CHAPTER : III

SECTION : I

Kinetics of oxidation of nicotinic acid hydrazide

CHAPTER - III

This chapter contains the present work on the kinetics and mechanism of oxidation of two hydrazides, namely nicotinic acid hydrazide and isonioctinic acid hydrozide, by chloramine-T in alkaline solution. The experiments were designed to determine --

1) The order of reaction w.r.t. the chloramine - T concentration.
2) The order of reaction w.r.t. the substrate concentration.
3) The order of reaction w.r.t. the hydroxide ion concentration.
4) Effect of the addition of chloride ions.
5) Effect of change in ionic strength of the medium.
6) The effect of change in temperature on the rate of the reaction, from which the kinetic and thermodynomic parameters have been calculated.

SECTION - I

3.1 KINETICS OF OXIDATION OF NICOTINIC ACID HYDRAZIDE:

Preliminary experiments were performed in order to decide the suitable temperature and concentrations of the reactants. It was observed that the reaction proceeds with measurable velocity at 25°c, when the concentrations of nicotinic acid hydrazide (NAH) was 1.0×10^{-2} M, chloramine - T (CAT) was 1.0×10^{-3}M and that of NaOH was 1.0×10^{-2} M. To maintain the constant ionic strength μ of the solution, 0.1 M $NaClO_4$ was added. The kinetic data has been recorded in Table 3.1.1 given below :

TABLE 3.1.1

$[NAH] = 1.0 \times 10^{-2}M$ $[NaOH] = 1.0 \times 10^{-2}$ M $[NaClO_4] = 1.0 \times 10^{-1}M$
$[CAT] = 1.0 \times 10^{-3}$ M $[Na_2S_2O_3.5H_2O] = 1.0 \times 10^{-3}M$ Temp = 25°c

Time (min)	Vol(in ml) of $Na_2S_2O_3$	k x 10^{-2} min^{-1}
0	11.2	--
5	8.35	5.87
10	6.24	5.85
15	4.66	5.85
20	3.50	5.81
25	2.62	5.81
30	1.97	5.79
35	1.48	5.78
40	1.11	5.77
45	0.84	5.76
50	0.63	5.75
Mean k x 10^{-2}		5.804×10^{-2}

A perusal of the above data closely shows that pseudo first order specific rate is almost constant. In this experiment the hydrazide concentration is in excess (10 times) over the CAT concentration.

1) EFFECT OF CHLORAMINE - T CONCENTRATION :-

It was necessary to determine the order of reaction w.r.t. CAT, keeping the concentrations of nicotinic acid hydrazide and that of NaOH unchanged in order to investigate the effect of CAT concentration on the rate of the reaction. For this perpose, the reaction was carried out at 5 different concentrations of CAT by keeping the concentrations of other reagents constant. Table 3.1.2 embodies the results of these kinetic runs. The values of first order rate constants (viz k) have been evaluated from the initial slope of the curves, shown in fig.3.1.1 as well as calculated at different times by integration method which are in good agreement with each other:

TABLE 3.1.2

[NAH] = 1.0×10^{-2} M. [$Na_2S_2O_3$] = 1.0×10^{-3} M Temp. 25^o c
[NaOH] = 1.0×10^{-2} M. [$NaClO_4$] = 1.0×10^{-1} M

Conc of CAT = M $\times 10^{-3}$	0.5	1.0	1.5	2.0	2.5
Time in(min)	Vol (in ml) of $Na_2S_2O_3$.				
0	6.40	11.20	16.60	22.10	27.50
5	4.78	8.35	12.40	16.48	20.50
10	3.58	6.24	9.28	12.30	15.31
15	2.68	4.66	6.98	9.20	11.44
20	2.01	3.50	5.20	6.88	8.54
25	1.51	2.62	3.90	5.18	6.40
30	1.13	1.97	2.94	3.90	4.80
35	0.85	1.48	2.20	2.93	3.60
40	0.64	1.11	1.67	2.20	2.70
45	0.48	0.84	1.26	1.66	2.05
Mean:k$\times 10^{-2}$	5.78	5.804	5.78	5.801	5.82

An examination of the above data shows that when the hydrazide concentration is in excess, the pseudo first order rate constant (k) calculated in each case is almost constant. Hence the rate of disappearance of CAT obeys the first order kinetics.

In order to confirm the order of reaction w.r.t. CAT, the values of $-\frac{dc}{dt}$ were determined by plotting the volume of $Na_2S_2O_3$ (equivalent to CAT) against time for different initial concentrations of CAT and recorded in the table 3.1.3.

TABLE 3.1.3

Initial conc. of CAT C_o =M x 10^{-3}	-dc/dt (by graph)	Log C_o	Log (- dc/dt)
0.5×10^{-3}	3.07×10^{-4}	$\bar{4}.699$	$\bar{4}.487$
1.0×10^{-3}	6.00×10^{-4}	$\bar{3}.000$	$\bar{4}.778$
1.5×10^{-3}	8.8×10^{-4}	$\bar{3}.176$	$\bar{4}.944$
2.0×10^{-3}	11.6×10^{-4}	$\bar{3}.301$	$\bar{3}.064$
2.5×10^{-3}	14.3×10^{-4}	$\bar{3}.398$	$\bar{3}.155$

The value of the order of reaction w.r.t. [CAT] has been evaluated from the plot of log $\frac{-dco}{dt}$ vs log C_o fig3.1.2, where C_o is the initial concentration of CAT, which comes out to be 0.95. This confirms the first order behaviour of the reaction w.r.t. CAT.

2. EFFECT OF HYDRAZIDE (NAH) CONCENTRATION:

In order to investigate the effect of hydrazide concentration on the rate of oxidation of NAH, the hydrazide concentration was varied from 0.5×10^{-2} M to 1.5×10^{-2} M, keeping the concentration of CAT and that of NaOH constant. The results of these kinetic runs are recorded in table 3.1.4. and depicted graphically in Fig 3.1.3

TABLE 3.1.4

$[CAT] = 1.0 \times 10^{-3}$M $[Na_2S_2O_3] = 1.0 \times 10^{-3}$M. Temp. 25°c

$[NaOH] = 1.0 \times 10^{-2}$M $[NaClO_4] = 1.0 \times 10^{-1}$M.

[NAH], $M \times 10^{-2}$ =	0.5	0.75	1.0	1.25	1.5
Time	Vol. (in ml) of $Na_2S_2O_3$				
0	11.20	11.20	11.20	11.20	11.20
5	9.66	9.00	8.35	7.80	7.24
10	8.35	7.25	6.24	5.43	4.69
15	7.22	5.85	4.66	3.79	3.04
20	6.25	4.72	3.50	2.65	1.97
25	5.40	3.82	2.62	1.85	1.28
30	4.70	3.10	1.97	1.30	0.83
35	4.10	2.50	1.48	0.91	0.54
40	3.57	2.03	1.11	0.64	--
45	3.12	1.65	0.84	--	--
Mean k $\times 10^{-2}$	2.895	4.302	5.804	7.20	8.69

The results contained in Table 3.1.4 show that the first order rate constant increases with increase in the initial concentration of hydrazides.

The plots of log 'C' against time 't' (fig 3.1.3) are linear. The second order rate constant k_2,

$$k_2 = \frac{k_1}{[\text{Hydrazide}]_o}$$

where k_2 = second order rate constant and

k_1 = first order rate constant.

was found to be constant.

TABLE 3.1.5

[NAH]	$k_1 x 10^{-2}$	$k_2 x 10^{-2}$
$0.5x10^{-2}$	2.895	5.79
$0.75x\ 10^{-2}$	4.302	5.74
$1.00x\ 10^{-2}$	5.804	5.80
$1.25x\ 10^{-2}$	7.20	5.76
$1.50x10^{-2}$	8.69	5.79

Table 3.1.5 indicates first order dependence of the rate on hydrazide concentration.

The order in [hydrazide NAH] was determined by van't Hoff differential method. The volume of $Na_2S_2O_3$ (equivalent to CAT) was plotted against time for different initial concentrations of hydrazide. From these curves, the value of $-\frac{dc}{dt}$ in each case was determined from the initial slope which indicated the value of initial rate. These values are given in Table 3.1.6.

The values of $-\frac{dc}{dt}$ and $[\text{Hydrazide}]_o$ i.e. C_o are substituted in the vant't Hoff equation i.e.,

$$n = \frac{\log [dc / dt]_1 - \log [-dc / dt]_2}{\log [C_o]_1 - \log [C_o]_2}$$

where n = order of the reaction.

The results have been recorded in Table 3.1.7

TABLE 3.1.6

Initial conc of NAH $[C_o]$	$-\frac{dc}{dt}$	Log C_o	Log $-\frac{dc}{dt}$
0.5×10^{-2}	3.06×10^{-4}	$\bar{3}.699$	$\bar{4}.486$
0.75×10^{-2}	4.54×10^{-4}	$\bar{3}.875$	$\bar{4}.657$
1.00×10^{-2}	6.00×10^{-4}	$\bar{2}.000$	$\bar{4}.778$
1.25×10^{-2}	7.50×10^{-4}	$\bar{2}.0969$	$\bar{4}.875$
1.50×10^{-2}	9.02×10^{-4}	$\bar{2}.176$	$\bar{4}.955$

TABLE 3.1.7

Conc of NAH $[C_o]_1$ $M \times 10^{-2}$	$[Co]_2$ $M \times 10^{-2}$	$\left[-\frac{dc}{dt}\right]_1 \times 10^{-4}$	$-\left[\frac{dc}{dt}\right]_2 \times 10^{-4}$	Order of reaction (n)
0.5	0.75	3.06	4.54	0.971
0.5	1.00	3.06	6.00	0.970
0.5	1.25	3.06	7.50	0.977
0.5	1.50	3.06	9.02	0.983
0.75	1.00	4.54	6.00	0.968
0.75	1.25	4.54	7.50	0.982
0.75	1.50	4.54	9.02	0.990
1.00	1.25	6.00	7.50	1.000
1.00	1.50	6.00	9.02	1.005
1.25	1.50	7.50	9.02	1.012

The n values are fairly nearer to unity. The order of reaction w.r.t. |NAH| is also determined from the plot of Log $-\frac{dc}{dt}$ vs Log C_o (fig.3

where Co is the initial concentration of NAH, has been evaluated, which comes out to be 1.0. This confirms the first order behaviour of the reaction w.r.t. nicotinic acid hydrazide.

3) EFFECT OF SODIUM HYDROXIDE CONCENTRATION :-

In order to study the effect of alkali concentration on the rate of oxidation of NAH, the concentration of NaOH was varied from 0.5×10^{-2}M to 1.5×10^{-2}M by keeping the concentrations of other reactants constant. The results of these kinetic runs are recorded in Table 3.1.8.

TABLE 3.1.8

$[NAH] = 1.0\times10^{-2}M$ $[Na_2S_2O_3] = 1.0 \times 10^{-3}M.$ Temp. 25°c
$[CAT] = 1.0 \times 10^{-3}M.$ $[NaClO_4] = 1.0 \times 10^{-1}M.$

[NaOH] M x 10^{-2}	0.5	0.75	1.00	1.25	1.50
Time in (min)	Vol. (in ml) of $Na_2S_2O_3$				
0	11.20	11.20	11.20	11.20	11.20
5	8.17	8.27	8.35	8.44	8.53
10	5.97	6.12	6.24	6.37	6.50
15	4.37	4.53	4.66	4.82	4.95
20	3.20	3.36	3.50	3.65	3.78
25	2.35	2.49	2.62	2.76	2.89
30	1.72	1.85	1.97	2.10	2.21
35	1.27	1.38	1.48	1.60	1.70
40	0.94	1.04	1.11	1.22	1.30
45	--	0.77	0.84	0.93	1.00
Mean k = 10^{-2}	6.25	6.01	5.80	5.60	5.40

An examination of the results contained in the table 3.1.8 shows that the effect of hydroxide ion concentration is negligible and hence the rate of reaction is independent of alkali concentration.

