

CHAPTER - III SECTION - A  
KINETICS OF OXIDATION OF  
n-BUTYRIC ACID HYDRAZIDE

## C H A P T E R - III

### SECTION-A

#### 3.1 OXIDATION OF n-BUTYRIC ACID HYDRAZIDE :

A detailed kinetic study of oxidation of n-butyric and iso-butyric acid hydrazides has been presented in this chapter. Requisite concentrations of Hexacyanoferrate(III), n-butyric acid hydrazide, sodium hydroxide and potassium chloride were used to prepare the reaction mixture and optical density was measured at 420 nm wavelength as a function of time. Experiments were designed to include the following studies :

- 1) Overall order of the reaction and order w.r.t. reactants.
- 2) Effect of Hexacyanoferrate(III) concentration on the rate of the reaction.
- 3) Effect of Hydrazide concentration on the rate of reaction.
- 4) Effect of sodium hydroxide concentration.
- 5) Effect of temperature and evaluation of Thermodynamic parameters.
- 6) Effect of potassium chloride concentration.
- 7) Effect of dielectric constant of the medium.
- 8) End product analysis and free radical tests.

#### DETERMINATION OF ORDER OF THE REACTION :

The order of the reaction w.r.t. Hexacyanoferrate(III) was determined by isolation method. The concentration of Hexacyanoferrate

(III) was varied from  $3.0 \times 10^{-4} \text{M}$  to  $7.0 \times 10^{-4} \text{M}$ , keeping the concentrations of n-butyric acid hydrazide and sodium hydroxide constant. The reaction was studied at  $40^\circ\text{C}$ .

However, the order w.r.t. n-butyric acid hydrazide could not be determined by isolation method as Hexacyanoferrate(III), which is the absorbing species could not be used in large excess as compared to n-butyric acid hydrazide. Hence, comparable concentrations of Hexacyanoferrate(III) and n-butyric acid hydrazide were selected to determine overall order of the reaction. For this Hexacyanoferrate (III) concentration was kept constant ( $5.0 \times 10^{-4} \text{M}$ ), while, n-butyric acid hydrazide concentration was varied from  $4.0 \times 10^{-3} \text{M}$  to  $8.0 \times 10^{-3} \text{M}$ .

#### EFFECT OF HEXACYANOFERRATE(III) CONCENTRATION :

In order to investigate the effect of Hexacyanoferrate(III) concentration on the specific rate, it was also necessary to employ data of the kinetic runs to determine the order of the reaction w.r.t Hexacyanoferrate(III). Reaction was carried out at five different concentrations of Hexacyanoferrate(III) keeping the concentrations of hydrazide, NaOH and KCl unchanged.

Table A.1 embodies the results of kinetic runs, the data has been represented in Fig. A.1.

The values of first order rate constants (viz.k) have been evaluated at different time intervals by integration method using the formula

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \quad *$$

TABLE A - 1

$[n\text{-BAH}] = 5.0 \times 10^{-3} \text{ M}$                        $[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$   
 $[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$                       Temp = 40°C  
 $\lambda_{\text{max}} = 420 \text{ nm}$

[HCF(III)] M x 10 <sup>4</sup>	3.0	4.0	5.0	6.0	7.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.270	0.365	0.465	0.560	0.660
5	0.255	0.345	0.435	0.520	0.610
10	0.245	0.325	0.410	0.490	0.565
15	0.235	0.305	0.385	0.460	0.525
20	0.230	0.290	0.365	0.440	0.485
25	0.220	0.275	0.345	0.410	0.450
35	0.205	0.255	0.310	0.365	0.405
45	0.190	0.225	0.275	0.320	0.355
55	0.175	0.215	0.245	0.290	0.310
65	0.165	0.200	0.220	0.255	0.265
75	0.155	0.175	0.205	0.220	0.235
90	0.140	0.155	0.180	0.190	0.200
Mean <sub>min</sub> kx10 <sup>2</sup>	0.85	1.07	1.17	1.26	1.33

An examination of the above data shows that when hydrazide concentration is in excess and by increasing the initial concentration of hexacyanoferrate(III), the pseudo first order specific rate increases with increase in oxidant concentration, showing that the rate of disappearance of hexacyanoferrate(III) obeys the first order kinetics.

