CHAPTER-III

RESULTS

RESULTS

Introduction

The salicylic acid hydrazide (SAH) and O-chloro benzoic acid hydrazide (O-CBAH) were oxidised by chloramine-T at temperature $30^{O}C$. An aqueous alkaline methanol medium was used to study the reaction.

In a typical experiment, measured quantities of hydrazide, buffer solution, methanol and distilled water were taken in a reaction flask. The reaction flask was placed in the thermostat maintained at the temperature $30^{O}C$ for half an hour to attain constant temperature. A measured quantity of chloramine-T solution was also thermostated in the same bath. After adding chloramine-T in a reaction mixture, immediately 5 ml of reaction mixture was taken out and added in acidified potassium iodide solution in iodometric flask. After 10 minutes, liberated iodine was titrated against a standard solution 'of sodium thio-sulphate using freshly prepared starch solution as an indicator. Then after definite time intervals aliquots of 5 ml reaction mixture were titrated using same method.

(I) EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION [HYDRAZIDES]

In order to investigate the effect of change in hydrazide concentration on the rate of oxidation of hydrazides by chloramine-T; kinetic runs were carried out by changing the hydrazide concentration, keeping the concentration of chloramine-T and all other components constant at temperature $30^{o}C$. The salicylic acid hydrazide concentration was varied from 0.5×10^{-3} M to 3.0×10^{-3} M and O-chlorobenzoic acid hydrazide concentration was varied from 1.5×10^{-3} M to 4.5×10^{-3} M (Table Nos. 3.1.1, 3.1.2, 3.2.1 and 3.2.2). The results of these kinetic runs were calculated by using the formula

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

where

a = initial volume of $Na_2S_2O_3$ (equivalent to chloramine-T),

x = difference in initial reading and reading at particular time interval, and

t = time.

The results obtained in table Nos. 3.1.1 and 3.2.1, show that the first order rate constants increase with increase in the concentrations of hydrazides. The second order rate constant (k_2)

$$k_2 = \frac{k_1}{[\text{conc. of hydrazide}]}$$

where

k_2 = second order rate constant,

and k_1 = first order rate constant.

The second order rate constants were found to be constant for each hydrazide. These observations indicate that the rates of reactions are first order with respect to hydrazides.

The order (n) of the reaction was confirmed by following methods. First order rate constant (k_1) was calculated by using relation,

$$k_1 = \left[-dc/dt\right] \times 2.303$$

where $\left[-dc/dt\right]$ is the slope of the plot log (a-x) Vs time (t) (fig.3.1.1 and 3.2.1).

The order (n) with respect to hydrazide was also determined by Van't Hoff euqation :

$$\text{i.e. order (n)} = \frac{\log\left[-dc_0/dt\right]_1 - \log\left[-dc_0/dt\right]_2}{\log\left[c_0\right]_1 - \log\left[c_0\right]_2}$$

The order of reaction with respect ot hydrazide concentration is confirmed by the slope of the plot of log [-dc/dt] vs log [conc. of Hydrazide] (fig. 3.1.3 and 3.2.3).

In case of both the hydrazides, the order was found to be 1 (one). In the tables 3.1.2 and 3.2.2 the values of change in substrate concentration, [-dc/dt] and order (n) calculated, are given.

TABLE NO. 3.1.1

EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION ON THE OXIDATION OF SALICYLIC ACID HYDRAZIDE BY CHLORAMINE-T.

[CAT] = 5.0×10^{-4} M [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4} M

Temperature = 30^oC pH = 8.88

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

Sr. No.	SAH conc. = $M \times 10^3$	$k_1 \times 10^4$ min^{-1}	$k_2 \times 10^1$ min^{-1}
1	0.5	0.99	1.99
2	1.0	2.22	2.22
3	1.5	3.61	2.41
4	2.0	4.46	2.23
5	2.5	5.99	2.39
6	3.0	7.64	2.54

TABLE NO. 3.2.1

EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION ON THE OXIDATION OF ORTHO-CHLORO BENZOIC ACID HYDRAZIDE BY CHLORAMINE-T .

[CAT] = 5.0×10^{-4} M   [$Na_2S_2O_3, 5H_2O$] = 5.0×10^{-4} M

Temperature = $30^{o}C$ pH = 8.88

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

Sr. No.	O-CBAH conc. = $M \times 10^3$	$k_1 \times 10^4$ min^{-1}	$k_2 \times 10^2$ min^{-1}
1	1.5	0.62	4.14
2	2.0	0.87	4.34
3	2.5	1.05	4.18
4	3.0	1.31	4.37
5	3.5	1.50	4.28
6	4.5	1.82	4.05

TABLE NO. 3.1.2

EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION ON THE OXIDATION OF SALICYLIC ACID HYDRAZIDE BY CHLORAMINE-T .

Conc. of substrate [SAH] = $M \times 10^{3}$	0.5	1.0	1.5	2.0	2.5
[-dc/dt] $\times 10^{4}$	0.397	0.875	1.42 0	1.933	2.541
[-dc/dt] x 2.303 = $k_1 \times 10^{4}$ min^{-1}	0.914	2.015	3.270	4.451	5.851
k_1 / [Substrate] = $k_2 \times 10^{1} min^{-1}$	1.828	2.015	2.180	2.226	2.340
log [-dc/dt]	$\bar{5}.5988$	$\bar{5}.9420$	$\bar{4}.1523$	$\bar{4}.2863$	$\bar{4}.4050$
log c	$\bar{4}.6990$	$\bar{3}.0000$	$\bar{3}.1761$	$\bar{3}.3010$	$\bar{3}.3979$
'n'	-	1.14	1.19	1.07	1.22

Mean 'n' = 1.15 $\simeq$ 1

Slope (fig. 3.1.3) = 0.86 $\simeq$ 1

TABLE NO. 3.2.2

EFFECT OF CHANGE IN SUBSTRATE CONCENTRATION ON THE OXIDATION OF ORTHO-CHLORO BENZOIC ACID HYDRAZIDE BY CHLORAMINE-T .

Conc. of substrate [O-CBAH] = M x 10^3	1.5	2.0	2.5	3.0	3.5	4.5
[-dc/dt] x 10^4	0.317	0.400	0.500	0.605	0.697	0.870
[-dc/dt] x 2.303 = k_1 x 10^4 min^{-1}	0.730	0.921	1.151	1.393	1.605	2.003
k_1 / [Substrate] = k_2 x $10^2 min^{-1}$	4.87	4.60	4.60	4.64	4.59	4.45
log [-dc/dt]	$\bar{5}.5011$	$\bar{5}.6021$	$\bar{5}.6990$	$\bar{5}.7818$	5.8432	$\bar{5}.9395$
log c	$\bar{3}.1761$	$\bar{3}.3010$	$\bar{3}.3979$	$\bar{3}.4771$	$\bar{3}.5441$	$\bar{3}.6532$
' n '	-	0.81	1.00	1.05	0.92	0.96