4. EFFECT OF CHLORIDE ION ON THE RATE OF OXIDATION OF NAH.

To investigate the effect of addition of chloride ion (NaCl, i.e. salt effect) on the rate of oxidation of hydrazide (NAH), the concentration of sodium chloride was variec from 0.0 M to 4.0 x 10^{-2}M, keeping all the other concentrations constant. The results of which are recorded in the Table 3.1.9

TABLE 3.1.9

[CAT] = 1.0×10^{-3}M |$Na_2S_2O_3$| = 1.0×10^{-3}M |NAH| = 1.0×10^{-2}M

[NaOH] = 1.0×10^{-2}M [$NaClO_4$] = 1.0×10^{-1}M Temp. 25^oc

[NaCl] M x 10^{-2}	0.0	1.0	2.0	3.0	4.0
Time in in mins.	Vol.. (in ml) of $Na_2S_2O_3$				
0	11.20	11.20	11.20	11.20	11.20
5	8.35	8.37	8.33	8.31	8.30
10	6.24	6.27	6.20	6.18	6.16
15	4.66	4.70	4.62	4.60	4.58
20	3.50	3.53	3.45	3.42	3.40
25	2.62	2.65	2.58	2.55	2.53
30	1.97	2.00	1.93	1.90	1.89
35	1.48	1.51	1.45	1.42	1.41
40	1.11	1.14	1.09	1.06	1.05
45	0.84	0.86	0.82	0.79	0.79
Mean k x 10^{-2}	5.80	5.75	5.86	5.915	5.94

The above data shows that there is no salt effect on the rate of reaction.

5. EFFECT OF CHANGE IN IONIC STRENGTH OF THE MEDIUM

To study the effect of change in ionic strength of the medium on the rate of the reaction, the concentration of sodium perchlorate is varied from 1.0 x 10^{-1} to 4.0 x 10^{-1}M, keeping all other concentrations constant, and results are recorded in Table 3.1.10

TABLE 3.1.10

$[CAT] = 1.0 \times 10^{-3} M$ $[Na_2S_2O_3] = 1.0 \times 10^{-3} M$
$[NAH]$ $1.0 \times 10^{-2} M$ $[NaOH] = 1.0 \times 10^{-2} M$ Temp. 25°c.

$[NaClO_4]$ M x 10^{-1}	1.0	2.0	3.0	4.0
Time in mins.	Vol. (in ml) of $Na_2S_2O_3$			
0	11.20	11.20	11.20	11.20
5	8.35	8.32	8.31	8.27
10	6.24	6.19	6.18	6.12
15	4.66	4.61	4.60	4.53
20	3.50	3.44	3.42	3.36
25	2.62	2.57	2.55	2.49
30	1.97	1.92	1.90	1.85
35	1.48	1.44	1.42	1.38
40	1.11	1.08	1.06	1.04
45	0.84	0.81	0.80	0.78
Mean k x 10^{-2}	5.80	5.883	5.91	5.99

Perusal of the data contained in this table shows that, the change of ionic strength (μ) of the medium has no effect on the rate of the reaction.

6. EFFECT OF TEMPERATURE.

In order to determine the various energy parameters like energy of activation (Ea), temperature coefficient, frequency factor (A), enthalpy of activation ($\Delta H^{\ddagger}$), free energy of activation ($\Delta G^{\ddagger}$), entropy of activation ($\Delta S^{\ddagger}$), the reaction was carried out at 5 different temperatures ranging from 20^{o} to 40^{o} C The results of these kinetic runs have been tabulated in table 3.1.11 and depicted graphically in Fig.3.1.5.

TABLE 3.1.11

$[NAH] = 1.0\times10^{-2}$ M $[NaOH] = 1.0\times10^{-2}$ M $[Na_2S_2O_3] = 1.0\times10^{-3}$ M

$[CAT] = 1.0\times10^{-3}$ M $[NaClO_4] = 1.0\times10^{-1}$ M

Temp. C^{o}	20^{o}	25^{o}	30^{o}	35^{o}	40^{o}
Time(min)	Vol (in ml) of $Na_2S_2O_3$				
0	11.20	11.20	11.20	11.20	11.20
2	-	-	-	8.87	8.07
4	-	-	-	7.03	5.85
5	9.09	8.35	7.41	-	-
6	-	-	-	5.57	4.23
8	-	-	-	4.42	3.09
10	7.39	6.24	4.91	3.51	2.23
13	-	-	-	2.48	1.40
15	6.00	4.66	3.26	-	-
16	-	-	-	1.76	0.88
20	4.88	3.50	2.16	1.11	0.48
25	3.98	2.62	1.44	0.63	-
30	3.24	1.97	0.96	-	-
35	2.65	1.48	0.64	-	-
40	2.17	1.11	-	-	-
45	1.78	0.84	-	-	-
Mean k x 10^{-2}	4.12	5.804	8.22	11.60	16.00

It is seen from the results that, the specific rate has approximately doubled for 10^{o}C rise in temperature. The calculated values of $\frac{1}{T} \times 10^{3}$ and Log k are represented in table 3.1.12.

TABLE 3.1.12

Temp. K^{o}	$k \times 10^{-2}$ min^{-1}	$\frac{10^{3}}{T}$	Log k
293	4.12	3.412	- 1.385
298	5.80	3.355	- 1.236
303	8.22	3.300	- 1.085
308	11.60	3.246	- 0.935
313	16.00	3.194	- 0.796

A plot of log k vs $10^{3}/T$ as shown in Fig 3.1.6 is found to be linear indicating that, the reaction obeys Arrhenius relationship. The value of energy of activation (Ea) evaluated from slope of this curve comes out to be 12.48 k.cals mole^{-1}. The Arrhenius equation has been used directly to calculate energy of activation, the mean of which comes out to be 12.47 k.cals mole^{-1}.

$$Ea = \log \frac{k_2}{k_1} \times 2.303 \, R \left[\frac{T_1 \, T_2}{T_2 - T_1} \right] \qquad (1)$$

The value of energy of activation was used to calculate the frequency factor (A), and entropy of activation, $S^{\ddagger}$, by the following equations

$$k_r = A \, e^{-E/RT} \qquad (2)$$

and $$A = e . \frac{kT}{h} . e^{\Delta S^{\ddagger}/R} \qquad (3)$$

where (3) is valid for reactions in solution,[131] and k_r is the specific rate constant, k is the Boltzman constant, 'h' is the plank's constant and 'e' is the constant having a value of 2.718, other symbols carry their usual meanings.

The free energy for the reaction, $\Delta G^{\ddagger}$, was calculated by the equation.

$$k_r = \frac{kT}{h} \cdot e^{\Delta G^{\ddagger}/RT}$$

$$\therefore \Delta G^{\ddagger} = 4.576 \left(\mathrm{Log} \frac{kT}{h} - \mathrm{Log}\, k_r \right) T \qquad (4)$$

Entropy of activation $\Delta S^{\ddagger}$ is given by the relationship

$$\Delta S^{\ddagger} = R \left(\ln A - \ln \frac{kT}{h} - 1 \right) \qquad (5)$$

Enthalpy of activation, $\Delta H^{\ddagger}$, was calculated from the equation

$$k_r = \frac{kT}{h} \cdot e^{\Delta H^{\ddagger}/RT} \; e^{\Delta S^{\ddagger}/R} \qquad (6)$$

The values of log $\left[\frac{k_r}{kT/h} \right]$ and $\frac{1}{T}$ are tabulated in Table 3.1.13.

TABLE 3.1.13

Temp. K°	$\frac{k_r}{kT/h}$	$\frac{10^3}{T}$	Log $\frac{k_r}{kT/h}$
293	1.123×10^{-16}	3.412	- 15.9496
298	1.555×10^{-16}	3.355	- 15.808
303	2.169×10^{-16}	3.300	- 15.6638
308	3.007×10^{-16}	3.246	- 15.522
313	4.087×10^{-16}	3.194	- 15.389

The plot of log $\left[\frac{k_r}{kT/h} \right]$ VS $\frac{1}{T}$, shown in figure 3.1.7, is linear and from the slope of the straight line the enthalpy change $(\Delta H^{\neq})$ for the formation of the activated complex has been calculated, which was found to be 11.97 k.cals. mole^{-1}.

The various energy parameters obtained, have been recorded in Table 3.1.14.

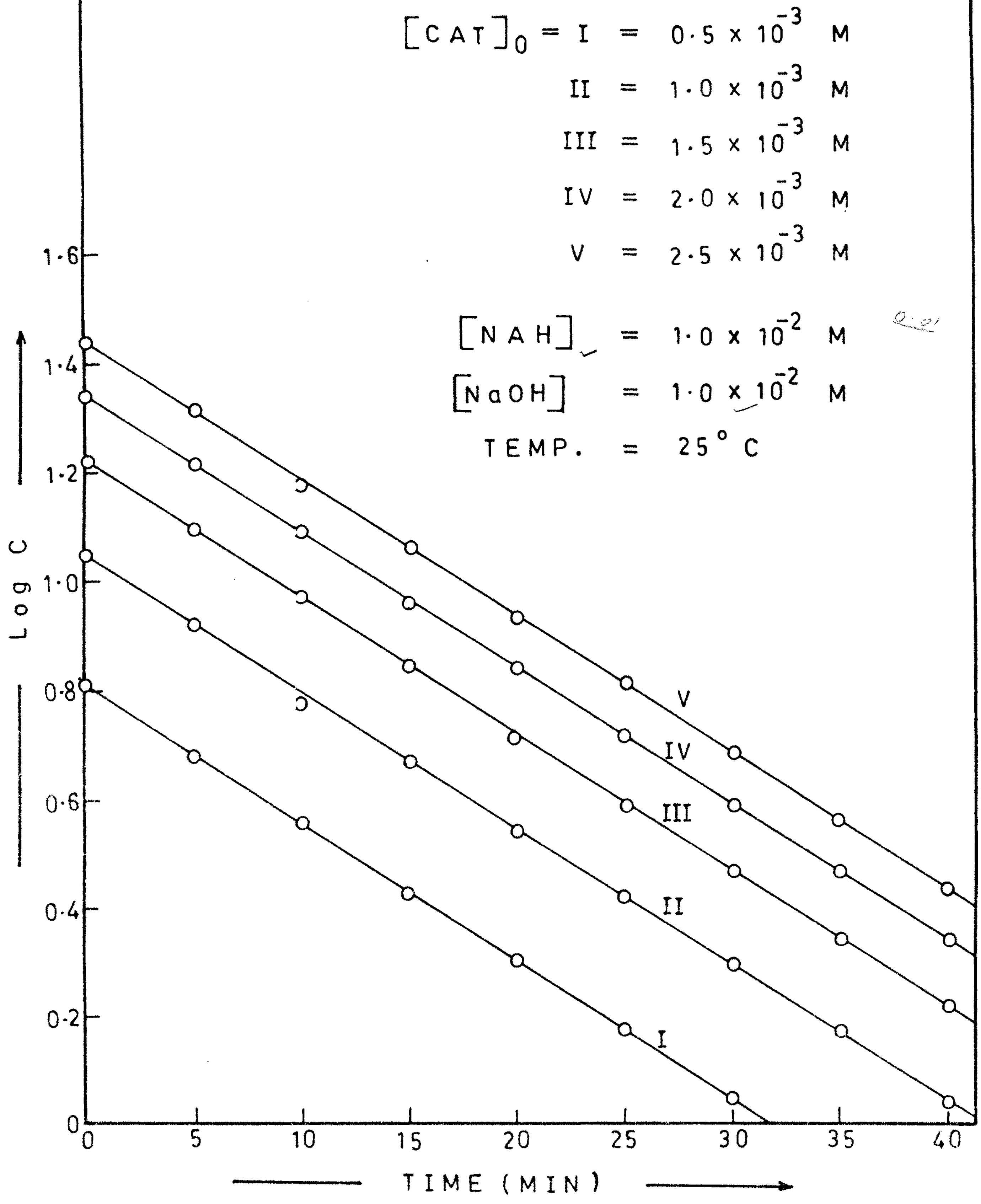
TABLE 3.1.14

Temp. K^{o}	Energy of activation (Ea) k.cals mole^{-1}	Temp. coefficients	Frequency factor (A) Ax10^{6}sec^{-1}	Free energy of activitation $\Delta G^{\ddagger}$ k.cals	Entropy of activation $\Delta S^{\ddagger}$ e.u.
293			1.371	19.016	-32.39
298	12.19	1.995	1.348	19.148	-32.43
303	12.65	2.00	1.349	19.269	-32.486
308	12.56	1.946	1.360	19.386	-32.51
313			1.355	19.511	-32.54
Mean	12.47	1.980	1.356	19.266	-32.47

Enthalpy change $(\Delta H^{\ddagger})$ by graph = 11.97 k.cals mole^{-1}

Energy of activation (Ea) by graph = 12.48 k.cals mole^{-1}

FIG. 3·1·1 — EFFECT OF CAT CONCENTRATION.