The most important step in the elucidation of the mechanism of the reaction is the determination of the order of reaction. It can be determined by one of the several methods available, provided that the reaction is not complicated by consecutive reaction, reverse reaction, side reaction or other factors which influence the rate.

The order w.r.t. hexacyanoferrate(III) was determined by van't Hoff differential method. The optical density of the hexacyanoferrate(III) was plotted against time for initial concentrations of Hexacyanoferrate(III), from these curves, the value of initial rate  $-\frac{dA}{dt}$  in each case was determined from initial slope, from which the value of  $-\frac{dc}{dt}$  was calculated by multiplying  $\frac{1}{\epsilon}$ , which was obtained by plotting optical density vs concentration of Hexacyanoferrate(III) and value was found to be ( $\epsilon = 961$ ). Liters mole<sup>-1</sup> cm<sup>-1</sup>.

The values of  $-\frac{dc}{dt}$  and concentration of hexacyanoferrate(III) i.e. 'C' are substituted in the Van't Hoff equation i.e.,

$$n = \frac{\log \left( \frac{-dc_{01}}{dt} \right) - \log \left( \frac{-dc_{02}}{dt} \right)}{\log C_1 - \log C_2}$$

and the order of reaction 'n' was calculated. The values of initial

rates  $-\frac{dc}{dt}$  for different initial concentrations of Hexacyanoferrate (III) and the values of 'n' calculated thereby are recorded in Table A.2 and Table A.3.

TABLE A-2

[HCF(III)] M x 10 <sup>4</sup>	(-dc/dt) x 10 <sup>6</sup>	Log C <sub>o</sub>	Log(-dc/dt) <sub>o</sub>
3.0	3.0120	- 3.5228	- 5.521
4.0	4.0150	- 3.3979	- 5.396
5.0	5.0190	- 3.3010	- 5.299
6.0	6.0230	- 3.2218	- 5.220
7.0	7.0270	- 3.1549	- 5.138

TABLE A-3

[HCF(III)] M x 10 <sup>4</sup>	(-dc/dt) x 10 <sup>6</sup>	Order of reaction 'n'
3.0	3.012	]-----0.99
4.0	4.015	
4.0	4.015	]-----1.00
5.0	5.019	
5.0	5.019	]-----1.00
6.0	6.023	
6.0	6.023	]-----1.00
7.0	7.027	

In order to confirm the order of reaction w.r.t. Hexacyano-ferrate(III) from the plot of  $\log - dc/dt$  vs  $\log C_0$  represented in Figure A-2. The value of the order w.r.t. Hexacyanoferrate(III) has been evaluated, which comes out to be 0.97. This confirms the first order behaviour w.r.t. Hexacyanoferrate(III).

#### EFFECT OF HYDRAZIDE CONCENTRATION :

The effect of n-butyric acid hydrazide concentration on the rate of the reaction was studied by taking five different initial concentrations i.e.  $4.0 \times 10^{-3}M$  to  $8.0 \times 10^{-3}M$  keeping the concentration of hexacyanoferrate(III) and sodium hydroxide constant. The results of these kinetic runs are recorded in Table A-4 and depicted graphically in Fig. A-3.

The results given in Table A-4 show that, first order rate constant increases with increase initial concentration of hydrazide. The plots of  $\log O.D.$  against time [Fig. A-3] are linear. The second order rate constant

$$k_2 = \frac{k_1}{[\text{Hydrazide}]_0}$$

where,  $k_2$  = second order rate constant

$k_1$  = first order rate constant.

was found to be constant (Table A-5) indicating the first order dependance of the rate on hydrazide concentration.

TABLE A - 4

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp} = 40^\circ\text{C}$$

[ n-BAH] M x 10 <sup>3</sup>	4.0	5.0	6.0	7.0	8.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.470	0.465	0.465	0.465	0.460
5	0.440	0.435	0.430	0.425	0.420
10	0.415	0.410	0.400	0.395	0.385
15	0.405	0.385	0.375	0.365	0.350
20	0.385	0.365	0.350	0.335	0.320
25	0.370	0.345	0.325	0.310	0.290
35	0.335	0.310	0.285	0.265	0.245
45	0.305	0.275	0.250	0.230	0.205
55	0.275	0.245	0.220	0.200	0.175
65	0.250	0.220	0.195	0.175	0.160
75	0.230	0.205	0.170	0.150	0.145
90	0.200	0.180	0.145	0.125	0.115
Mean <sub>min</sub> k x 10 <sup>2</sup>	0.94	1.17	1.41	1.60	1.75