Mean 'n' = 0.95 $\simeq$ 1

Slope (fig. 3.2.3) = 0.98 $\simeq$ 1

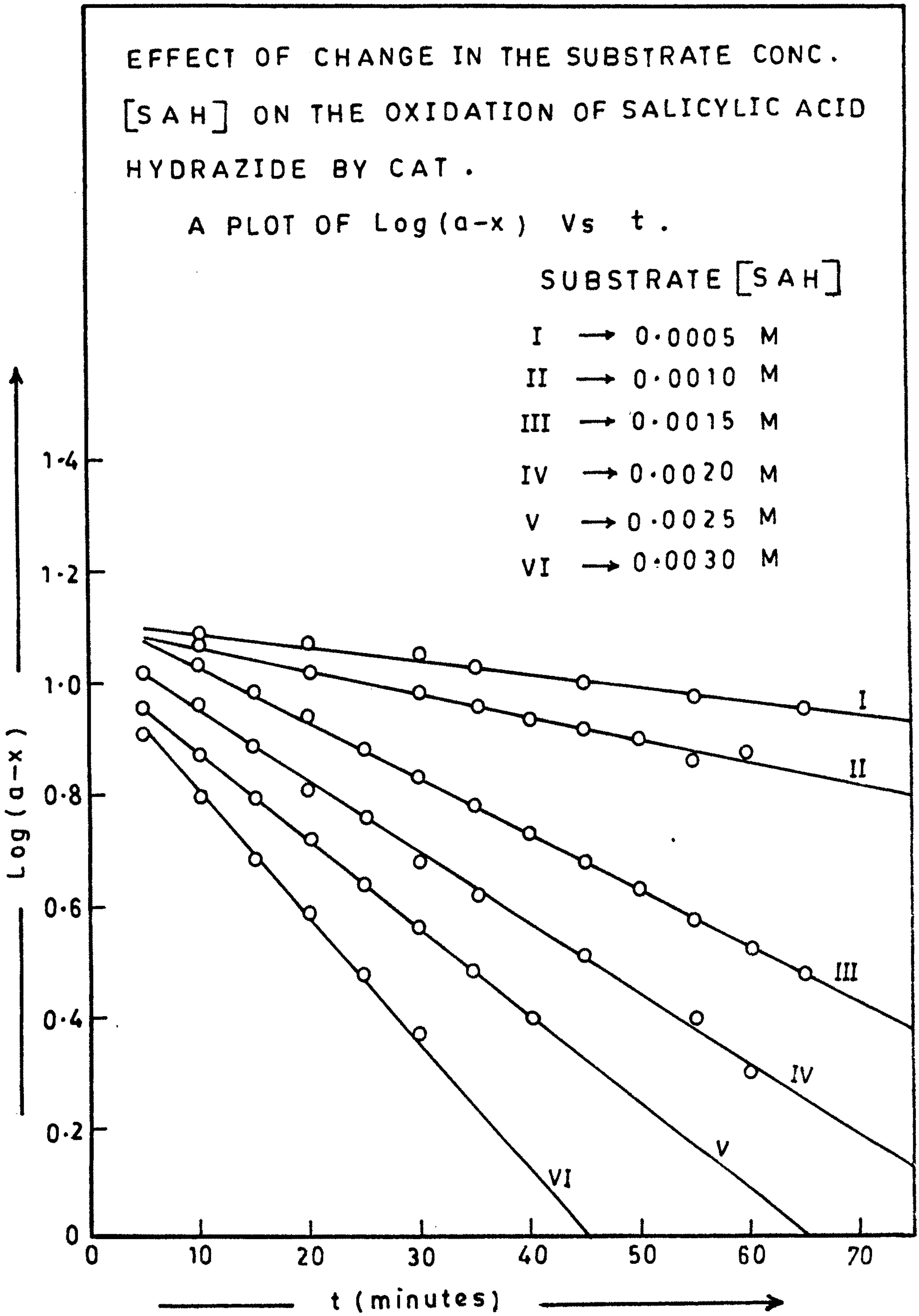
EFFECT OF CHANGE IN THE SUBSTRATE CONC. [SAH] ON THE OXIDATION OF SALICYLIC ACID HYDRAZIDE BY CAT.
A PLOT OF Log(a-x) Vs t.
SUBSTRATE [SAH]
I → 0·0005 M
II → 0·0010 M
III → 0·0015 M
IV → 0·0020 M
V → 0·0025 M
VI → 0·0030 M
Log(a-x)
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
0
10
20
30
40
50
60
70
t (minutes)
I
II
III
IV
V
VI

Fig. 3·1·1

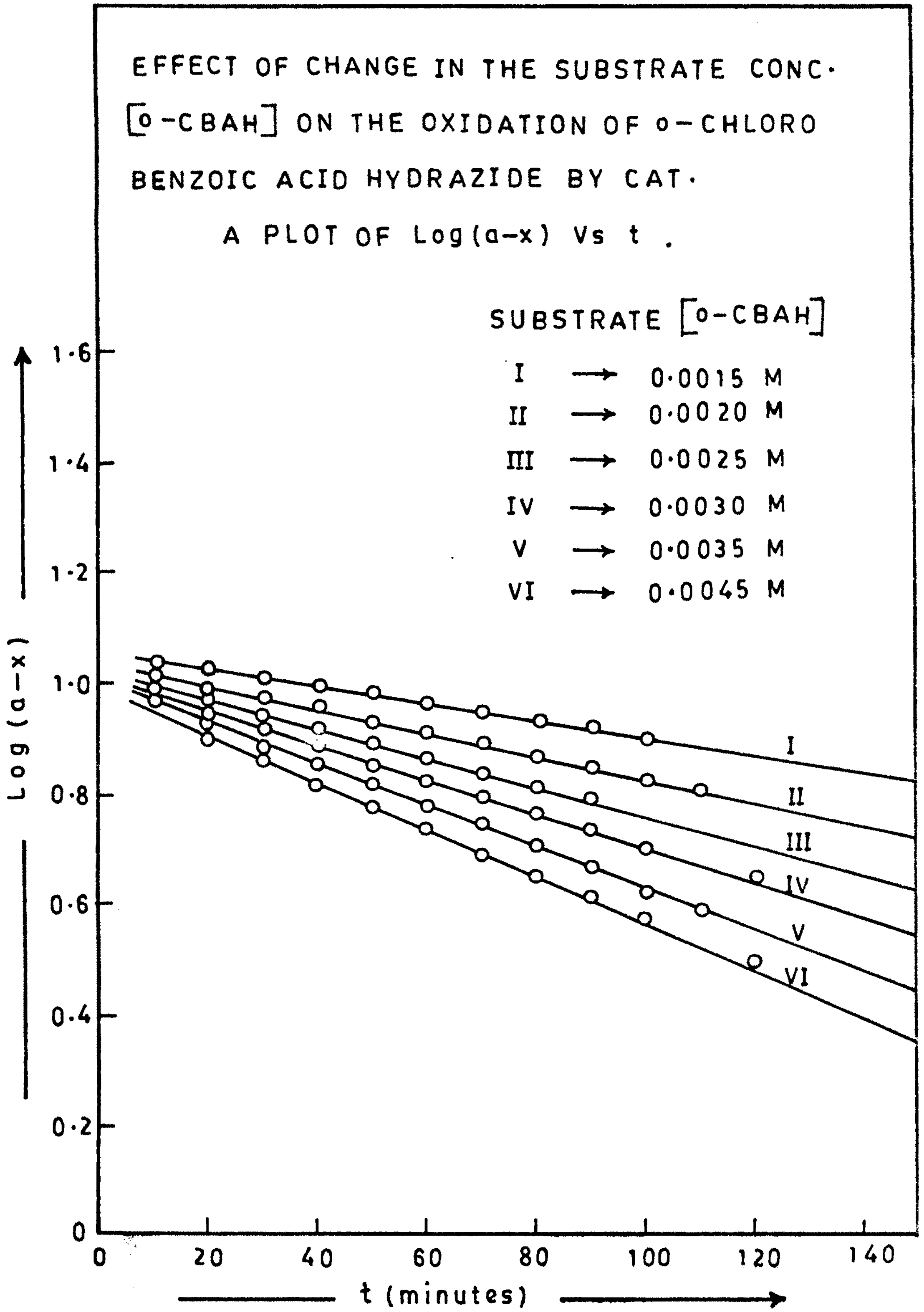
EFFECT OF CHANGE IN THE SUBSTRATE CONC.
[o-CBAH] ON THE OXIDATION OF o-CHLORO
BENZOIC ACID HYDRAZIDE BY CAT.
A PLOT OF Log(a-x) Vs t .
SUBSTRATE [o-CBAH]
I → 0·0015 M
II → 0·0020 M
III → 0·0025 M
IV → 0·0030 M
V → 0·0035 M
VI → 0·0045 M
Log (a-x)
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
0
20
40
60
80
100
120
140
t (minutes)
I
II
III
IV
V
VI

