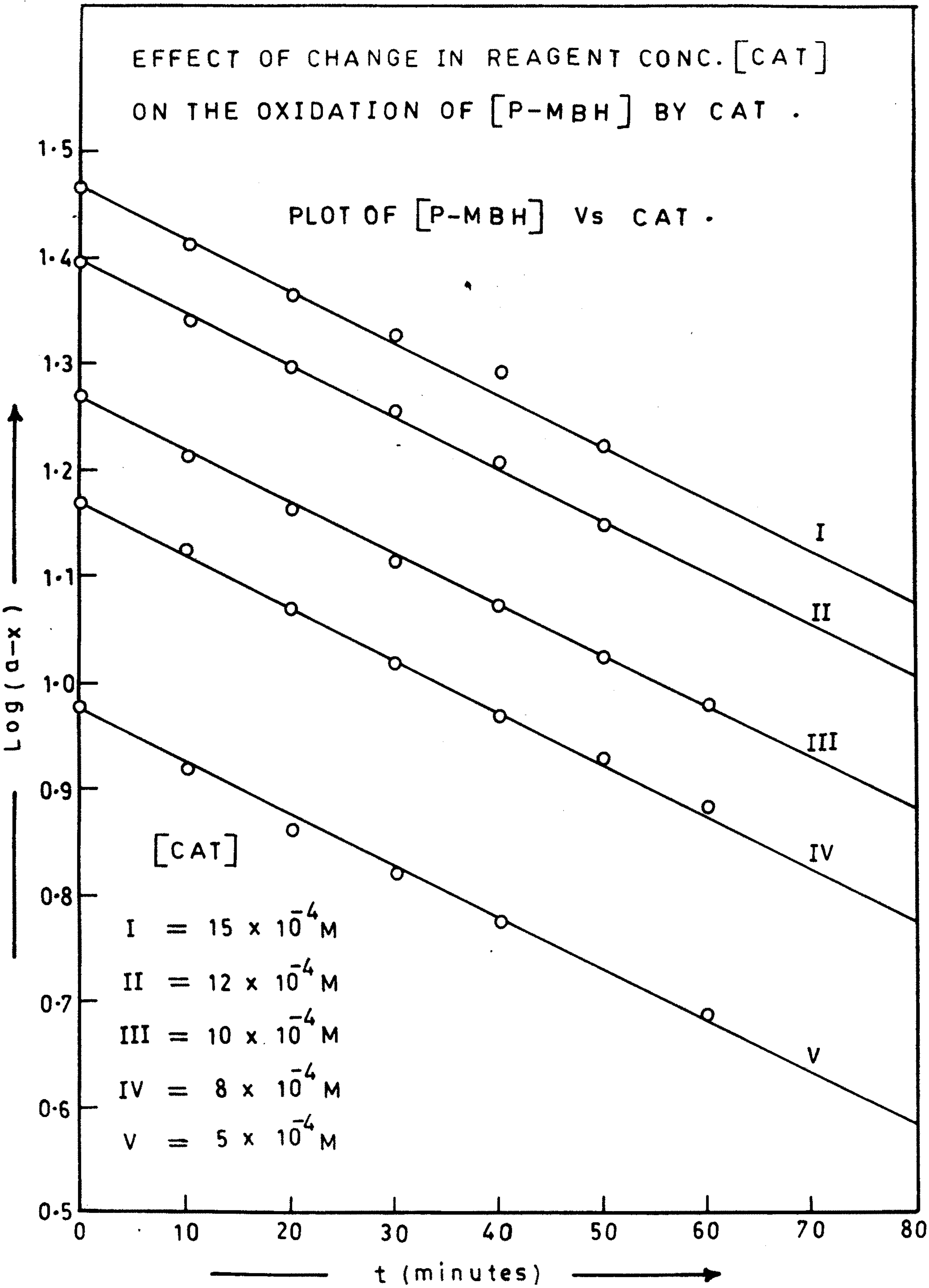

EFFECT OF CHANGE OF REAGENT CON. [CAT]
ON OXIDATION OF 3-5 DNBH BY CAT.
PLOT OF [3-5 DNBH] Vs [CAT].
Log(a-x)
1·7
1·5
1·3
1·1
0·9
0·7
0·5
0·3
0·1
0
5
10
15
20
25
30
35
40
t (minutes)
I
II
III
IV
V
[CAT]
I = 15 x 10⁻⁴ M
II = 12 x 10⁻⁴ M
III = 10 x 10⁻⁴ M
IV = 8 x 10⁻⁴ M
V = 5 x 10⁻⁴ M

Fig. 11



EFFECT OF CHANGE IN REAGENT CONC. [CAT]
ON THE OXIDATION OF [P-MBH] BY CAT.
PLOT OF [P-MBH] Vs CAT.
Log (a-x)
t (minutes)
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0
10
20
30
40
50
60
70
80
I
II
III
IV
V
[CAT]
I = 15 x 10^{-4} M
II = 12 x 10^{-4} M
III = 10 x 10^{-4} M
IV = 8 x 10^{-4} M
V = 5 x 10^{-4} M

Fig. 12

(IV) EFFECT OF CHANGE IN THE SOLVENT COMPOSITION (METHANOL/WATER) ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

To investigate the effect of change in solvent composition on rate constant (k) of the reaction, the reactions were carried out by changing the percentage composition of methanol and water in the reaction mixture. To know the effect of change in solvent composition on the oxidation of 3-5 dinitrobenzhydrazide, kinetic runs were carried out in four different mediums in which percentage compositions of methol/water were different from 70/30 (v/v) to 40/60 (v/v). In the same way kinetic runs were carried in the case of p-methoxy benzhydrazide in five different mediums in which percentage composition of methanol/water were different from 70/30 v/v to 30/70 (v/v).