TABLE A - 5

[n-BAH] M x 10 <sup>3</sup>	k <sub>1</sub> x 10 <sup>2</sup> min <sup>-1</sup>	k <sub>2</sub> min <sup>-1</sup> mole <sup>-1</sup>
4.0	0.94	2.35
5.0	1.17	2.34
6.0	1.41	2.35
7.0	1.60	2.29
8.0	1.75	2.19

ORDER WITH RESPECT TO HYDRAZIDE :

To investigate the order of the reaction w.r.t. hydrazide; the kinetic data of Table A-4, was subjected to van't Hoff differential method. From the initial slopes of plots of optical density vs time curves, the values of  $(-dc/dt)_0$  corresponding to various initial concentrations of hydrazides were evaluated which are given in Table A-6 and Table A-7 respectively.

A plot of  $\log (-dc/dt)_0$  vs  $\log C_0$ , where  $C_0$  is the initial concentration of n-Butyric acid hydrazide, was shown in Fig. A-4. The value of the order w.r.t. n-BAH has been evaluated which comes out to be 0.97. This confirms first order behaviour of the reaction w.r.t. n-butyric acid hydrazides.

TABLE A-6

$[n\text{-BAH}]$ $M \times 10^3$	$(-dc/dt) \times 10^6$	$\text{Log } C_o$	$\text{log } (-dc/dt)_o$
4.0	4.020	- 2.3979	- 5.396
5.0	5.019	- 2.3010	- 5.299
6.0	6.030	- 2.2218	- 5.220
7.0	7.035	- 2.1549	- 5.153
8.0	8.040	- 2.0969	- 5.095

TABLE A-7

$[n\text{-BAH}]$ $M \times 10^3$	$(-dc/dt) \times 10^6$	Order of reaction 'n'
4.0	4.020	] ----- 0.99
5.0	5.019	
5.0	5.019	] ----- 1.01
6.0	6.030	
6.0	6.030	] ----- 1.00
7.0	7.035	
7.0	7.035	] ----- 1.00
8.0	8.04	

#### EFFECT OF SODIUM HYDROXIDE CONCENTRATION :

In order to study the effect of alkali concentration on the oxidation of n-butyric acid hydrazide, the concentration of sodium hydroxide was varied from  $2.0 \times 10^{-4}M$  to  $6.0 \times 10^{-4}M$  by keeping the concentrations of other reactants constant. The results of these runs are recorded in Table A-8.

An examination of the results in the above table reveals that an increase in the concentration of the NaOH enhances the reaction rate. The kinetics of oxidation of n-butyric acid hydrazide by Hexacyanoferrate(III) was found to be directly proportional to the concentration of sodium hydroxide.

#### EFFECT OF TEMPERATURE :

In order to determine the temperature coefficient, energy of activation ( $E_a$ ), 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  $30^\circ C$  to  $50^\circ C$ . The results of these kinetic runs have been tabulated in Table A-9, and graphically represented in Fig. A-5.

It is seen from the above results that mean value of temperature coefficients for  $10^\circ C$  rise comes out to be 1.98.

A plot of  $\log k$  vs  $1/T$  is found to be linear as shown in Fig. A-6, indicating that the reaction obeys Arrhenius relationship. The values of energy of activation ( $E_a$ ), evaluated from slope of this

TABLE A - 8

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{n-BAH}] = 5.0 \times 10^{-2} \text{ M}$$

$$[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp} = 40^\circ\text{C}$$

[NaOH] M x 10 <sup>4</sup>	2.0	3.0	4.0	5.0	6.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.465	0.465	0.465	0.465	0.465
5	0.440	0.435	0.440	0.435	0.425
10	0.425	0.415	0.415	0.410	0.400
15	0.410	0.400	0.390	0.385	0.370
20	0.390	0.375	0.370	0.365	0.350
25	0.375	0.360	0.355	0.345	0.325
35	0.345	0.330	0.325	0.310	0.280
45	0.315	0.300	0.285	0.275	0.260
55	0.285	0.270	0.255	0.245	0.240
65	0.260	0.245	0.230	0.220	0.215
75	0.240	0.220	0.205	0.205	0.195
90	0.215	0.190	0.185	0.180	0.175
Mean <sub>1</sub> min <sup>2</sup> x 10 <sup>2</sup>	0.90	1.03	1.11	1.17	1.39