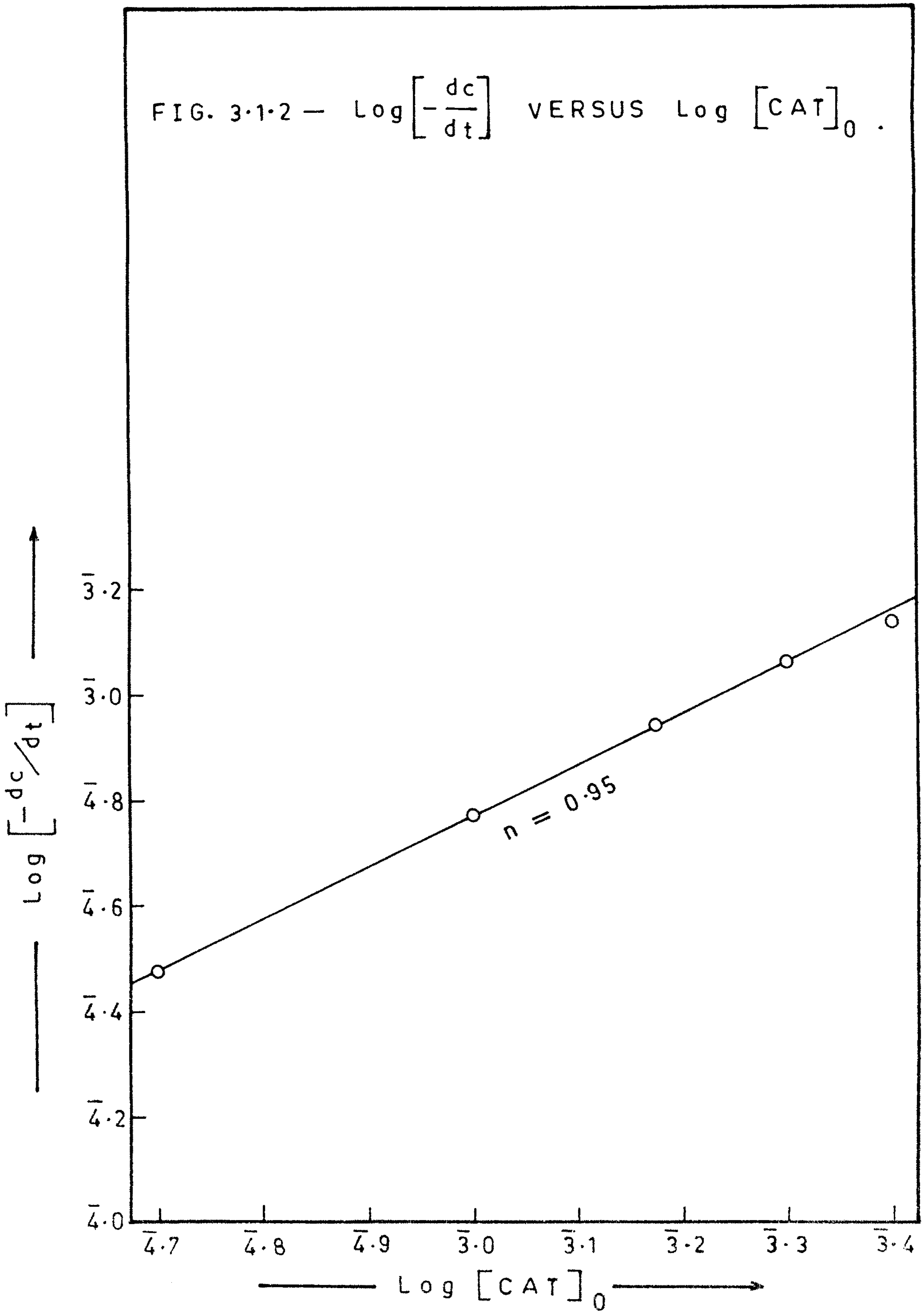


FIG. 3·1·2 — Log$\left[-\frac{dc}{dt}\right]$ VERSUS Log $[CAT]_0$.

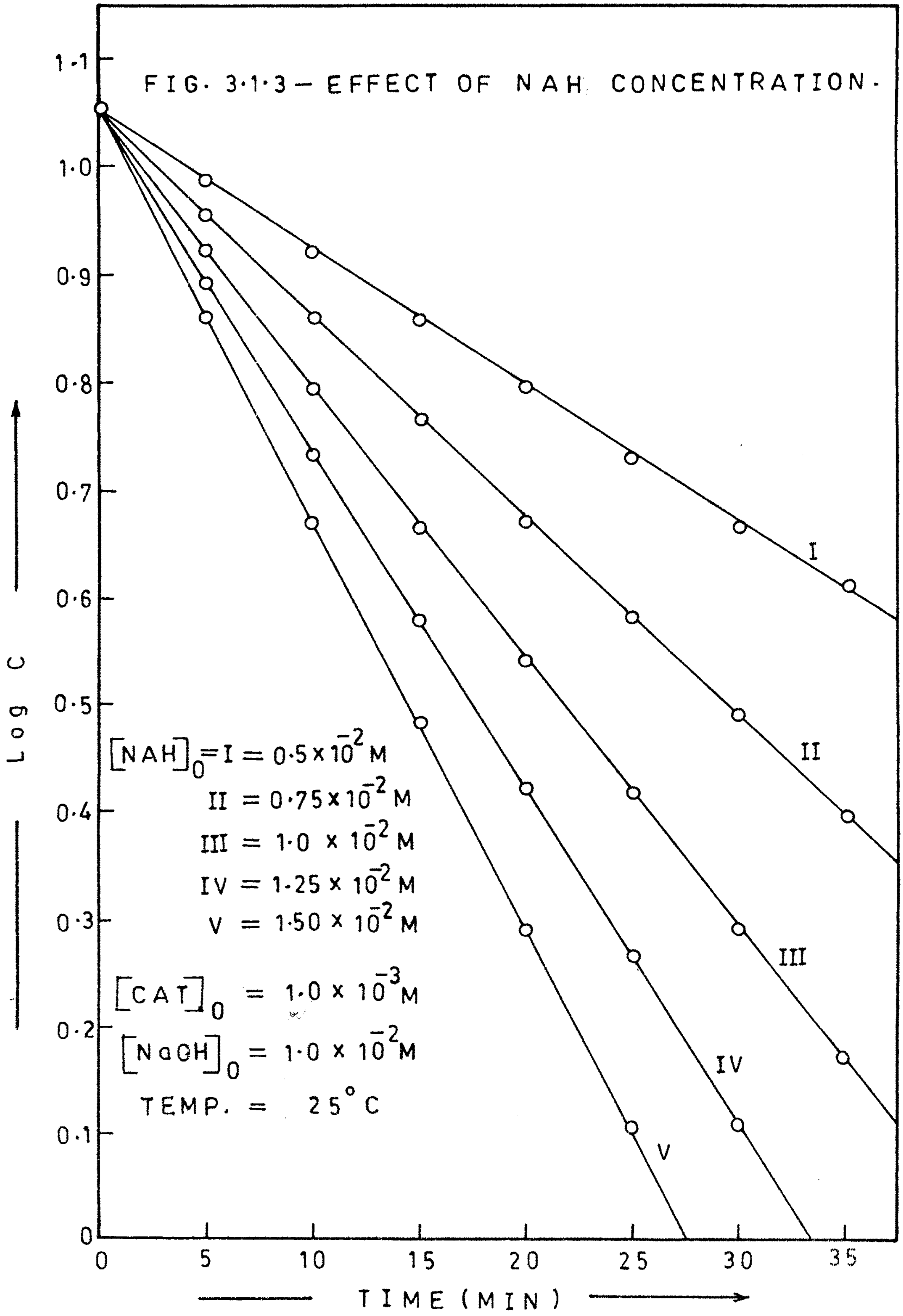
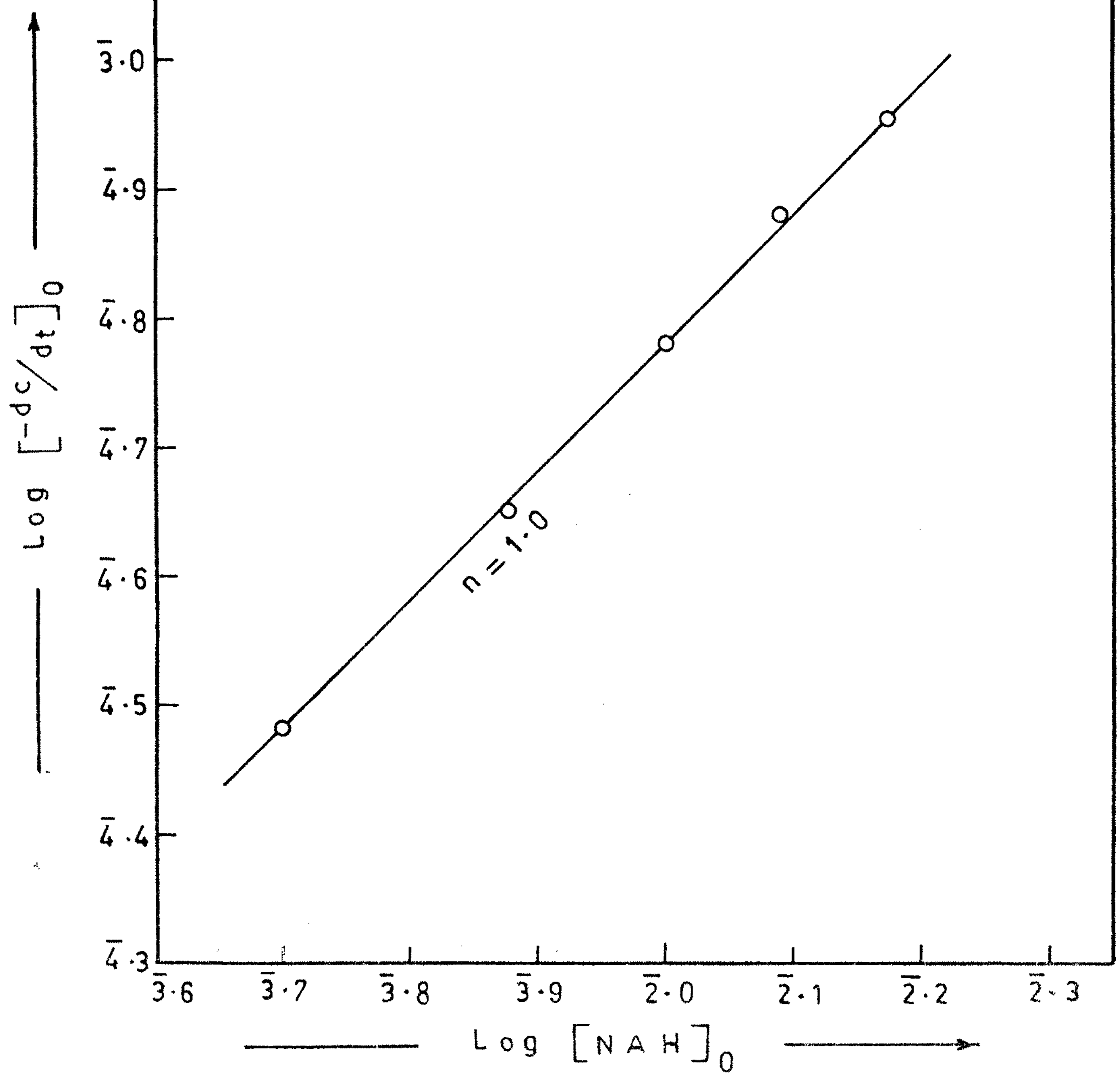


FIG. 3·1·3 — EFFECT OF NAH CONCENTRATION.