Fig. 3:2:1

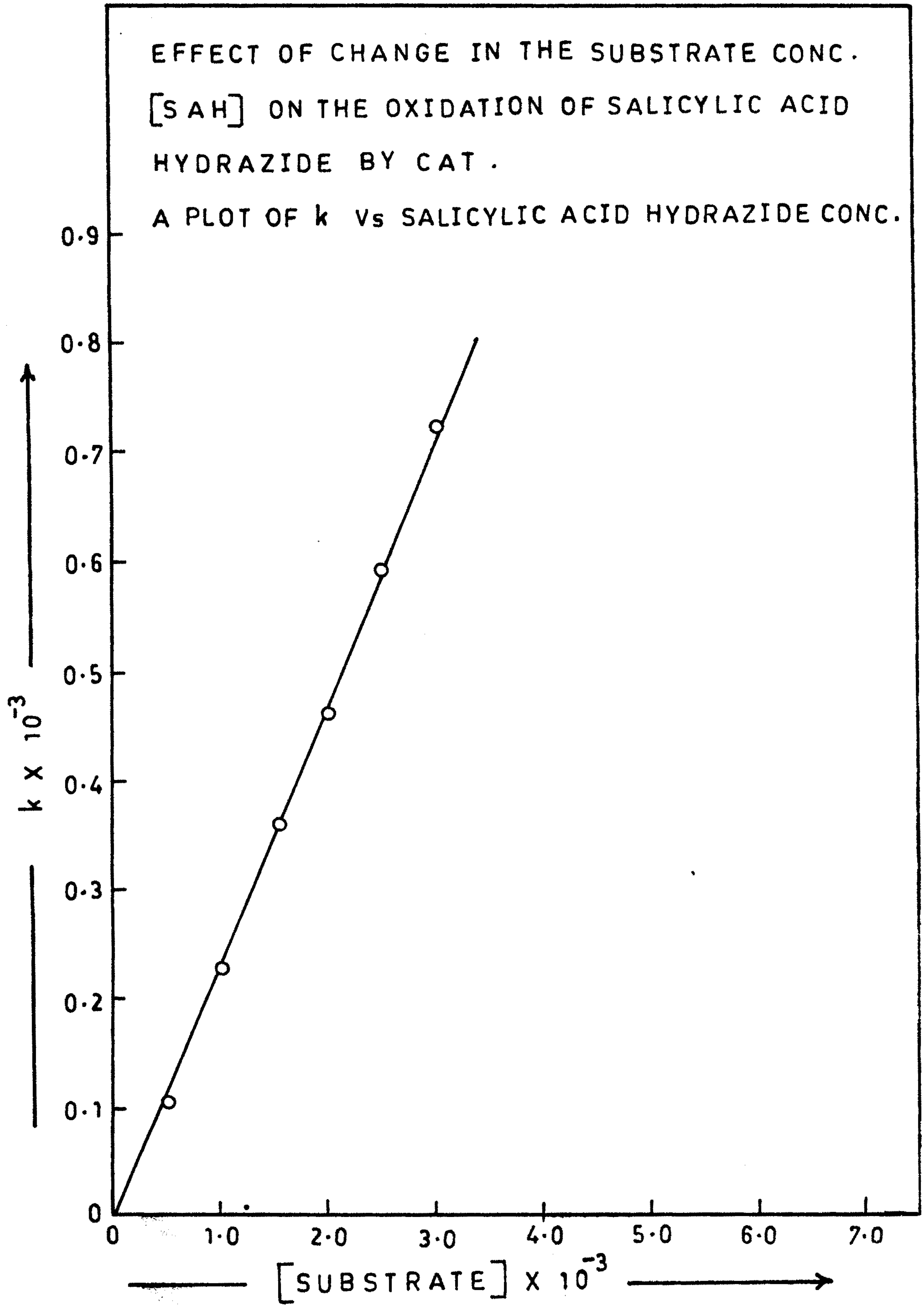
EFFECT OF CHANGE IN THE SUBSTRATE CONC.
[SAH] ON THE OXIDATION OF SALICYLIC ACID
HYDRAZIDE BY CAT.
A PLOT OF k Vs SALICYLIC ACID HYDRAZIDE CONC.
k X 10^-3
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
[SUBSTRATE] X 10^-3

Fig. 3·1·2

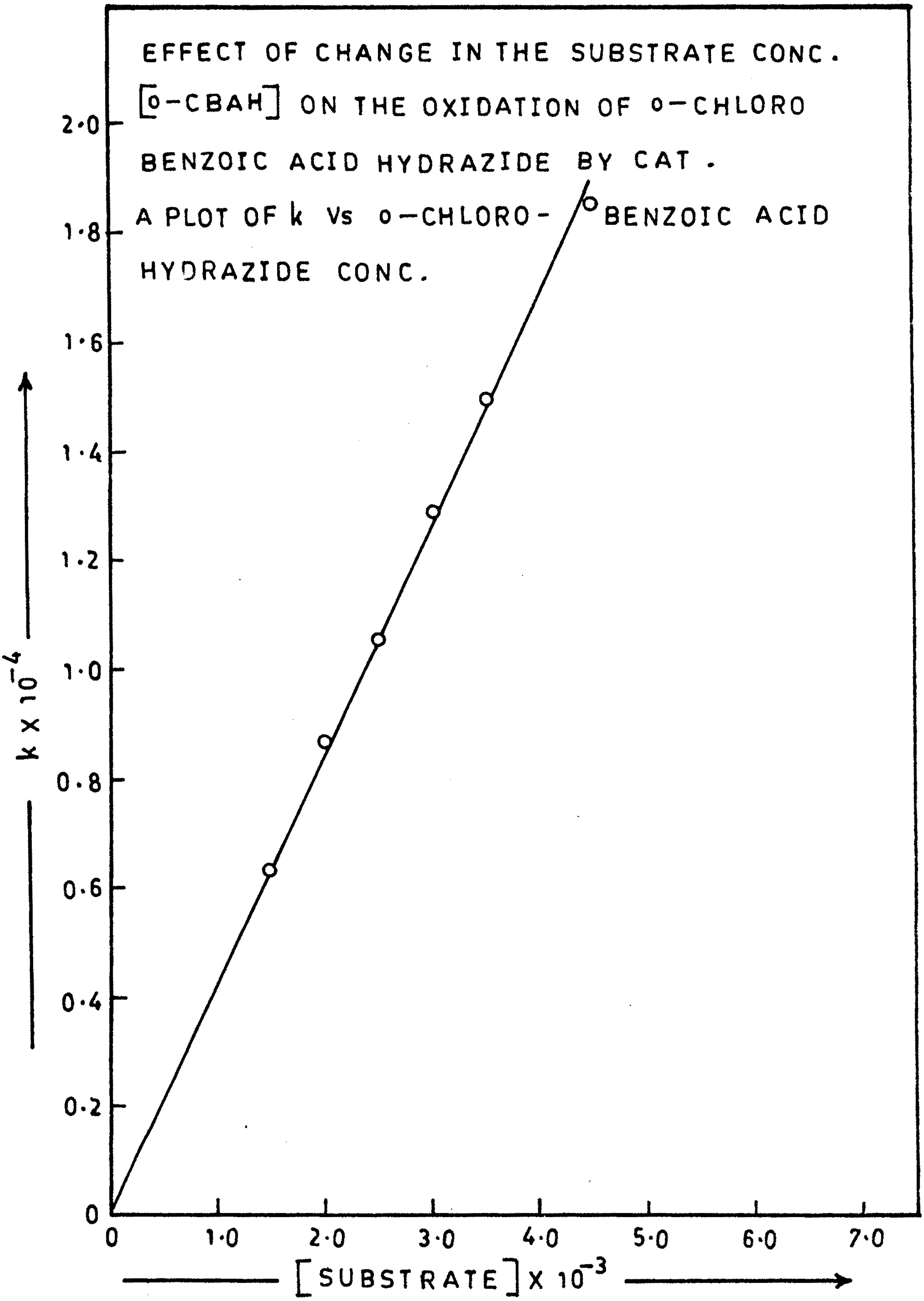
EFFECT OF CHANGE IN THE SUBSTRATE CONC. [o-CBAH] ON THE OXIDATION OF o-CHLORO BENZOIC ACID HYDRAZIDE BY CAT.
A PLOT OF k Vs o-CHLORO-BENZOIC ACID HYDRAZIDE CONC.
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
k x 10⁻⁴
1·0
2·0
3·0
4·0
5·0
6·0
7·0
[SUBSTRATE] x 10⁻³