TABLE A - 9

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{n-BAH}] = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$$

Temperature	30°C	35°C	40°C	45°C	50°C
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.465	0.465	0.465	0.465	0.465
5	0.450	0.445	0.435	0.425	0.410
10	0.435	0.425	0.410	0.385	0.365
15	0.425	0.405	0.385	0.355	0.325
20	0.410	0.390	0.365	0.325	0.285
25	0.400	0.370	0.345	0.295	0.255
35	0.380	0.340	0.310	0.250	0.220
45	0.360	0.310	0.275	0.210	0.180
55	0.350	0.295	0.245	0.185	0.150
65	0.340	0.275	0.220	0.155	-
75	0.320	0.260	0.205	0.140	-
90	0.300	0.235	0.180	-	-
Mean <sub>min</sub> <sup>-1</sup> kx10 <sup>2</sup>	0.58	0.87	1.17	1.76	2.23

curve comes out to be  $13.56 \text{ k cal mole}^{-1}$ . The Arrhenius equation has been used directly to calculate the energy of activation, which comes out to be  $13.30 \text{ k cal mole}^{-1}$ . On the basis of this calculated value, the frequency factor (A), free energy of activation and entropy of activation ( $\Delta S^\ddagger$ ) have been calculated by the application of the following equations :

$$\begin{aligned} \text{i)} \quad & k_r = Ae^{-E/RT} \\ \text{ii)} \quad & k_r = (kT/h)e^{\Delta G^\ddagger/RT} \\ \text{iii)} \quad & A = e (kT/h)e^{\Delta S^\ddagger/R} \end{aligned}$$

where equation (iii) is applicable to the reactions taking place in solutions. In the above equations ' $k_r$ ' is the specific rate, ' $k$ ' is the Boltzmann constant, ' $h$ ' is the Planck's constant and ' $e$ ' is a constant (2.178) to be introduced in the equation, when the reaction takes place in solution, other symbols carry their usual meanings.

The free energy of the reaction,  $\Delta G^\ddagger$  was calculated by the equation :

$$\text{iv)} \quad k_r = \frac{kT}{h} e^{-\Delta G^\ddagger/RT}$$

equation (ii) can be expressed in terms of enthalpy change as

$$k_r = \left[ \frac{kT}{h} \right] e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}$$

$$\text{Log } \frac{k_r}{kT/h} = \frac{-\Delta H^\ddagger}{2.303 RT} \quad \text{OR} \quad + \frac{\Delta S^\ddagger}{2.303 R}$$

TABLE A - 10

Temp. T(K°)	1/T x 10 <sup>3</sup>	k <sub>r</sub> x 10 <sup>2</sup> min <sup>-1</sup>	log k <sub>r</sub>	log $\frac{k_r}{kT/h}$
303	3.3003	0.5800	- 2.2365	- 15.0367
308	3.2467	0.8700	- 2.0605	- 14.8677
313	3.1948	1.1700	- 1.9318	- 14.7460
318	3.1446	1.7600	- 1.7545	- 14.5756
323	3.0959	2.2300	- 1.6517	- 14.4796

The values of  $\log \left[ \frac{k_r}{kT/h} \right]$  have been plotted against 1/T which is shown in Fig. A-7. The plot is linear and from the slope of the straight line the enthalpy change for the formation of activated complex ( $\Delta H^\ddagger$ ) has been calculated. The value of the  $\Delta H^\ddagger$  [11.75 k cal /mole<sup>-1</sup>] was obtained. The above equation was used to calculate  $\Delta S^\ddagger$ . The various energy parameters obtained have been recorded in Table-11

A large negative value of entropy of activation is indicative of the formation of an activated complex involving two oppositely charged ions.