FIG. 3·1·4 — Log $\left[-\frac{dc}{dt}\right]$ VERSUS Log $[NAH]_0$.



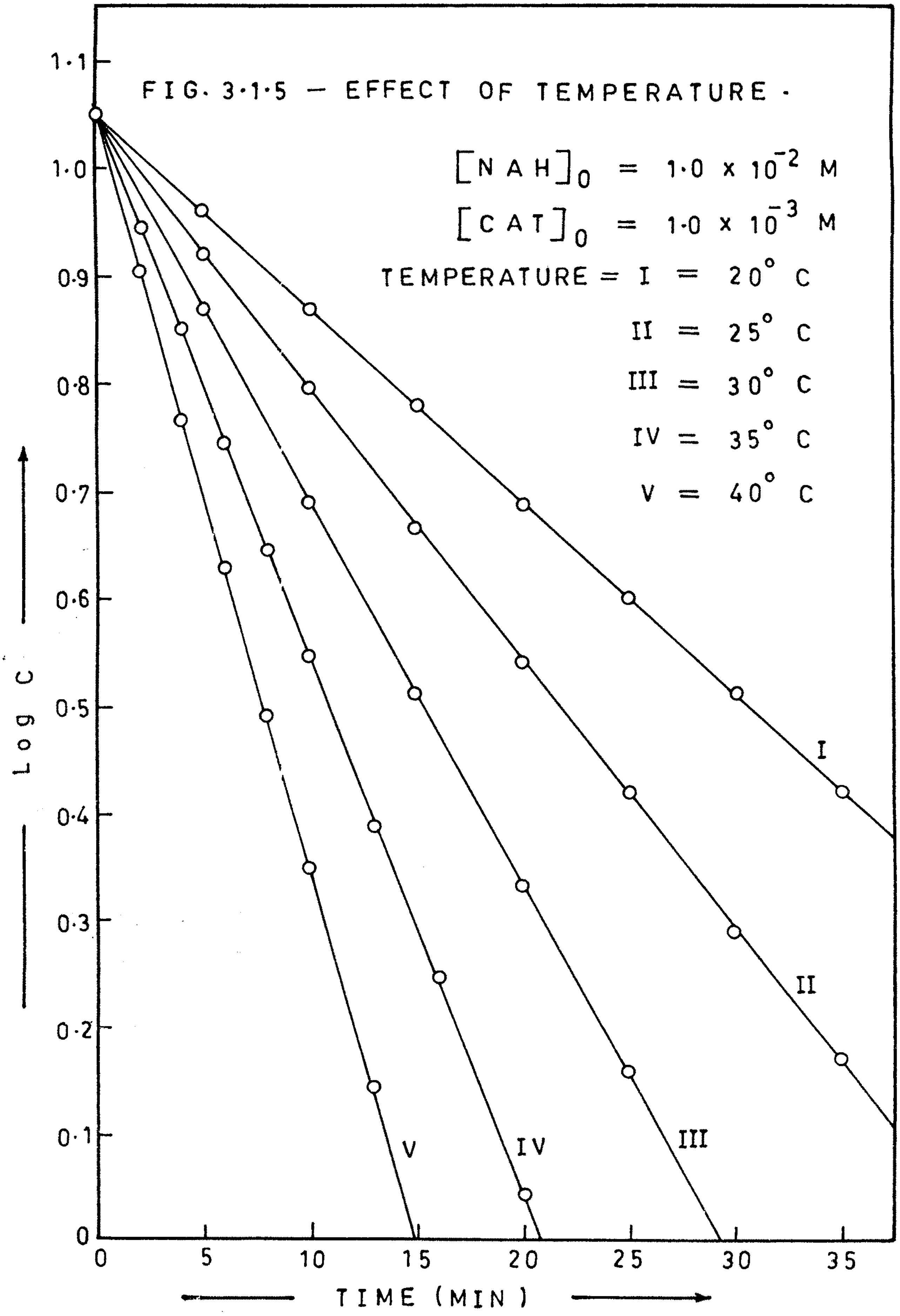


FIG. 3.1.5 — EFFECT OF TEMPERATURE.

FIG. 3·1·6 Log k VERSUS $\frac{1}{T} \times 10^3$.

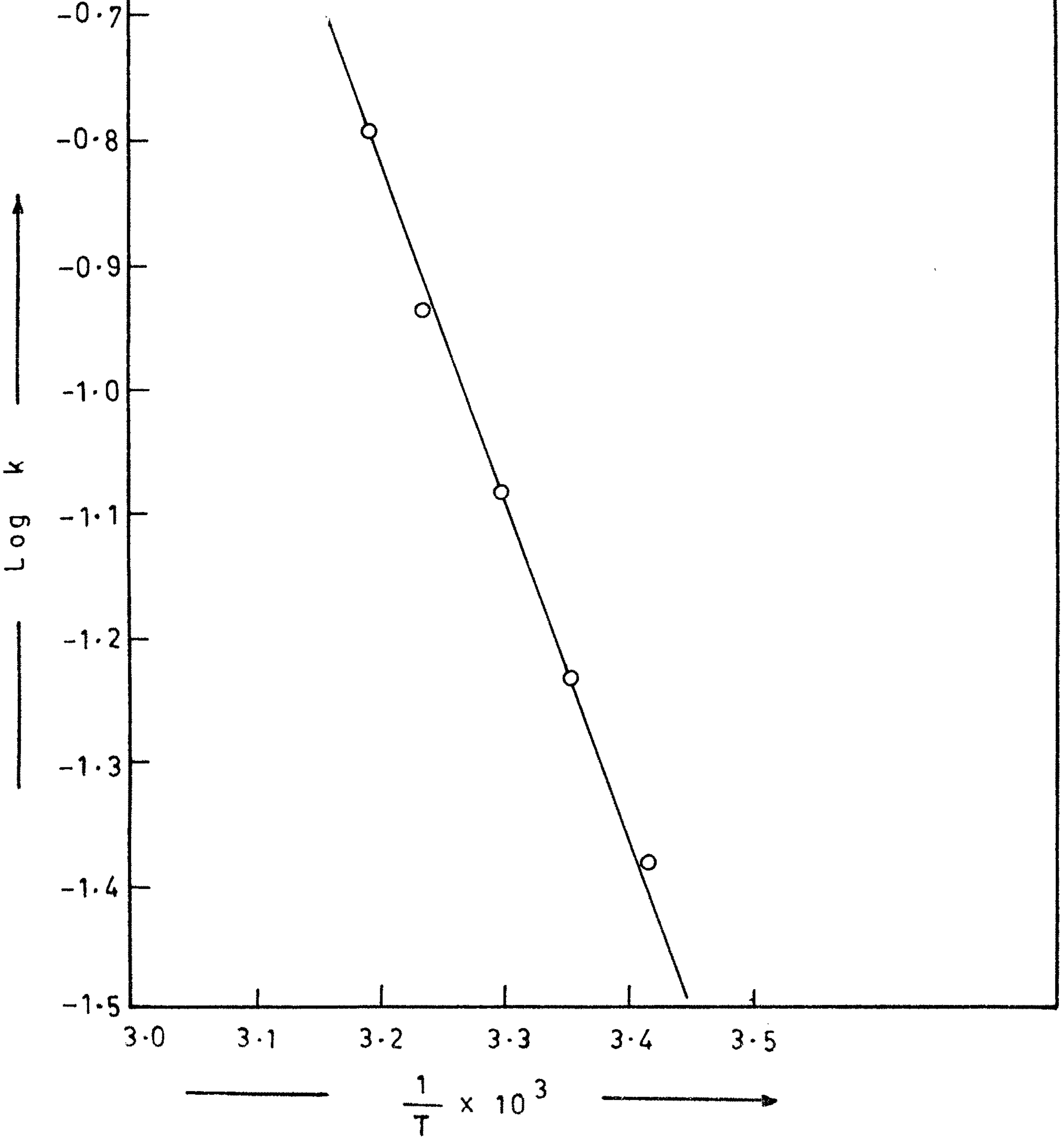
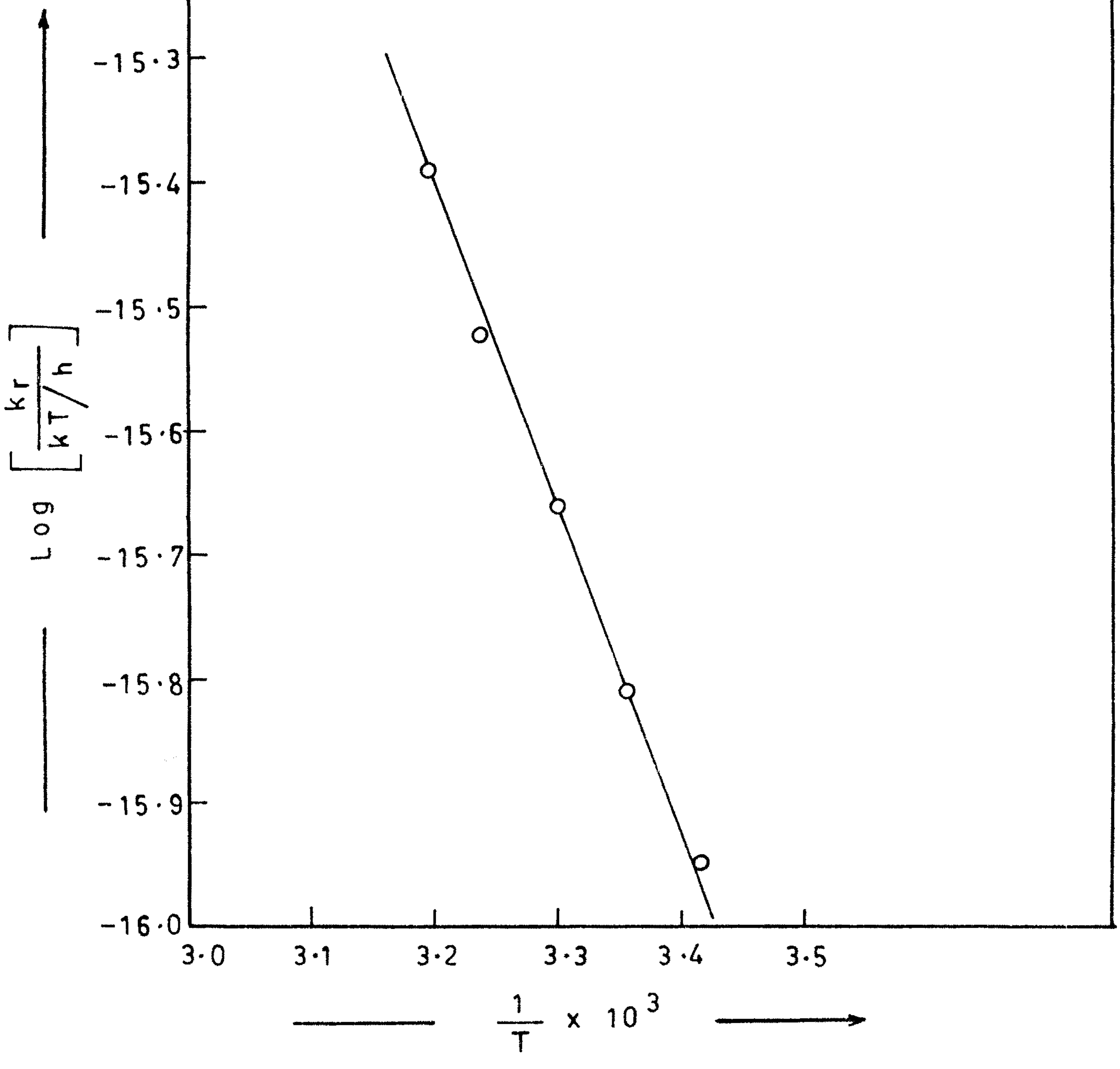


FIG. 3·1·7 — $\mathrm{Log}\left[\frac{k_r}{kT/h}\right]$ VERSUS $\frac{1}{T} \times 10^3$.