Fig. 3:2:2

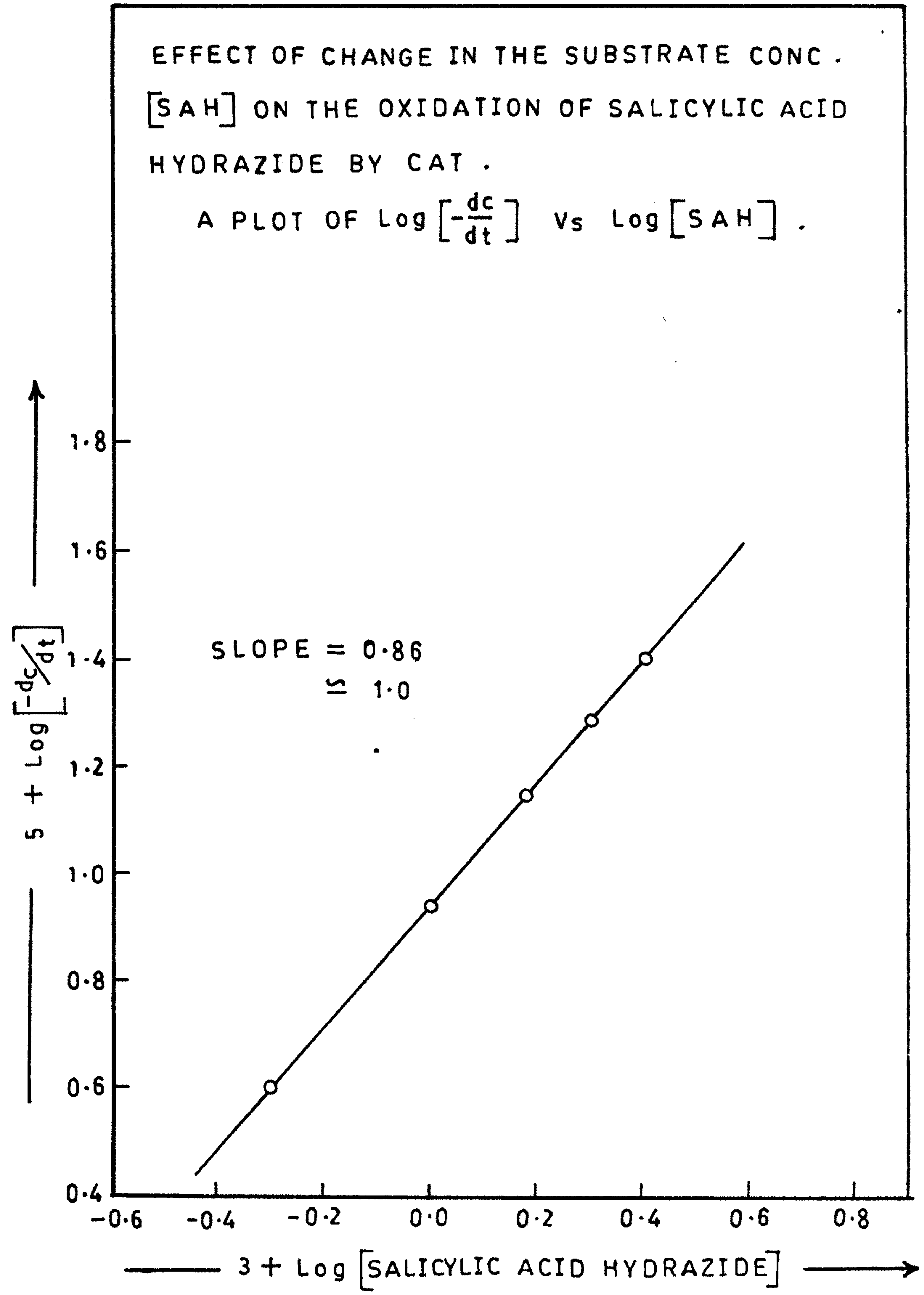
EFFECT OF CHANGE IN THE SUBSTRATE CONC. [SAH] ON THE OXIDATION OF SALICYLIC ACID HYDRAZIDE BY CAT.
A PLOT OF Log $\left[-\frac{dc}{dt}\right]$ Vs Log [SAH].
SLOPE = 0·86
≅ 1·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
−0·6
−0·4
−0·2
0·0
0·2
0·4
0·6
0·8
5 + Log $\left[-dc/dt\right]$
3 + Log [SALICYLIC ACID HYDRAZIDE]

Fig. 3:1:3

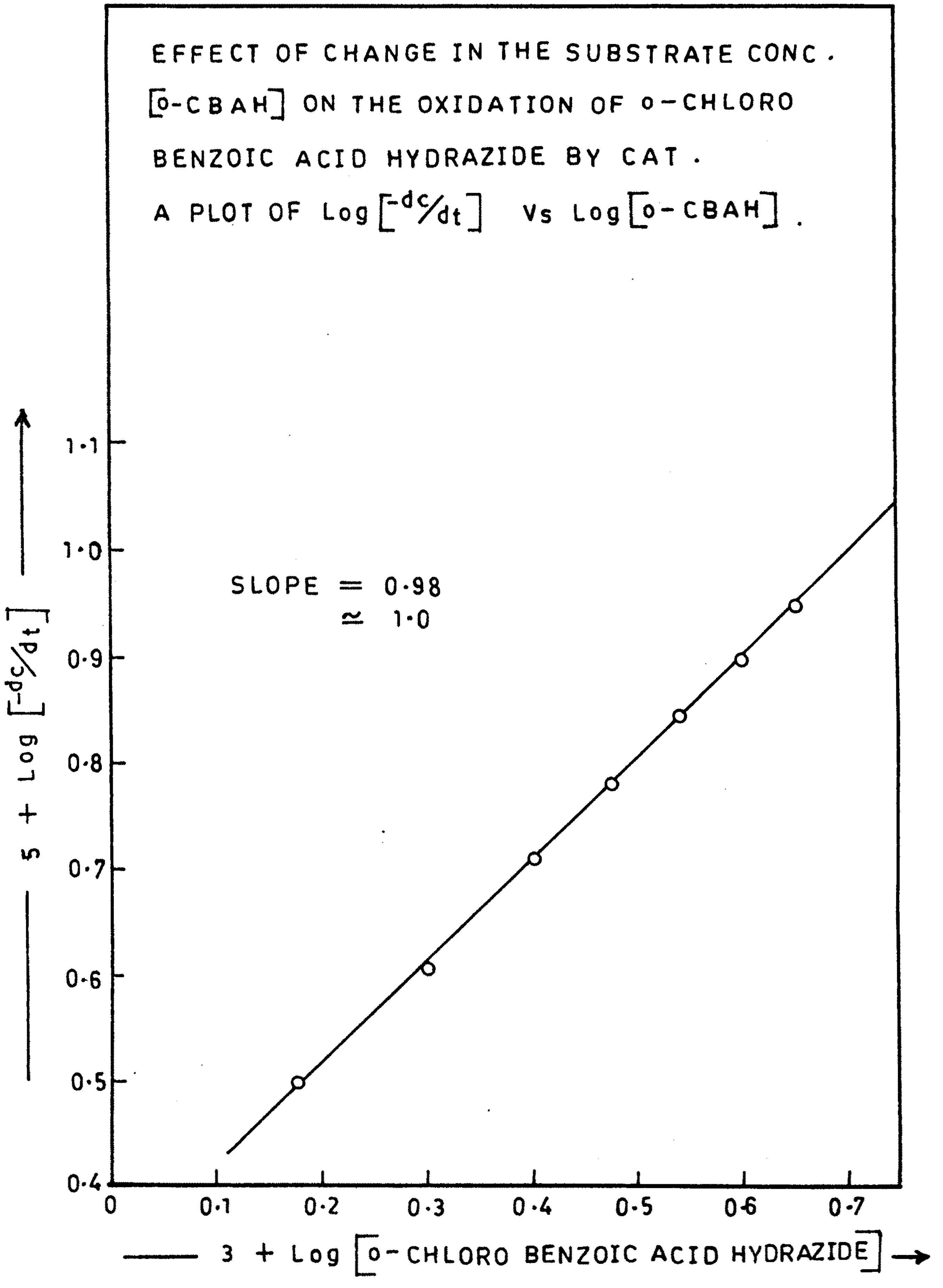
EFFECT OF CHANGE IN THE SUBSTRATE CONC.
[o-CBAH] ON THE OXIDATION OF o-CHLORO
BENZOIC ACID HYDRAZIDE BY CAT.
A PLOT OF Log [-dc/dt] Vs Log [o-CBAH].
SLOPE = 0·98
≃ 1·0
5 + Log [-dc/dt]
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
3 + Log [o-CHLORO BENZOIC ACID HYDRAZIDE]

Fig. 3:2:3

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

The first order rate constants were determined as a function of temperature in the range 30°C to 50°C. The results of these kinetic runs for these hydrazides are shown in tables 3.1.3 and 3.2.3. The plot of log k Vs 1/T is found to be linear indicating that this reaction obeys Arrhenius relationship. It is observed that the specific rate has approximately doubled for 10°C rise in temperature. On the basis of the calculated values of rate constants with respect to temperatures, different thermodynamic parameters were calculated.

To find out these parameters following equations were used :-

1) Energy of activation (Ea),

$$Ea = \log \frac{k_2}{k_1} \left[\frac{T_2 \times T_1}{T_2 - T_1} \right] \times 4.576$$

where k_1 and k_2 are the rate constants at the temperatures T_1 and T_2 respectively.

2) Frequency factory (A).

$$\log A = \log k_1 + \frac{Ea}{4.576\ T}$$

3) Entropy of activations $[\Delta S^{\neq}]$.

$$\Delta S^{\neq} = 4.576 \left[\log k_1 - 10.576 - \log T + \frac{Ea}{4.576\ T}\right]$$

4) Enthalpy of activation $[\Delta H^{\neq}]$.

$$\Delta H^{\neq} = Ea - RT$$

5) Free energy of activation $[\Delta G^{\neq}]$.

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

The calculated values of different Arrhenius parameters are given in tables 3.1.4 and 3.2.4.

These values are also calculated graphically. A plot log k Vs 1/T (fig. 3.1.5 and 3.2.5) is a straight line. The energy of activation is calculated from the slope of this straight line.

$$Ea = \text{Slope} \times 2.303 \times R\ .$$

Similarly a plot of log $[k/T]$ Vs 1/T is a linear plot (Fig.3.1.6 and 3.2.6). From the slope of this linear plot enthalpy $[\Delta H^{\neq}]$ was calculated using following equation.