#### EFFECT OF CHLORIDE ION CONCENTRATION :

To investigate the effect of addition of chloride ion on the rate of oxidation of hydrazide, the concentration of potassium chloride was varied from 0.0 M to 6.0 x 10<sup>-4</sup>M, keeping all other concentrations constant. An examination of the results contained in the Table A-12 show that effect of variation of chloride ion concentra-

TABLE A-11

THERMODYNAMIC - PARAMETERS

Temp. T ( K° )	k <sub>r</sub> x 10 <sup>2</sup>	Temp. coeffi- cient per 10°C	E <sub>a</sub> k cal/mole <sup>-1</sup>		ΔH <sup>‡</sup> k cal/mole <sup>-1</sup>	A x 10 <sup>-5</sup> sec <sup>-1</sup>	ΔS <sup>‡</sup> e.u.	ΔG <sup>‡</sup> k cal/mole <sup>-1</sup>
			Graph	Calculated				
303	0.5800				Graph	5.898	- 32.17	21.505
308	0.8700	2.017		13.226		6.137	- 32.12	21.650
313	1.1700	2.023	13.568	13.715	11.758	5.792	- 32.27	21.858
318	1.7600	1.906		12.959		6.184	- 32.17	21.988
323	2.2300					5.120	- 32.57	22.278
Mean		1.98	13.56	13.30	11.75	5.82	- 32.26	21.85



TABLE A - 12

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{n-BAH}] = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp.} = 40^\circ\text{C}_M$$

[KCl]= Mx10 <sup>4</sup>	0.0	2.0	4.0	6.00
Time in min.	O.D.	O.D.	O.D.	O.D.
0	0.465	0.465	0.465	0.465
5	0.435	0.430	0.425	0.425
10	0.410	0.405	0.400	0.345
15	0.385	0.380	0.375	0.370
20	0.365	0.360	0.355	0.350
25	0.345	0.340	0.335	0.330
35	0.310	0.300	0.295	0.290
45	0.275	0.270	0.265	0.255
55	0.245	0.240	0.230	0.220
65	0.220	0.215	0.210	0.205
75	0.205	0.200	0.195	0.190
90	0.180	0.175	0.170	0.165
Mean <sub>min</sub> kx10 <sup>2</sup>	1.17	1.28	1.34	1.42

TABLE A - 13

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{n-BAH}] = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp.} = 40^\circ\text{C}$$

Ethanol % (v/v)	0.0	10.0	20.0	30.00
Time in min.	O.D.	O.D.	O.D.	O.D.
0	0.465	0.465	0.465	0.465
5	0.435	0.430	0.425	0.420
10	0.410	0.405	0.395	0.390
15	0.385	0.375	0.370	0.365
20	0.365	0.355	0.345	0.340
25	0.345	0.335	0.325	0.315
35	0.310	0.305	0.285	0.270
45	0.275	0.265	0.255	0.240
55	0.245	0.235	0.220	0.215
65	0.220	0.210	0.195	0.185
75	0.205	0.200	0.180	0.175
90	0.180	0.175	0.160	0.145
Mean <sub>1</sub> min $\times 10^2$	1.17	1.32	1.45	1.57

tion on the rate of oxidation of hydrazide was found to be concentration dependence.

EFFECT OF DIELECTRIC CONSTANT OF MEDIUM :

The effect of dielectric constant (D) of the medium on the rate of oxidation of n-butyric acid hydrazide was studied by addition of ethanol (0.0 to 30%) to the reaction mixture, keeping the other concentrations constant. The results are depicted in the Table A-13.

It is observed from the Table A-13 that rate of oxidation of n-butyric acid hydrazide was found to be increased with increase in dielectric constant of the medium. The values of dielectric constant (D) were reported by GOSTA-AKERLOF<sup>1</sup>.

The results are depicted in the following table :

TABLE A - 14

Ethanol % (v/v)	Dielectric constant(D)	$K \times 10^2$ $\text{min}^{-1}$	$\frac{10^2}{D}$	$2 + \log k$
0.0	72.12	1.17	1.367	2.0681
10.0	67.86	1.32	1.473	2.1205
20.0	62.41	1.45	1.602	2.1613
30.0	56.73	1.57	1.763	2.1958

Results recorded in the above table clearly show that decrease in dielectric constant increases the specific rate of the reaction, which may be due to the fact that the rate determining step may have involved between the ions of similar charges.