CHAPTER : III

SECTION : II

Kinetics of oxidation of isonicotinic acid hydrazide.

SECTION II

KINETICS OF OXIDATION OF ISO NICOTINIC ACID HYDRAZIDE. (INAH)

Preliminary experiments were performed in order to decide the suitable temperature and concentration ranges of the reactants. It was observed that the reaction proceeds with measurable velocity at 25°c and at concentrations of INAH of $1.0\text{x}10^{-2}$M, that of CAT = $1.0\text{x}10^{-3}$M and that of NaOH = $1.0\text{x}10^{-2}$ M. The kinetic data is recorded in the table 3.2.1. given below.

TABLE 3.2.1

$[INAH]=1.0\text{x}10^{-2}$ M $[NaOH]=1.0\text{x}10^{-2}$ M $[Na_2S_2O_3]= 1.0 \text{ x } 10^{-3}$ M
$[CAT] = 1.0 \text{ x } 10^{-3}$M $[NaClO_4] = 1.0\text{x}10^{-1}$M Temp. 25°c

Time (min)	Vol.(ml)of $Na_2S_2O_3$	k x 10^{-2} min^{-1}
0	11.0	-
5	8.4	5.39
10	6.5	5.26
15	5.0	5.25
20	3.9	5.18
25	3.0	5.19
30	2.4	5.07
35	1.9	5.01
40	1.5	4.98
45	1.2	4.92
50	1.0	4.80
Mean $kx10^{-2}$		5.10 min^{-1}

An examination of the above data closely shows that pseudo first order specific rate is almost constant. In this experiment the hydrazide concentration is in excess (10 times) over that of CAT concentration.

1. EFFECT OF CHLORAMINE -T CONCENTRATION:

In order to investigate the effect of concentration of cAT on the reaction, kinetic runs were performed in which concentration of the CAT was varied, whereas that of [INAH] and [NaOH] was kept constant. Using these experimental data the value of k was determined. Table 3.2.2 embodies the results of these kinetic runs and for the sake of comparision the data of the Table 3.2.1 has also been incorporated in it. The values of first order rate constant (k) have been evaluated from the initial slope of the curves, shown in Fig.3.2.1, as well as calculated at different times by integration method, which are in good agreement with each other.

TABLE 3.2.2

[INAH]=1.0×10^{-2}M [$Na_2S_2O_3$]= 1.0×10^{-3} M Temp 25^{o}c
[NaOH] = 1.0×10^{-2} M [$NaClO_4$] = 1.0×10^{-1}M

Conc. of CAT = M $\times10^{-3}$	0.5	1.0	1.5	2.0	2.5
Time (min)	Vol (in ml) of $Na_2S_2O_3$				
0	6.3	11.0	16.2	21.8	27.4
5	4.8	8.4	12.4	16.7	21.0
10	3.7	6.5	9.5	12.8	16.1
15	2.85	5.0	7.3	9.9	12.4
20	2.20	3.9	5.6	7.6	9.6
25	1.7	3.0	4.3	5.9	7.4
30	1.3	2.4	3.4	4.7	5.7
35	1.05	1.9	2.7	3.7	4.5
40	0.8	1.5	2.1	3.0	3.5
45	0.65	1.2	1.7	2.4	2.8
50	0.50	1.0	1.4	1.9	2.3
Mean k$\times10^{-2}$	5.2	5.10	5.19	5.13	5.19

To confirm the order of reaction w.r.t. CAT, the values of - dc/dt were determined by plotting the volume of $Na_2S_2O_3$ (equivalent to CAT) against time for different initial concentrations of oxidant. These values are tabulated in the Table 3.2.3.

TABLE 3.2.3

Initial conc. CAT, Co	$-\frac{dc}{dt}$	Log Co	Log $\left[-\frac{dc}{dt}\right]$
0.5×10^{-3}	3.0×10^{-4}	$\bar{4}.699$	$\bar{4}.477$
1.0×10^{-3}	5.9×10^{-4}	$\bar{3}.000$	$\bar{4}.770$
1.5×10^{-3}	8.7×10^{-4}	$\bar{3}.176$	$\bar{4}.941$
2.0×10^{-3}	1.14×10^{-3}	$\bar{3}.301$	$\bar{3}.060$
2.5×10^{-3}	1.45×10^{-3}	$\bar{3}.398$	$\bar{3}.161$

The order of reaction w.r.t., CAT has been determined from the plot of Log $\left[\frac{-dc}{dt}\right]$ vs log Co (Fig.3.2.2.) which comes out to be 1. This establishes the first order behaviour of the reaction w.r.t.CAT.

2.EFFECT OF HYDRAZIDE (INAH) CONCENTRATION

In order to investigate the effect of hydrazide concentration on the rate of oxidation of isonicotinic acid hydrazide, the hydrazide concentration was varied from 0.5 x 10^{-2} M. to 1.5 x 10^{-2} M, keeping the concentrations of CAT and NaOH constant. The results of these kinetic runs are recorded in Table 3.2.4.and depicted graphically in Fig.3.2.3.

TABLE 3.2.4

[CAT] = 1.0×10^{-3}M [$NaClO_4$] = 1.0×10^{-1} M Temp 25°c
[NaOH]= 1.0×10^{-2} M [$Na_2S_2O_3$]= 1.0 $\times10^{-3}$M

[INAH] M x 10^{-2}	0.5	0.75	1.0	1.25	1.50
Time(min)	Vol (in ml) of $Na_2S_2O_3$				
0	11.2	11.2	11.2	11.2	11.2
5	9.7	9.2	8.4	8.1	7.6
10	8.5	7.6	6.5	5.9	5.2
15	7.5	6.3	5.0	4.3	3.6
20	6.6	5.2	3.9	3.15	2.5
25	5.9	4.3	3.0	2.3	1.7
30	5.3	3.6	2.4	1.7	1.2
35	4.7	3.0	1.9	1.25	0.8
40	4.2	2.5	1.5	0.95	0.7
45	3.8	2.1	1.2	0.7	-
50	3.4	1.8	1.0	-	-
Mean k$\times10^{-2}$=	2.57	3.79	5.10	6.33	7.54

The results contained in Table 3.2.4 show that the first order rate constant increases with increase in hydrazide concentration. The plots of Log C vs time (Fig.3.2.3) are found to be linear. The second order rate constant k_2.

$$k_2 = \frac{k_1}{(\text{Hydrazide})_o}$$

where k_2 = second order rate constant and

k_1 = first order rate constant,

is found to be constant (Table 3.2.5), indicating the first order dependence of the rate on hydrazide concentration.

TABLE 3.2.5

$[\text{INAH}]_o$ $\text{M} \times 10^{-2}$	$k_1 \times 10^{-2}$ min^{-1}	$k_2 \times 10^{-2}$ min^{-1}
0.50	2.57	5.14
0.75	3.79	5.05
1.00	5.10	5.10
1.25	6.33	5.03
1.50	7.54	5.06

The order w.r.t. isonicotinic acid hydrazide was also determined by van't Hoff differential method. The values of -dc /dt and initial concentrations of hydrazide (Co) are given in the table 3.2.6 and these values are substituted in the van't Hoff's equation, i.e.

$$n = \frac{\text{Log}\,[-dc/dt]_1 - \log\,[-dc/dt]_2}{\log\,(Co)_1 - \log\,(Co)_2}$$

The order of reaction was calculated, which is found to be almost unity(One)

The volume of $Na_2S_2O_3$ (equivalent to CAT) was plotted against time for different initial concentrations of hydrazide. From the curves, the value of -dc/dt, the initial rate, in each case was determined from the initial slope as given in Table 3.2.7.

TABLE 3.2.6.

[INAH] $[Co]_1$ $Mx10^{-2}$	$[Co]_2$ $Mx10^{-2}$	$-[dc/dt]_1$ $x10^{-4}$	$-[dc/dt]_2$ $x10^{-4}$	Order of reaction. (n)
0.5	0.75	3.09	4.47	0.97
0.5	1.00	3.09	5.90	0.955
0.5	1.25	3.09	7.76	1.004
0.5	1.50	3.09	8.71	0.94
0.75	1.00	4.47	5.90	0.99
0.75	1.25	4.47	7.76	1.04
0.75	1.50	4.47	8.71	0.97
1.00	1.25	5.90	7.76	1.05
1.00	1.50	5.90	8.71	0.99
1.25	1.50	7.76	8.71	0.94

TABLE 3.2.7

$[INAH]_o$ (Co) $M\times10^{-2}$	$d\,co/dt\times10^{-4}$	Log Co	Log [- dc/dt]
0.50	3.09	$\bar{3}.699$	$\bar{4}.49$
0.75	4.47	$\bar{3}.875$	$\bar{4}.65$
1.00	5.90	$\bar{2}.000$	$\bar{4}.77$
1.25	7.76	$\bar{2}.0969$	$\bar{4}.89$
1.50	8.71	$\bar{2}.176$	$\bar{4}.94$

In order to confirm the order of reaction w.r.t. isonicotinic acid hydrazide, fram the plot of log [- dc/dt] vs Co (represented in Fig 3.2.4), the value of the order w.r.t. INAH has been evaluated which comes out to be 0.975. This confirms the first order behaviour of the reaction w.r.t. [INAH].

3. EFFECT OF SODIUM HYDROXIDE CONCENTRATION :

In order to study the effect of alkali concentration on the rate of oxidation of INAH, the concentration of NaOH is varied from 0.5 x 10^{-2}M to 1.5 x 10^{-2} keeping the concentration of other reactants constant. The results of these kinetic runs are recorded in Table 3.2.8.

TABLE 3.2.8

[INAH] =1.0×10^{-2}M [$NaClO_4$] = 1.0×10^{-1} M Temp = 25°C

[CAT] = 1.0×10^{-2}M [$Na_2S_2O_3$] = 1.0×10^{-3}M

[NaOH] Mx10^{-2} =	0.5	0.75	1.0	1.25	1.50
Time (min)	Vol (in ml) of $Na_2S_2O_3$				
0	11.2	11.1	11.0	11.2	11.2
5	8.4	8.5	8.4	8.65	8.8
10	6.4	6.5	6.6	6.9	6.9.
15	4.9	5.0	5.0	5.2	5.45
20	3.7	3.9	3.9	4.05	4.3
25	2.85	3.0	3.0	3.2	3.5
30	2.2	2.3	2.4	2.5	2.8
35	1.7	1.8	1.9	2.0	2.3
40	1.3	1.4	1.5	1.6	1.85
45	1.0	1.1	1.2	1.3	1.50
50	0.8	0.9	1.0	1.1	1.20
Mean kx10^{-2}	5.43	5.22	5.10	4.97	4.645

Examination of the above results show that, the effect of hydroxide ion concentration is negligible and hence the rate of reaction is independent of alkali concentration.