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

The large negative values of entropy of activation $[\Delta S^{\neq}]$ and smaller values of frequency factor are indicative of the formation of an activated complex involving oppositely charged species or neutral molecule.

TABLE NO. 3.1.3

EFFECT OF THE TEMPERATURE ON THE OXIDATION OF SALICYLIC ACID HYDRAZIDE BY CHLORAMINE-T .

[SAH] = 1.5×10^{-3} M   [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4} M

[CAT] = 8.0×10^{-4} M   pH = 8.88

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

Temp.	$k_1 \times 10^4 min^{-1}$	$10^3/T$	log k	log k/T
303	2.282	3.300	$\bar{4}.3583$	- 6.1231
308	3.013	3.2467	$\bar{4}.4790$	- 6.0096
313	3.958	3.1949	$\bar{4}.5975$	- 5.8961
318	5.271	3.1447	$\bar{4}.7219$	- 5.7805
323	6.657	3.0960	$\bar{4}.8233$	- 5.6859

TABLE NO. 3.2.3

EFFECT OF THE TEMPERATURE ON THE OXIDATION OF ORTHO-CHLORO BENZOIC ACID HYDRAZIDE BY CHLORAMINE-T.

[O-CBAH] = 1.5×10^{-3} M　　[$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4}

[CAT] = 8.0×10^{-4} M　　pH = 8.88

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

Temp.	$k_1 \times 10^4 min^{-1}$	$10^3/T$	log k	log k/T
303	0.671	3.300	$\bar{5}.8267$	- 6.6547
308	0.998	3.2467	$\bar{5}.9991$	- 6.4894
313	1.430	3.1949	$\bar{4}.1553$	- 6.3402
318	2.081	3.1447	$\bar{4}.3183$	- 6.1842
323	3.040	3.0960	$\bar{4}.4829$	- 6.0263

TABLE NO.3.1.4 and 3.2.4

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

Parameters	Values for [SAH]	Values for [O-CBAH]
	I - Calculated	
Energy of activation (Ea)	10.41 Kcal/mole	14.70 Kcal/mole
Frequency factor (A)	7.31×10^{3} Sec^{-1}	2.68×10^{6} Sec^{-1}
Entropy [$\Delta S^{\neq}$]	- 42.13 e.u.	- 30.40 e.u.
Enthalpy [$\Delta H^{\neq}$]	9.78 Kcal/mole	14.08 Kcal/mole
Free energy [$\Delta G^{\neq}$]	22.97 Kcal/mole	23.60 Kcal/mole
	II - Graphical	
Energy of activation(Ea)	10.46 Kcal/mole	14.64 Kcal/mole
Enthalpy [$\Delta H^{\neq}$]	9.98 Kcal/mole	13.73 Kcal/mole

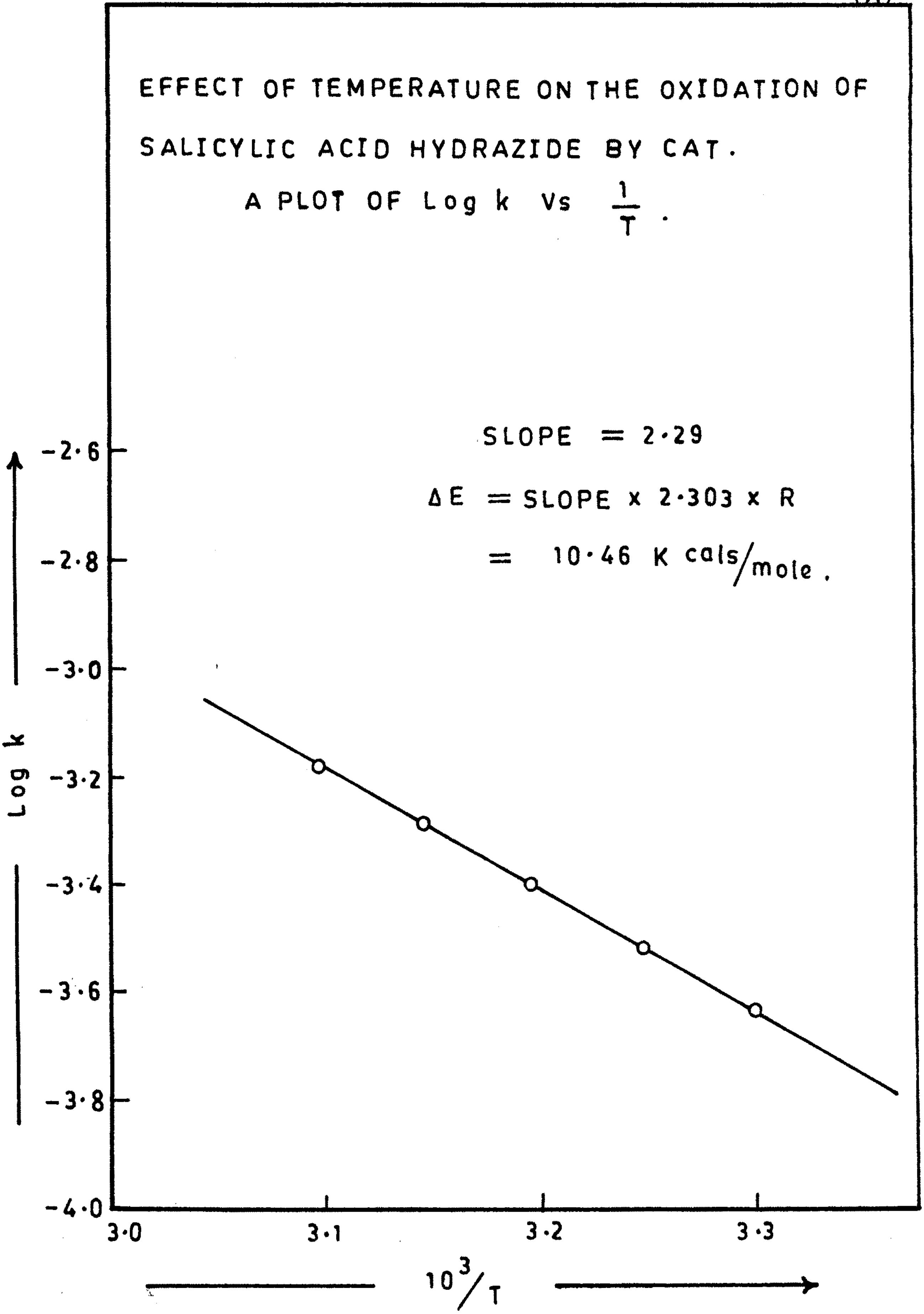
EFFECT OF TEMPERATURE ON THE OXIDATION OF SALICYLIC ACID HYDRAZIDE BY CAT.
A PLOT OF Log k Vs 1/T .
SLOPE = 2·29
ΔE = SLOPE x 2·303 x R
= 10·46 K cals/mole .
Log k
-2·6
-2·8
-3·0
-3·2
-3·4
-3·6
-3·8
-4·0
3·0
3·1
3·2
3·3
10^3/T