FIG:A-1 — EFFECT OF HCF(III) CONCENTRATION

$[n\text{-BAH}] = 5.0 \times 10^{-3} \text{ M}$   
 $[\text{OH}] = 5.0 \times 10^{-4} \text{ M}$   
TEMP = 40°C

$[\text{HCF (III)}] - \text{I} = 3.0 \times 10^{-4} \text{ M}$   
II = 4.0 × 10<sup>-4</sup> M  
III = 5.0 × 10<sup>-4</sup> M  
IV = 6.0 × 10<sup>-4</sup> M  
V = 7.0 × 10<sup>-4</sup> M

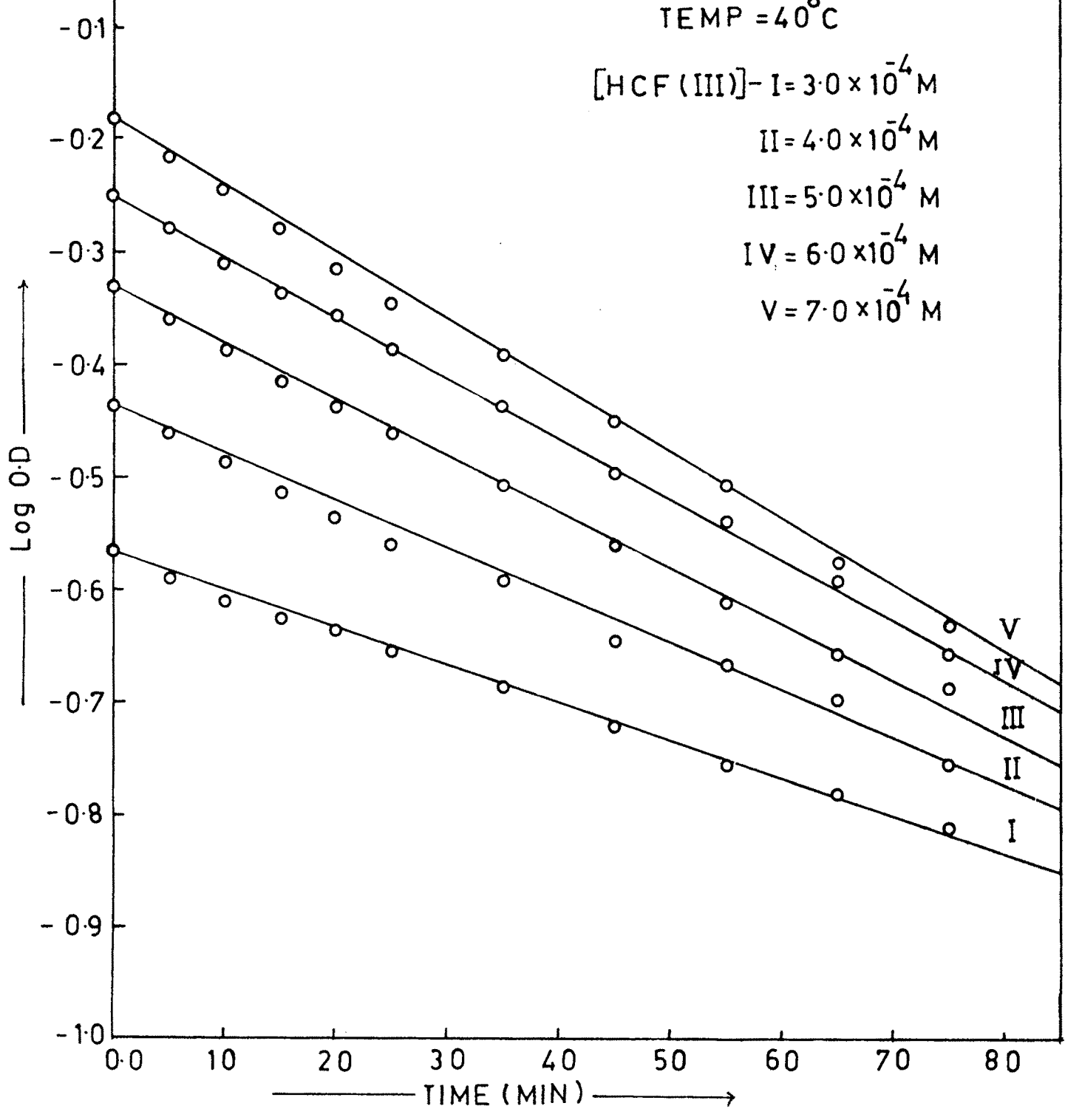


FIG:A-2 — PLOT OF  $\text{Log} \left[ -\frac{dc}{dt} \right]_0$  Vs  $\text{Log} C_0$