4. EFFECT OF CHLORIDE ION ON THE RATE OF OXIDATION OF INAH.

To investigate the effect of addition of chloride ion on the rate of oxidation of hydrazides, the concentration of NaCl was varied from O.O M to 4.0 x 10^{-2}M, keeping all the other concentrations constant. The results are listed in the Table 3.2.9.

TABLE 3.2.9

[INAH] = 1.0×10^{-2}M [NaOH] = 1.0×10^{-2}M [$Na_2S_2O_3$] = 1.0×10^{-3}M
[CAT] = 1.0 $\times10^{-3}$M [$NaClO_4$] = 1.0×10^{-1}M Temp. 25°c

[NaCl] M x 10^{-2}	0.00	1.0	2.0	3.0	4.0
Time(min)	Vol.(in ml) of $Na_2S_2O_3$				
0	11.0	11.2	11.2	11.2	11.2
5	8.4	8.7	8.6	8.55	8.5
10	6.5	6.75	6.6	6.5	6.5
15	5.0	5.3	5.1	5.0	5.0
20	3.9	4.0	3.95	3.9	3.8
25	3.0	3.15	3.1	3.0	3.30
30	2.4	2.5	2.4	2.4	2.35
35	1.9	2.0	1.9	1.9	1.8
40	1.5	1.6	1.5	1.5	1.4
45	1.2	-	-	-	-
50	1.0	-	-	-	-
Mean k$\times10^{-2}$	5.10	5.00	5.17	5.24	5.32

An examination of the results contained in the above table shows that the effect of chloride ion is quite negligible.

5. EFFECT OF CHANGE IN IONIC STRENGTH OF THE MEDIUM.

To study the effect of change in ionic strength of the medium on the rate of oxidation of hydrazide, the concentration of sodium perchlorate is varied from 0.1 M x 0.4 M, keeping all other concentrations constant. The results of which are recorded in the table 3.2.10

TABLE 3.2.10

[INAH] = 1.0×10^{-2} M [NaOH] = 1.0×10^{-2} M
[CAT] = 1.0×10^{-3} M [$Na_2S_2O_3$] = 1.0×10^{-3} M Temp. 25°c

[$NaClO_4$] M x 10^{-1}	1.0	2.0	3.0	4.0
μ	0.111	0.211	0.311	0.411
Time(min)	Vol (in ml) of $Na_2S_2O_3$			
0	11.2	11.2	11.2	11.2
5	8.4	8.6	8.5	8.4
10	6.5	6.6	6.5	6.35
15	5.0	5.1	4.95	4.8
20	3.9	3.95	3.8	3.65
25	3.0	3.0	2.9	2.8
30	2.4	2.4	2.2	2.1
35	1.9	1.9	1.7	1.6
40	1.5	1.5	1.3	1.3
45	1.2	-	1.0	-
50	1.0	-	-	-
Mean k$\times 10^{-2}$	5.10	5.19	5.40	5.58

A perusal of the data contained in this table shows that the change of ionic strength (μ) of the medium has marginal effect on the rate of oxidation of hydrazides.

6. EFFECT OF TEMPERATURE

In order to determine the temperature coefficient, energy of activiation (Ea), enthalpy of activation ($\Delta H^{\ddagger}$), frequency factor (A), free energy of activation ($\Delta G^{\ddagger}$)and entropy of activation ($\Delta S^{\ddagger}$), the reaction was studied at five different temperatures ranging from 20° to 40°C. The results of these kinetic runs have been tabulated in Table 3.2.11 and depicted graphically in Fig 3.2.5.

TABLE 3.2.11

[INAH] = 1.0×10^{-2} M [NaOH] = 1.0×10^{-2}M [$Na_2S_2O_3$] = 1.0×10^{-3} M
[CAT] = 1.0×10^{-3}M [$NaClO_4$] = 1.0×10^{-1}M

Temp C°	20°	25°	30°	35°	40°
Time(min)		Vol (in ml.) of $Na_2S_2O_3$			
0	11.2	11.0	11.2	11.2	11.2
2	-	-	-	-	8.3
4	-	-	-	-	6.2
5	9.25	8.4	7.7	6.6	-
7	-	-	-	-	4.0
10	7.7	6.5	5.3	4.0	2.6
15	6.4	5.0	3.65	2.5	1.25
20	5.35	3.9	2.55	1.6	0.50
25	4.5	3.0	1.8	1.0	-
30	3.8	2.4	1.25	0.6	-
35	3.2	1.9	0.9	-	-
40	2.7	1.5	-	-	-
Mean $k\times10^{-2}$	3.66	5.10	7.38	9.95	14.7

It is seen from the above results that the specific rate has approximately doubled for 10°C rise in temperature.

A plot of Log k vs $\frac{1}{T}$, as shown in Fig 3.2.6 is found to be linear showing that, the reaction obeys the Arrhenius relationship. The value of energy of activation (Ea) evaluated from the slope of this curve comes out to be 12.36 k.cals mole^{-1}. The Arrhenius equation has been used directly to calculate energy of activation, which comes out to be 12.51 k.cals mole^{-1}. On the base of this value, the frequency factory (A) and entropy of activation ($\Delta S^{\neq}$) have been calculated. The free energy of activation ($\Delta G^{\neq}$) was calculated as shown by the equations given in section I of temperature effect.

The values of Log $\frac{k_r}{kT/h}$ and $\frac{1}{T}$ are recorded in table 3.2.12 and a plot of $\frac{k_r}{kT/h}$ vs $\frac{1}{T}$ (Fig.3.2.7) gives a straight line and from the slope of which the enthalpy change for the formation of activated complex ($\Delta H^{\neq}$) has been calculated. The value of $\Delta H^{\neq}$, (12.21 k.cals mole^{-1}) obtained from the graph has been used to calculate $\Delta S^{\neq}$ from the equation.

TABLE 3.2.12

Temp. K^{o}	$\frac{1}{T} \times 10^3$	$\frac{k_r}{kT/h}$	Log $\frac{k_r}{kT/h}$
293	3.412	- 15.001	- 16.0004
298	3.355	- 14.632	- 15.8639
303	3.300	- 14.052	- 15.7104
308	3.246	- 13.417	- 15.5879
313	3.194	- 12.244	- 15.4253

The various energy parameters obtained, have been recorded in Table 3.2.13.

TABLE 3.2.13

Temp. K^{o}	Energy of activation (Ea) k.cals mole^{-1}	Temp coefficient	Frequency factor (A) Ax10 ^{5} sec^{-1}	Free energy $\Delta G^{\ddagger}$ k.cal	Entropy of activation $\Delta S^{\ddagger}$ e.u.
293			9.849	21.100	-33.047
298	12.38	2.016	9.616	21.26	-33.092
303	12.19	1.95	9.867	21.43	-33.108
308	12.98	1.99	9.541	21.63	-33.209
313			10.209	21.76	-33.11
Mean	12.51	1.98	9.816	21.44	-33.11

Enthalpy change ($\Delta H^{\ddagger}$) by graph = 12.21 k.cals

Energy of activation (Ea) by graph = 12.36 k.cals

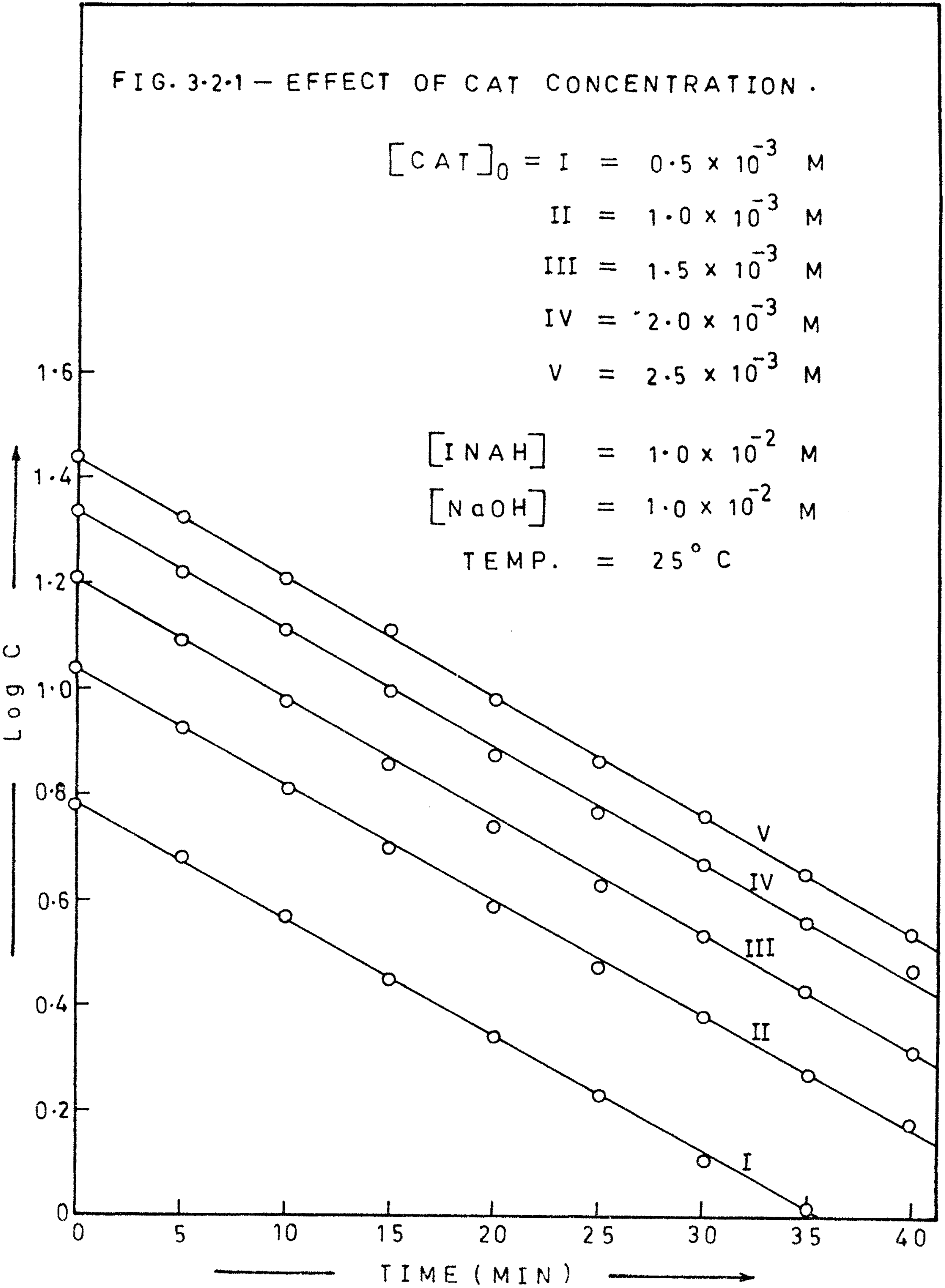


FIG. 3·2·1 — EFFECT OF CAT CONCENTRATION.