The results obtained were tabulated in tables 9 and 10. From the tables 9 and 10, it is clear that rate constant (k_1) increases with decrease in the percentage of methanol in the composition of the medium.

TABLE NO. 9

EFFECT OF THE CHANGE IN THE COMPOSITION OF METHANOL/WATER MIXTURE ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

Substrate concentration = [3.5 DNBH] = 1×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

pH = 8.88

Temperature = 40^{o} C

Sr.No.	Percentage of methanol	Percentage of water	$k_1 x 10^2$ min^{-1}
1	70	30	2.434
2	60	40	2.804
3	50	50	3.052
4	40	60	6.061

TABLE NO. 10

EFFECT OF CHANGE IN THE COMPOSITION OF METHANOL/WATER MIXTURE ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

Substrate concentration = [P.MBH] = 4×10^{-3}

Chloramine-T concentration = 5×10^{-4} M

pH = 8.88

Temperature = 40^{o} C

Sr.No.	Percentage of Methanol	Percentage of Water	$k_1 \times 10^2$ min^{-1}
1	70	30	0.882
2	60	40	1.043
3	50	50	1.239
4	40	60	1.380
5	30	70	1.641

(V) EFFECT OF pH ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

To investigate the effect of pH on the oxidation of hydrazides by chlorimine-T, kinetic runs were carried out in different buffer solutions with the pH range from 8.55 to 9.55. Buffer solutions were prepared by mixing equal volumes of 0.025 M sodium carbonate and 0.025 M sodium bicarbonate solutions. To prepare reaction mixtures of different pH, 10, 20, 30 and 40 mls of buffer solutions were added to 100 ml reaction mixtures, the pH of the reaction mixtures were found to be 8.55, 8.88, 9.28 and 9.55 respectively. The pH values were determined by digital pH meter.

The results of kinetic runs were tabulated in tables 11 and 12. From the results of table No.11, it is clear that oxidation of 3-5 dinitrobenzhydrazide is independant of pH in the range of 9.55 to 8.85. Similarly by observing results in the table 12 it can be said that oxidation of p-methoxybenzhydrazide is independent of pH in the range of 9.55 to 8.55.

TABLE NO. 11

EFFECT OF THE CHANGE IN THE pH OF MEDIUM ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

Substrate concentration= [3-5 DNBH] = 1×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temperature = $40^{o}C$

Medium = Methanol/water (50/50 v/v)

Sr. No.	mls of $NaHCO_3$(0.025N) in 100 ml mixture	mls of Na_2CO_3(0.025N) in 100 ml mixture	pH of the solution	$k_1 \times 10^2$ min^{-1}
1	20	20	9.55	2.806
2	15	15	9.28	3.022
3	10	10	8.88	3.052

TABLE NO. 12

EFFECT OF THE CHANGE IN THE pH OF MEDIUM ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

Substrate concentration = [P-MBH] = 4×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temperature = 40° C

Medium = Methanol/water (50/50 v/v)

Sr. No	mls of $NaHCO_3$(0.025N) in 100 ml mixture	mls of Na_2CO_3(0.025N) in 100 ml mixture	pH of the solution	$k_1 \times 10^2$ min^{-1}
1	20	20	9.55	1.167
2	15	15	9.28	1.052
3	10	10	8.88	1.239
4	5	5	8.55	1.100

(VI) EFFECT OF ADDITION OF SALT ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T

In order to investigate the effect of added salt on the oxidation of hydrazide by chloramine-T, different kinetic runs were carried out by adding different volumes of 0.1 N sodium chloride solution to reaction mixtures keeping all other concentrations constant at 40°C. These reaction mixtures were prepared with different concentrations of sodium chloride [0.002 M, 0.004 M, 0.006, 0.008 and 0.01 M] and, its effect on the rate constant(k) was observed. The results obtained were tabulated in the tables 13 and 14. From the results in the tables 13 and 14, it is clear that added sodium chloride have no effect on the rate of the reactions.

TABLE NO. 13

EFFECT OF ADDITION OF SODIUM CHLORIDE ON THE OXIDATION OF HYDRAZIDE BY CHLORAMINE-T

Substrate concentration = [3.5 D NBH] = 1×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temperature = $40^{o}C$

Medium = Methanol/water (50/50 v/v)

Conc. of NaCl = [NaCl] $\times 10^3$ M	2.0	4.0	6.0	8.0	10.0
$k_1 \times 10^2$ min^{-1}	2.8800	3.031	2.933	3.285	2.889

TABLE NO. 14

EFFECT OF ADDITION OF SODIUM CHLORIDE ON THE OXIDATION OF HYDRAZIDE BY CHLORAMINE-T

Substrate concentration = [P.MBH] = 4×10^{-3} M

Chloramine-T concentration = 5×10^{-4} M

Temperature = $40^{o}C$

Medium = Methanol/water (50/50 v/v)

Conc. of NaCl = [NaCl] $\times 10^3$ M	2.0	4.0	6.0	8.0	10.0
$k_1 \times 10^2$ min^{-1}	1.068	1.197	1.712	1.288	1.137