Fig. 3:1:5

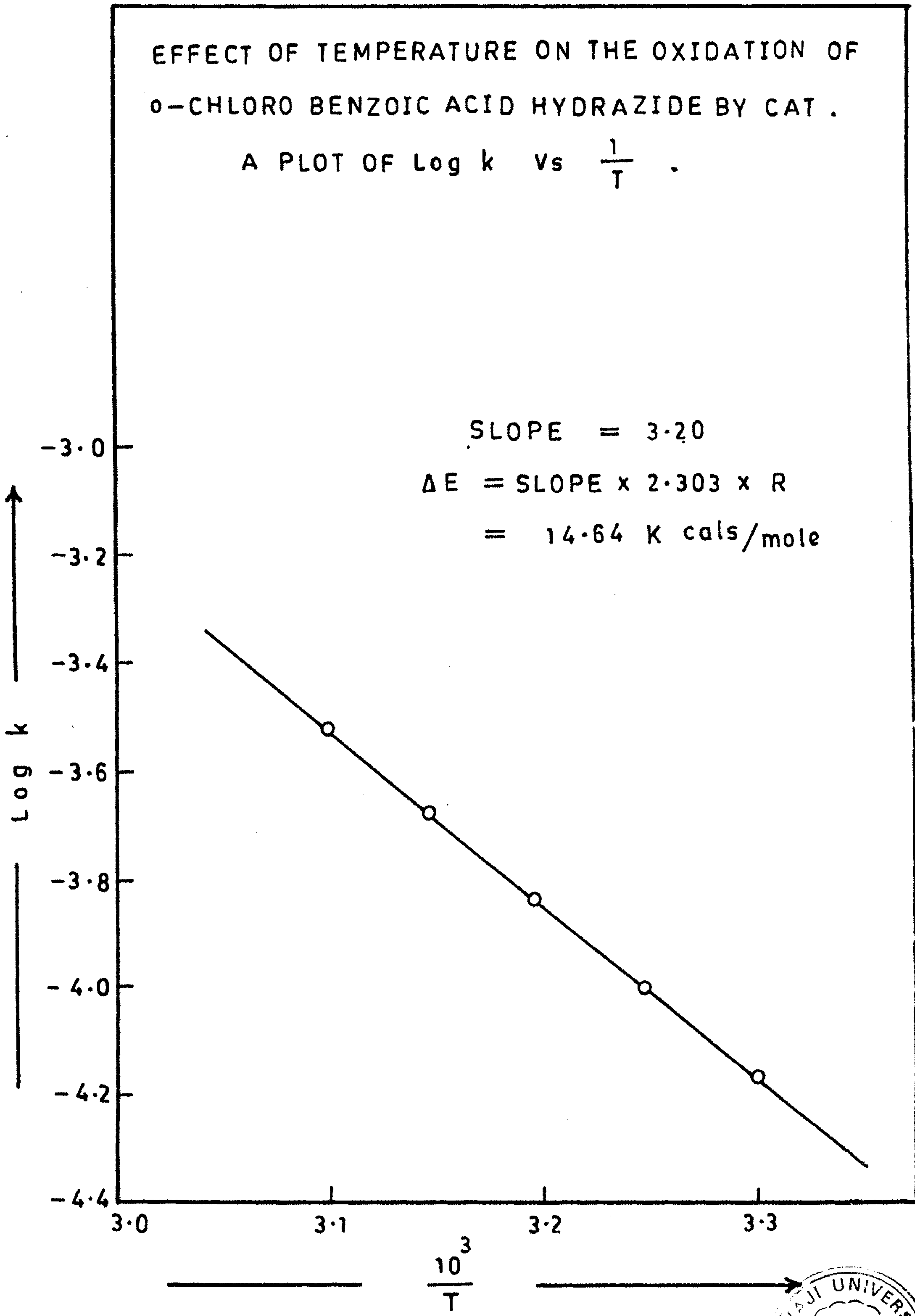
EFFECT OF TEMPERATURE ON THE OXIDATION OF
o-CHLORO BENZOIC ACID HYDRAZIDE BY CAT.
A PLOT OF Log k Vs 1/T .
SLOPE = 3·20
ΔE = SLOPE x 2·303 x R
= 14·64 K cals/mole
-3·0
-3·2
-3·4
-3·6
-3·8
-4·0
-4·2
-4·4
Log k
3·0
3·1
3·2
3·3
10^3/T

Fig. 3:2:5

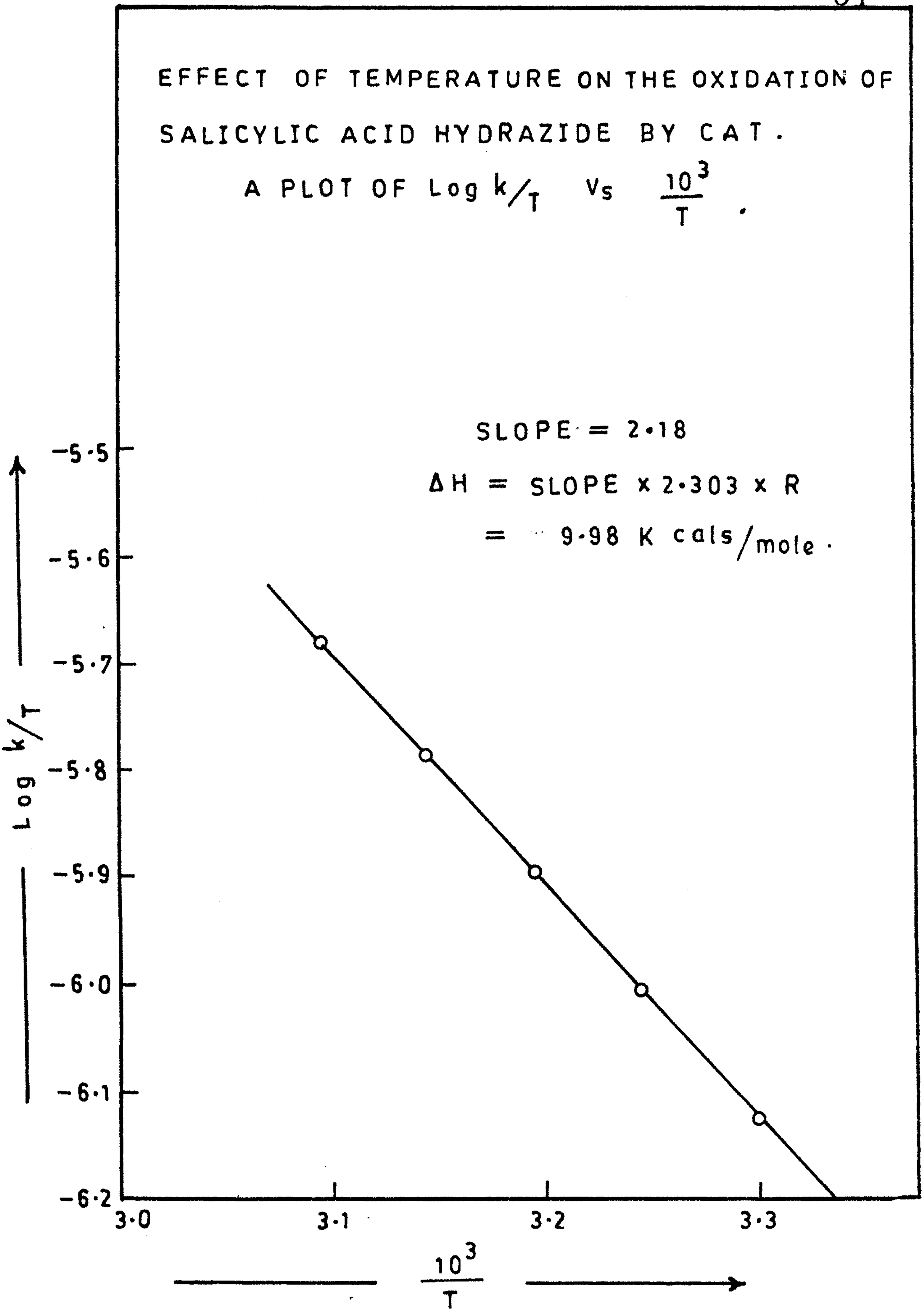
EFFECT OF TEMPERATURE ON THE OXIDATION OF SALICYLIC ACID HYDRAZIDE BY CAT.
A PLOT OF Log k/T Vs $\frac{10^3}{T}$.
SLOPE = 2·18
ΔH = SLOPE x 2·303 x R
= 9·98 K cals/mole.
-5·5
-5·6
-5·7
-5·8
-5·9
-6·0
-6·1
-6·2
Log k/T
3·0
3·1
3·2
3·3
$\frac{10^3}{T}$