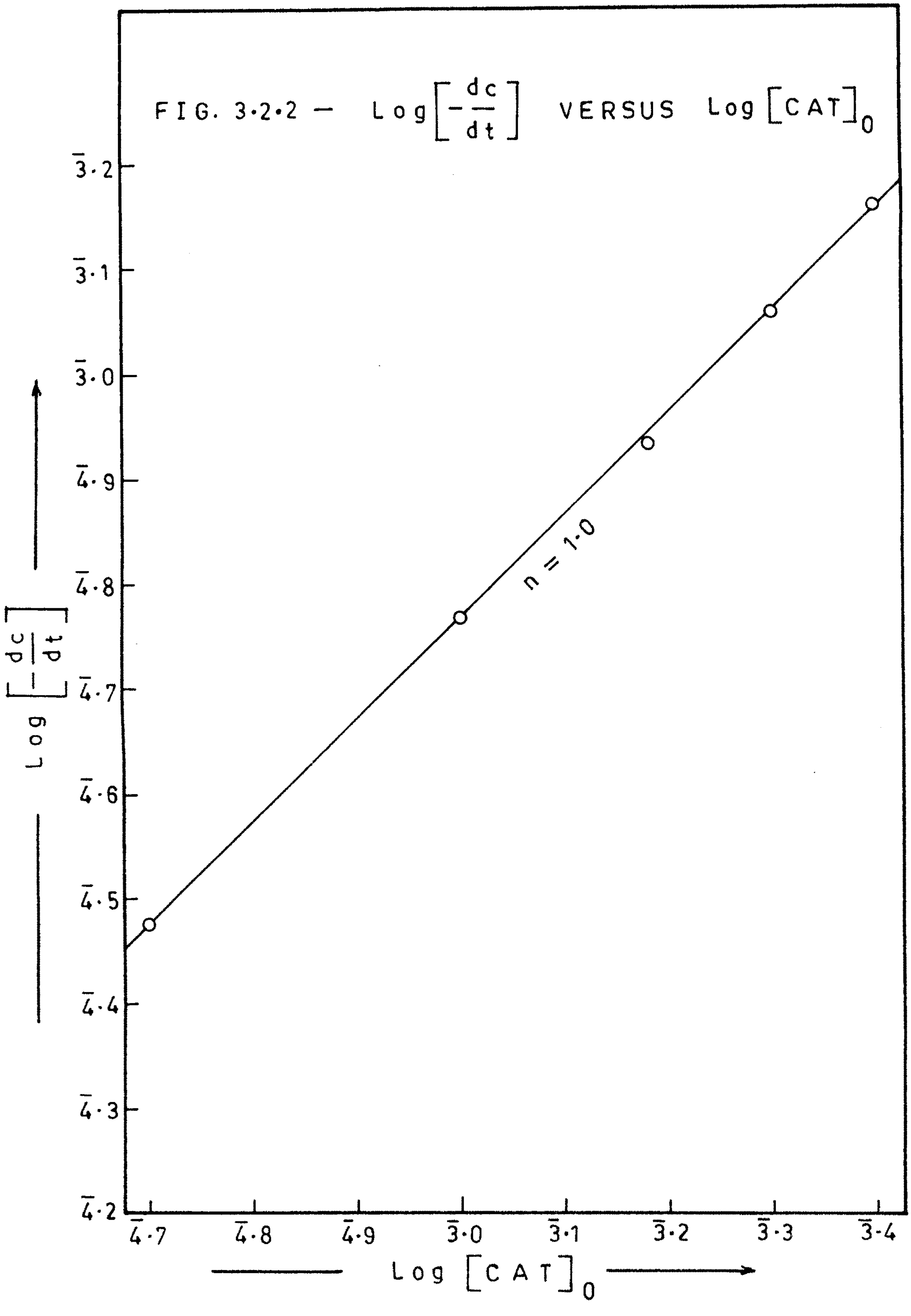


FIG. 3·2·2 — $\mathrm{Log}\left[-\frac{dc}{dt}\right]$ VERSUS $\mathrm{Log}\,[CAT]_0$

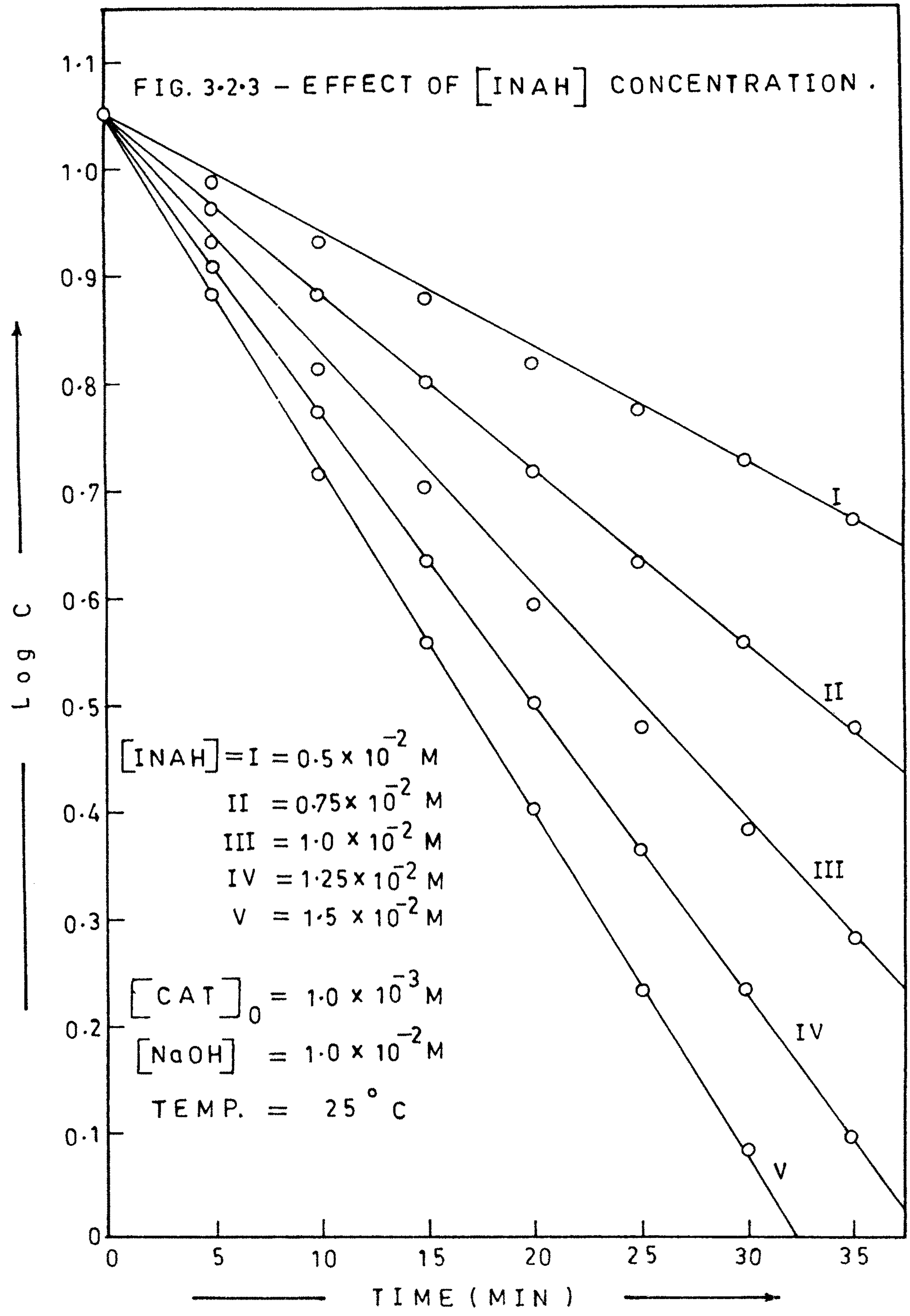
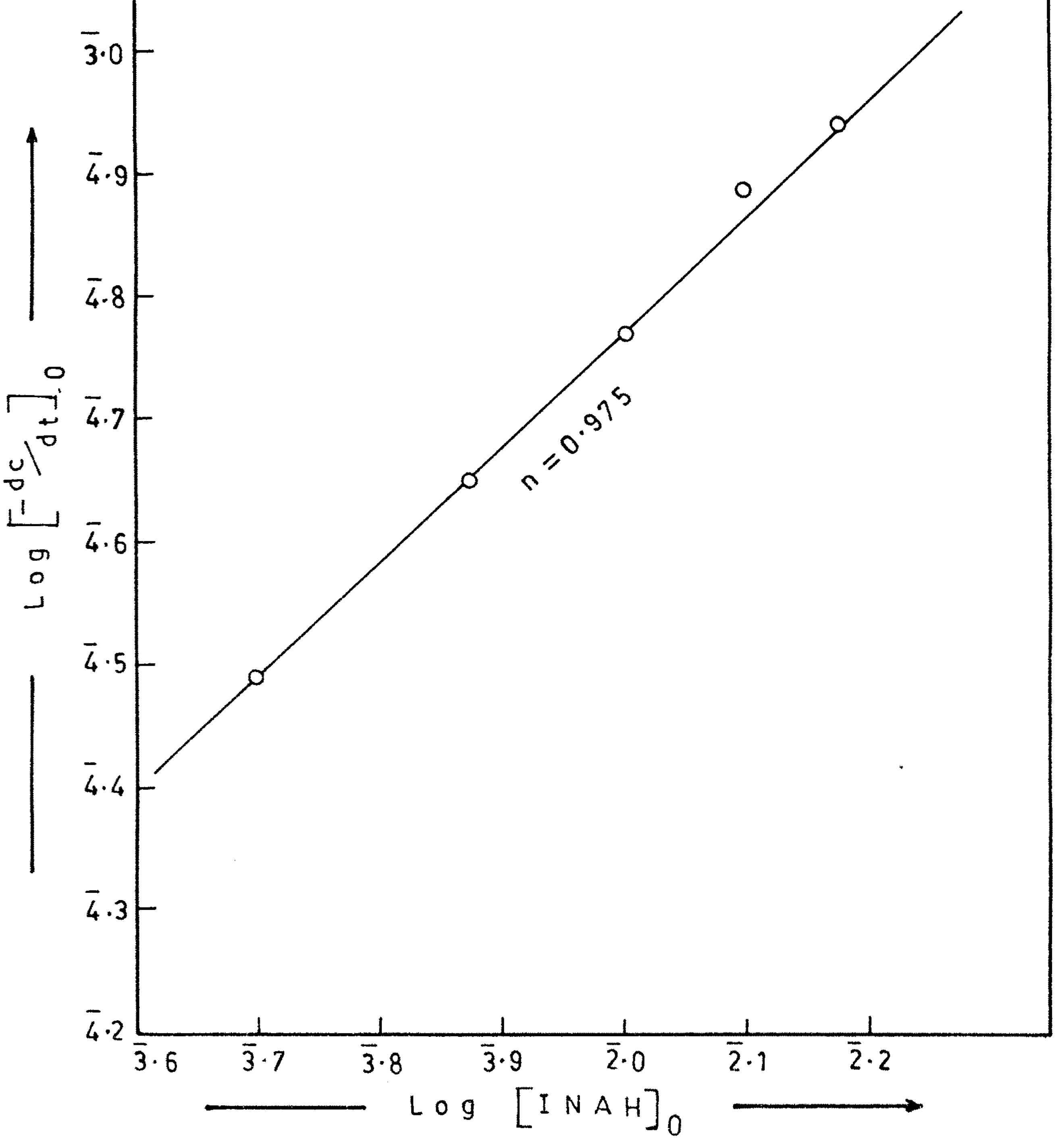


FIG. 3·2·3 – EFFECT OF [INAH] CONCENTRATION.

FIG. 3·2·4 — Log$\left[-\frac{dc}{dt}\right]_0$ VERSUS Log $[\mathrm{INAH}]_0$.



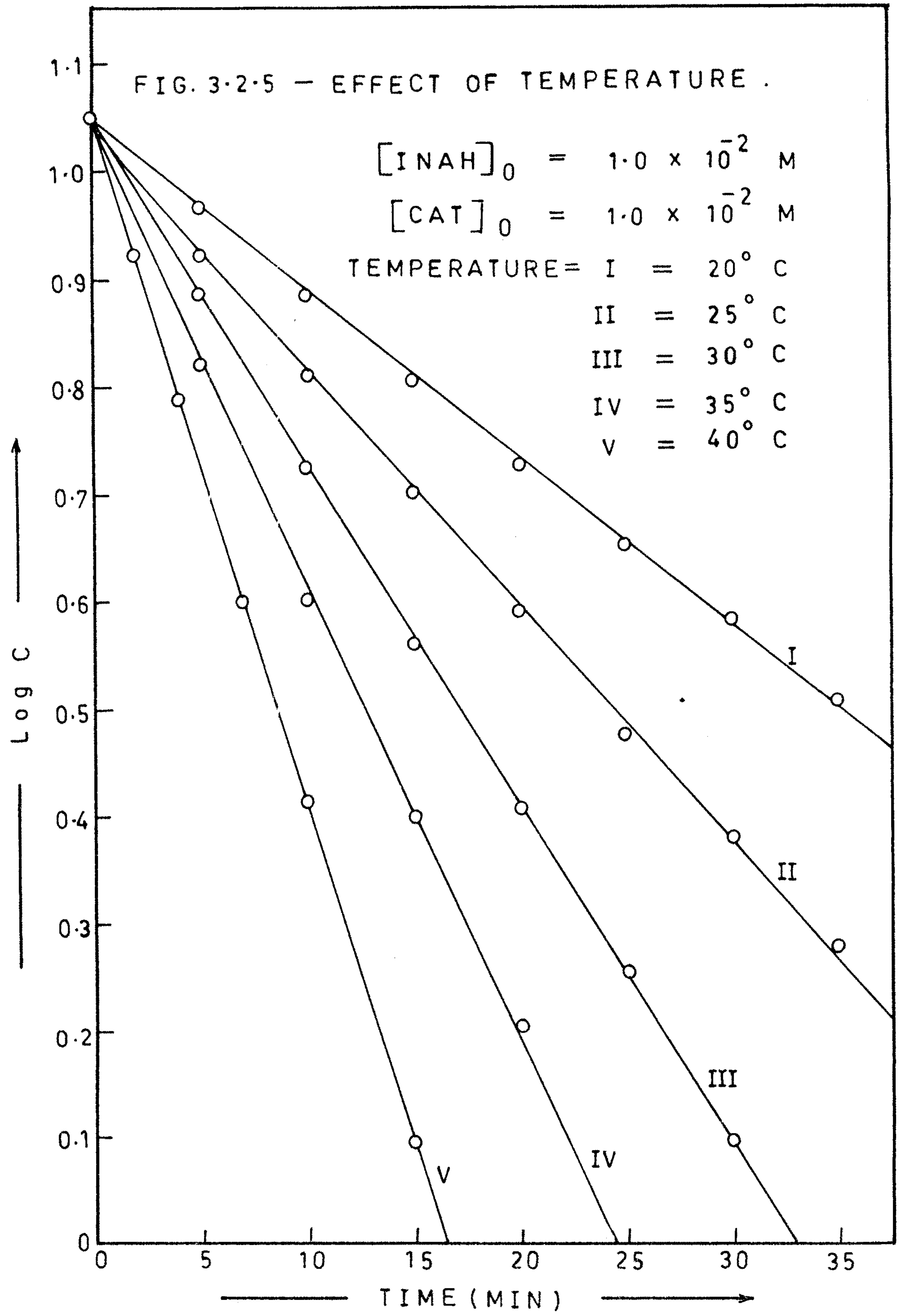


FIG. 3·2·5 — EFFECT OF TEMPERATURE.

FIG. 3·2·6 — Log k VERSUS $\frac{1}{T} \times 10^3$.

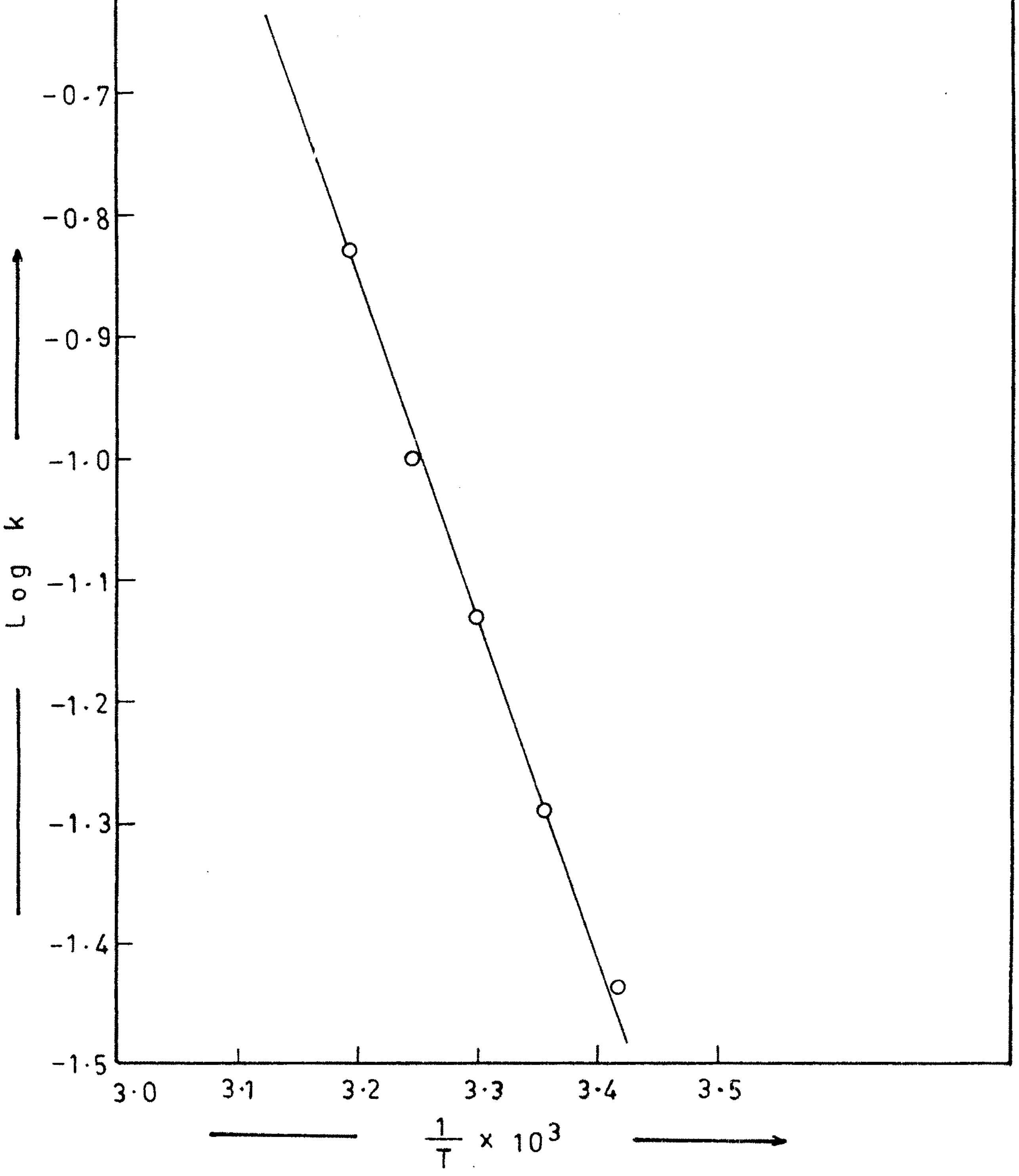
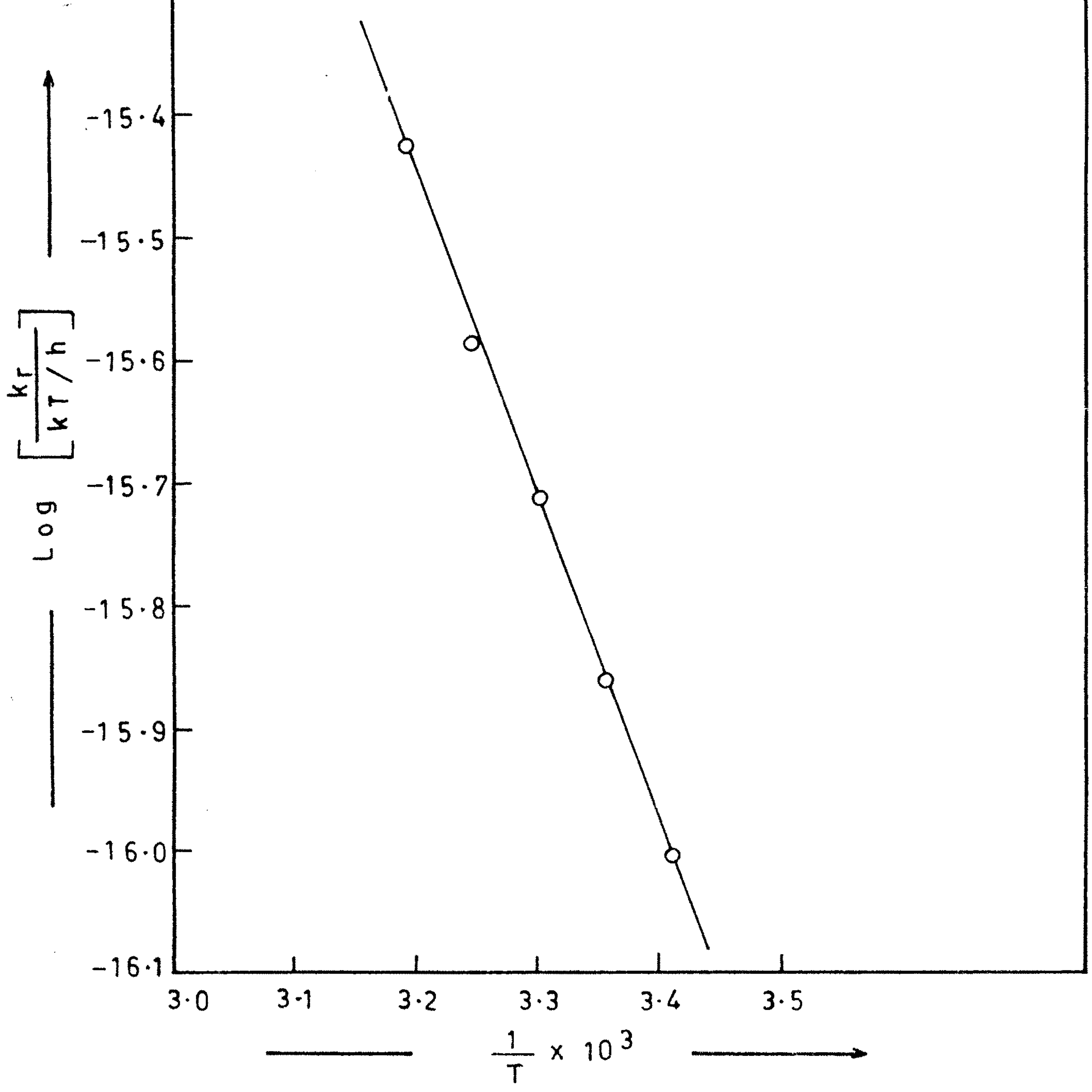


FIG. 3·2·7 — $\text{Log}\left[\frac{k_r}{kT/h}\right]$ VERSUS $\frac{1}{T} \times 10^3$.



1) STOICHIOMETRY :

The ratic of CAT to hydrazide was varied in the presence of NaOH and was equilibrated at 25°C for 24 hours. The estimation of unreacted CAT indicated that one mole of CAT was consumed for one mole of hydrazide. The stoichiometry was found to be 1:1 which can be represented as below:

$$2\ p\ \underset{\text{CAT}}{CH_3 - C_6H_4SO_2NClNa} + 2\ \underset{\text{Hydrazide}}{RCONHNH_2} \longrightarrow$$

$$2\ p\ \underset{\text{PTS}}{CH_3 - C_6H_4SO_2NH_2} + \underset{\text{Bishydrazide}}{RCONH - NHCOR} + NaCl$$

2) PRODUCT ANALYSIS :

The knowledge of the products formed in a reaction, subjected to the kinetic study, is an important step in elucidation of the mechanism of a reaction. Therefore, it was necessary to identify the products formed in the reaction.

Detection of p-toluene sulfonamide has been done by paper chromatographic method. Benzyl alcohol saturated with water was used as the solvent. 0.5% vaniline in 1% HCl solution in ethanol was used as the spraying reagent. The oxidation product, bishydrazide was identified by TLC with authentic samples prepared by the literature method. Nitrogen is detected by lime test.[130]