Fig. 3:1:6

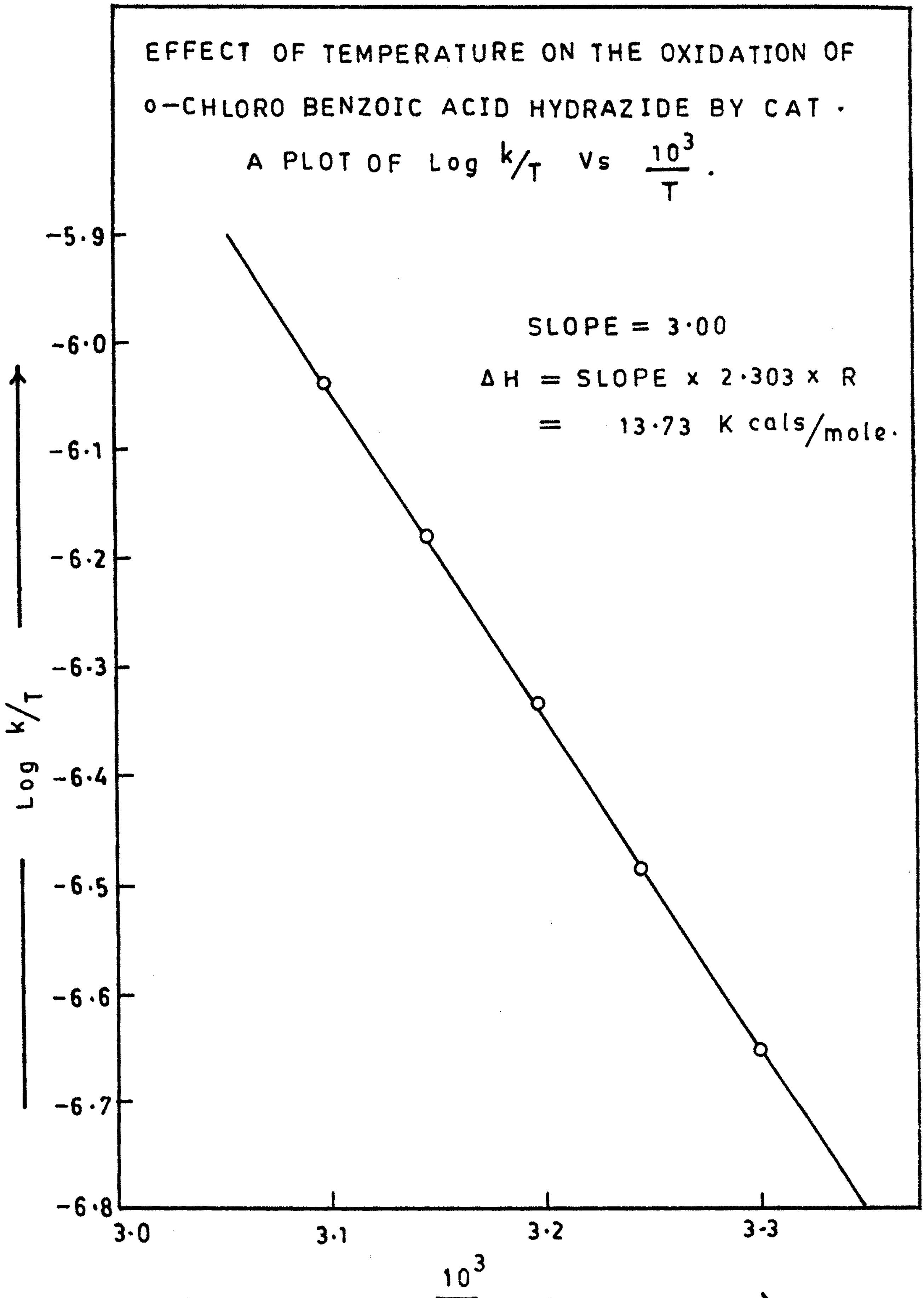
EFFECT OF TEMPERATURE ON THE OXIDATION OF
o-CHLORO BENZOIC ACID HYDRAZIDE BY CAT.
A PLOT OF Log k/T Vs 10³/T.
SLOPE = 3·00
ΔH = SLOPE x 2·303 x R
= 13·73 K cals/mole.
-5·9
-6·0
-6·1
-6·2
-6·3
-6·4
-6·5
-6·6
-6·7
-6·8
Log k/T
3·0
3·1
3·2
3·3
10³/T

Fig. 3:2:6

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

In order to study the effect of chloramine-T concentration on the oxidation of hydrazides, the reaction was examined by varying chloramine-T concentration from 2×10^{-4} M to 12×10^{-4} M, keeping all other concentrations constant at 30^{o}C. The results of these kinetic runs were shown in table 3.1.5 and 3.2.5. It is found that the rate constant (k) nearly remain the same. Similarly the plots of log (a-x) Vs T are linear. These lines are parallel even though there is change in the initial concentration. (Fig. 3.1.4 and 3.2.4).

TABLE NO. 3.1.5

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

[SAH] = 2.0×10^{-3} M   [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4} M

Temperature = $30^{o}C$ pH = 8.88

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

Conc.of Chloramine-T = [CAT] x 10^4 M	2.0	4.0	6.0	8.0	10.0	12.0
k x 10^4 min^{-1}	4.02	3.93	4.83	4.30	4.72	4.33

TABLE NO. 3.2.5

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

[O-CBAH] = 2.0×10^{-3} M   [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4}

Temperature = $30^{o}C$ pH = 8.88

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

Conc.of Chloramine-T = [CAT] x 10^4 M	2.0	4.0	6.0	8.0	10.0	12.0
k x 10^5 min^{-1}	8.60	8.46	8.66	8.53	8.87	8.66

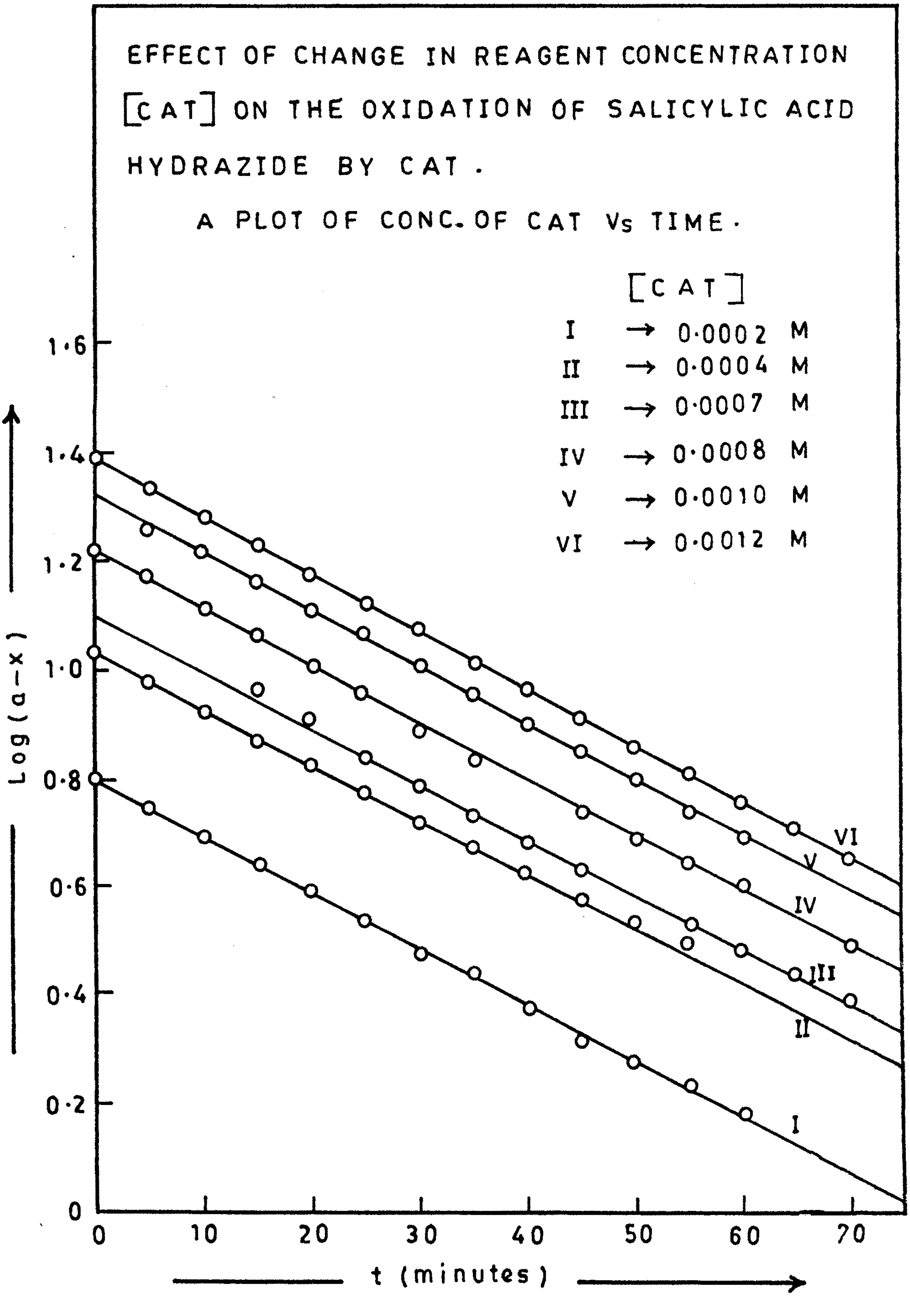
EFFECT OF CHANGE IN REAGENT CONCENTRATION [CAT] ON THE OXIDATION OF SALICYLIC ACID HYDRAZIDE BY CAT.
A PLOT OF CONC. OF CAT Vs TIME.
[CAT]
I → 0·0002 M
II → 0·0004 M
III → 0·0007 M
IV → 0·0008 M
V → 0·0010 M
VI → 0·0012 M
Log (a−x)
t (minutes)
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
0
10
20
30
40
50
60
70
I
II
III
IV
V
VI

Fig. 3:1:4

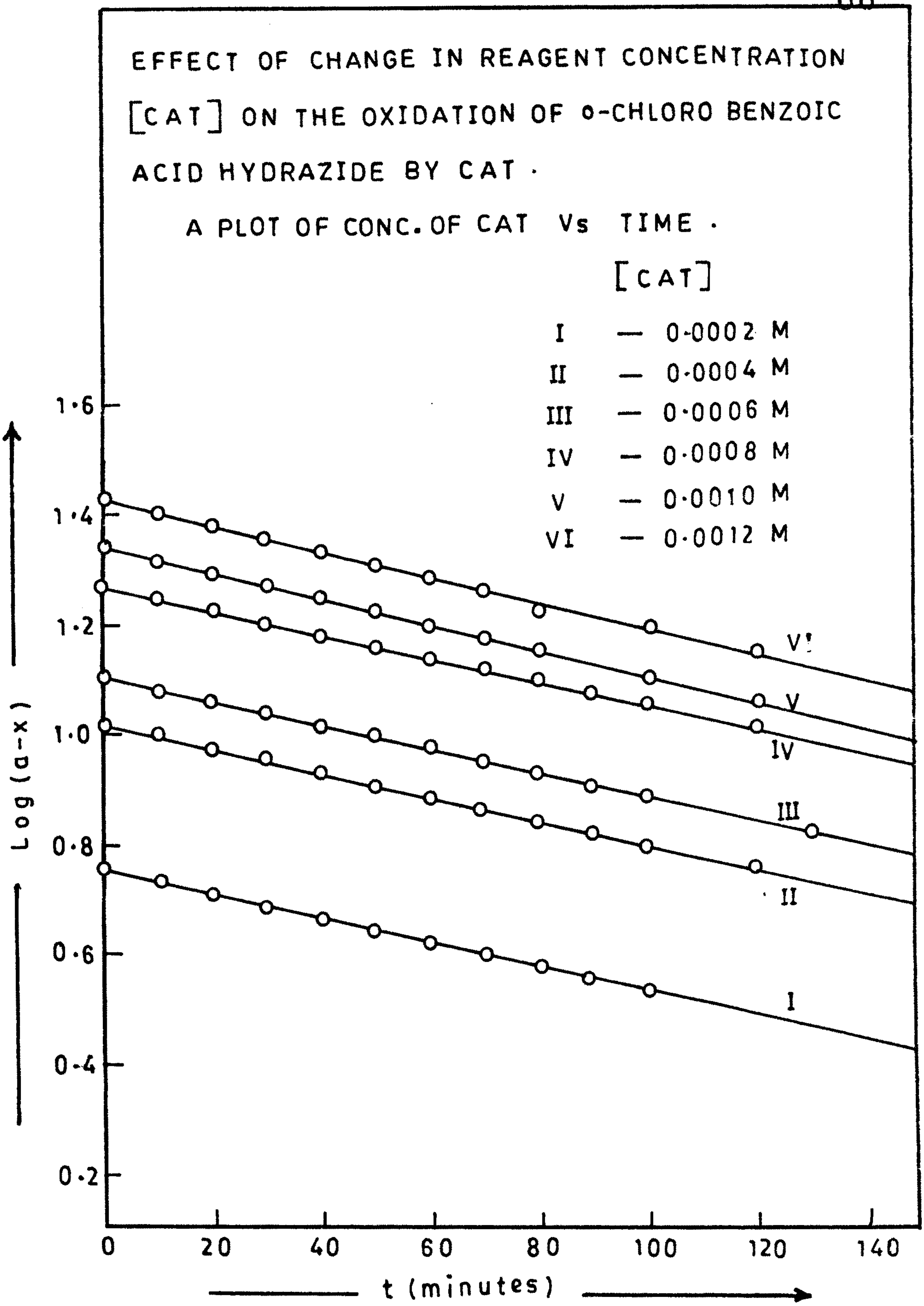
EFFECT OF CHANGE IN REAGENT CONCENTRATION
[CAT] ON THE OXIDATION OF o-CHLORO BENZOIC
ACID HYDRAZIDE BY CAT.
A PLOT OF CONC. OF CAT Vs TIME.
[CAT]
I — 0·0002 M
II — 0·0004 M
III — 0·0006 M
IV — 0·0008 M
V — 0·0010 M
VI — 0·0012 M
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
Log (a-x)
0
20
40
60
80
100
120
140
t (minutes)
VI
V
IV
III
II
I

Fig. 3:2:4

IV) OXIDATION OF HYDRAZIDES BY CHLORAMINE-T IN WATER-METHANOL MIXTURE AT 30°C.

In order to investigate the effect of change in solvent proportion (v/v) on the rate constant (k) of the reaction, the percentage composition of methanol and water in the reaction mixture were changed and the reaction is carried out. The kinetic runs were carried out as follows :-

The percentage composition of methanol/water were taken from 20/80 v/v to 80/20 v/v for these hydrazides.

The results of these kinetic runs have been represented in the tables 3.1.6 and 3.2.6. From these results it is clear that the rate constant (k) increases with the decrease in methanol percentage.

TABLE NO. 3.1.6

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T IN WATER-METHANOL MIXTURES.

[SAH] = 1.5×10^{-3} M   [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4} M

[CAT] = 8.0×10^{-4} M   pH = 8.88

Temperature = $30^{o}C$

Sr. No.	Percentage of Methanol	Percentage of Water	$k \times 10^4$ min^{-1}
1	30	70	2.615
2	40	60	2.398
3	50	50	2.288
4	60	40	1.889
5	70	30	1.265
6	80	20	0.711

TABLE NO. 3.2.6

OXIDATION OF HYDRAZIDES BY CHLORAMINE-T IN WATER-METHANOL MIXTURE AT 30°C.

[O-CBAH] = 1.5×10^{-3} M   [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4} M

[CAT] = 8.0×10^{-4} M   pH = 8.88

Temperature = 30°C

Sr. No.	Percentage of Methanol	Percentage of Water	$k \times 10^4$ min^{-1}
1	20	80	1.274
2	30	70	0.817
3	40	60	0.751
4	50	50	0.671
5	60	40	0.632
6	70	30	0.540

V) THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T AT DIFFERENT pH .

To study the effect of change in pH on the rate of oxidation of hydrazides by chloramine-T, different kinetic runs were carried out in the solutions of different pH ranging from 8.75 to 10.8. The pH values of these solutions were checked by digital pH meter.

The results of these kinetic runs have been given in the tables 3.1.7 and 3.2.7. It is clear that oxidations of SAH and O-CBAH are independent of the pH in the range of 8.75 to 10.8.

TABLE NO. 3.1.7

THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T IN THE SOLUTIONS OF DIFFERENT pH.

[SAH] = 1.5×10^{-3}M   [$Na_2S_2O_3$, $5H_2O$] 5.0×10^{-4} M

[CAT] = 8.0×10^{-4}M   Temperature = $30^{o}C$

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

Sr. No.	mls. of $NaHCO_3$ (0.025 M) in 100 ml mixture	mls. of Na_2CO_3 (0.025 M) in 100 ml mixture	pH of the solution	$k \times 10^4 min^{-1}$
1	11	9	8.86	2.46
2	10	10	8.88	2.28
3	8	12	9.80	1.14
4	6	14	9.90	1.47

TABLE NO. 3.2.7

THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T IN THE SOLUTIONS OF DIFFERENT pH.

[O-CBAH] = 1.5×10^{-3}M   [$Na_2S_2O_3$, $5H_2O$] 5.0×10^{-4} M

[CAT] = 8.0×10^{-4}M   Temperature = 30^{o}C

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

Sr. No.	mls. of $NaHCO_3$ (0.025 M) in 100 ml mixture	mls. of Na_2CO_3 (0.025 M) in 100 ml mixture	pH of the solution	$k \times 10^{4} min^{-1}$
1	14	6	8.75	7.26
2	12	8	9.25	6.14
3	10	10	9.37	6.71
4	9	11	10.30	7.42
5	7	13	10.71	7.69
6	4	16	10.80	7.22

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

In order to investigate the effect of addition of salt (NaCl) on the rate of oxidation of hydrazide, kinetic runs were carried out using different concentrations of salt and keeping constant the concentrations of all other ingradients at 30^{o}C. The results have been shown in the tables 3.1.8 and 3.2.8. From these results it is clear that the effect of salt is negligible on the oxidation of hydrazides by chloramine-T.

TABLE NO. 3.1.8

EFFECT OF ADDITION OF SALT ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

[SAH] = 1.5×10^{-3} M   [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4}M

[CAT] = 8.0×10^{-4}M   Temperature = 30^oC

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

Conc. of salt = [NaCl] x 10^3M	0.00	1.00	2.00	3.00
k x 10^4 min^{-1}	2.28	2.28	2.25	2.18

TABLE NO. 3.2.8

EFFECT OF ADDITION OF SALT ON THE OXIDATION OF HYDRAZIDES BY CHLORAMINE-T.

[O-CBAH] = 1.5×10^{-3} M   [$Na_2S_2O_3$, $5H_2O$] = 5.0×10^{-4}M

[CAT] = 8.0×10^{-4}M   Temperature = 30^oC

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

Conc. of salt = [NaCl] x 10^3M	2.0	4.0	6.0	8.0	10.0
k x 10^4 min^{-1}	0.70	0,70	0.68	0.69	0.70