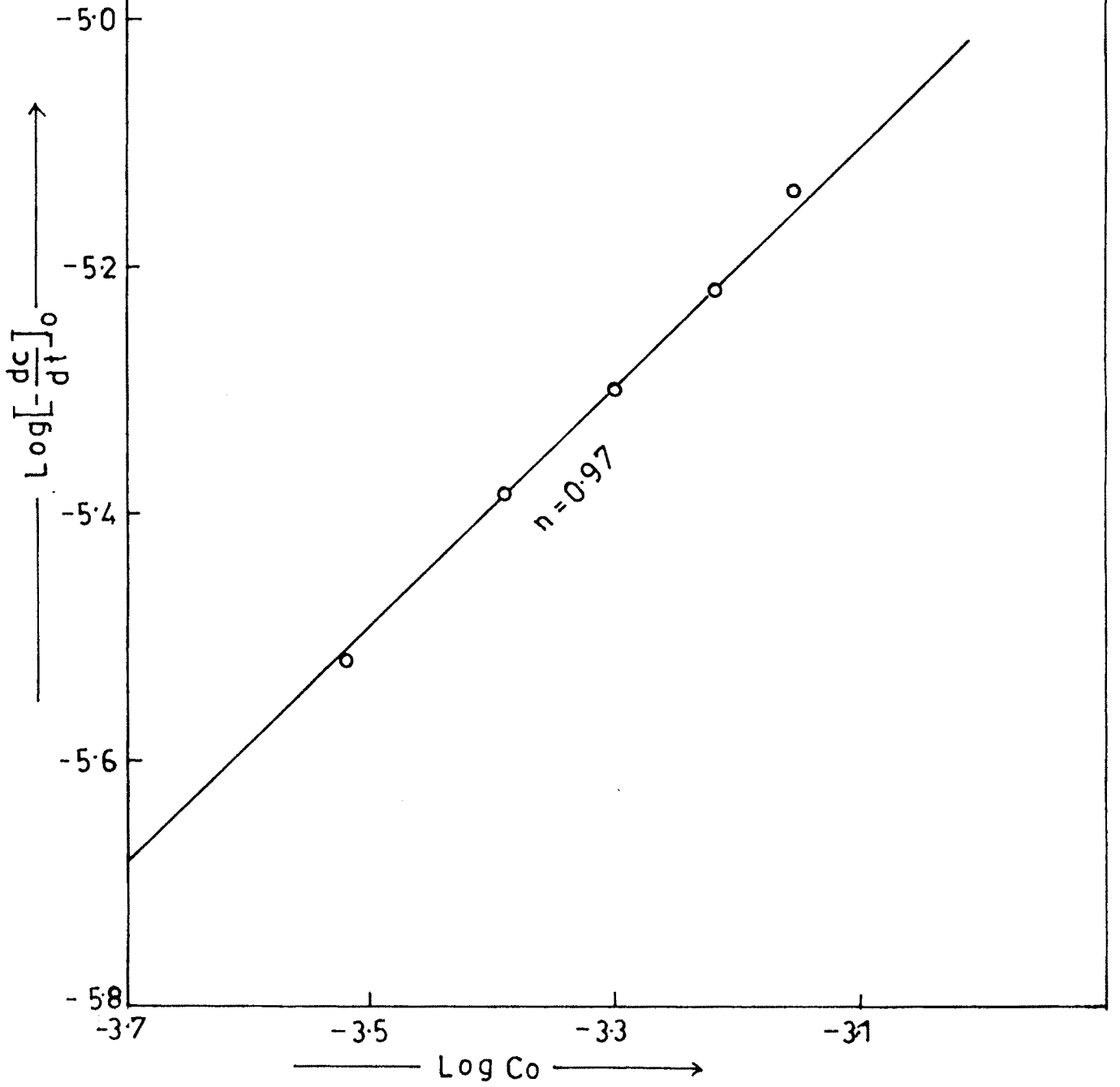


FIG:A-3 —EFFECT OF n-BAH CONCENTRATION

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{TEMP} = 40^\circ\text{C}$$

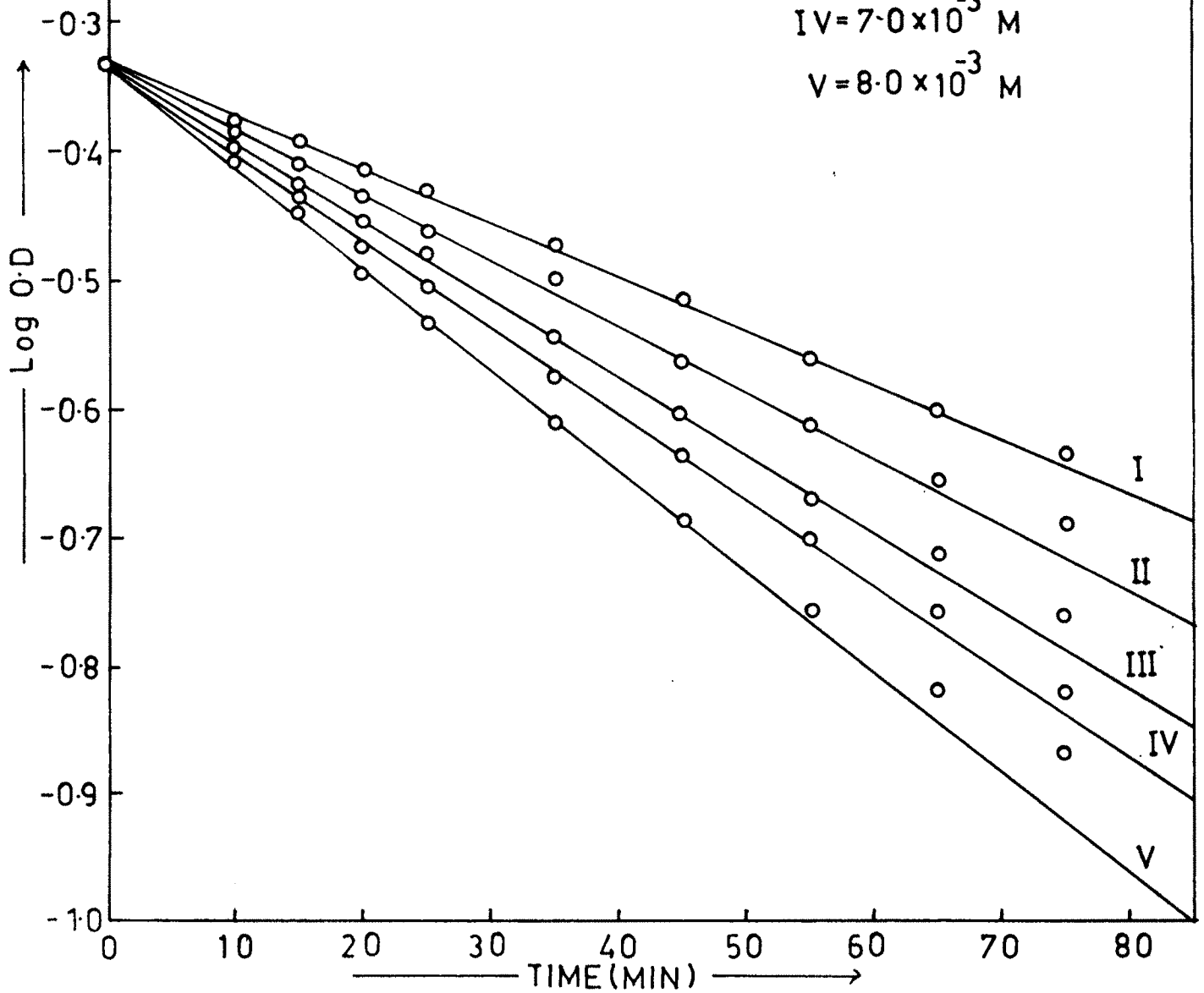
$$[\text{n-BAH}] - \text{I} = 4.0 \times 10^{-3} \text{ M}$$

$$\text{II} = 5.0 \times 10^{-3} \text{ M}$$

$$\text{III} = 6.0 \times 10^{-3} \text{ M}$$

$$\text{IV} = 7.0 \times 10^{-3} \text{ M}$$

$$\text{V} = 8.0 \times 10^{-3} \text{ M}$$



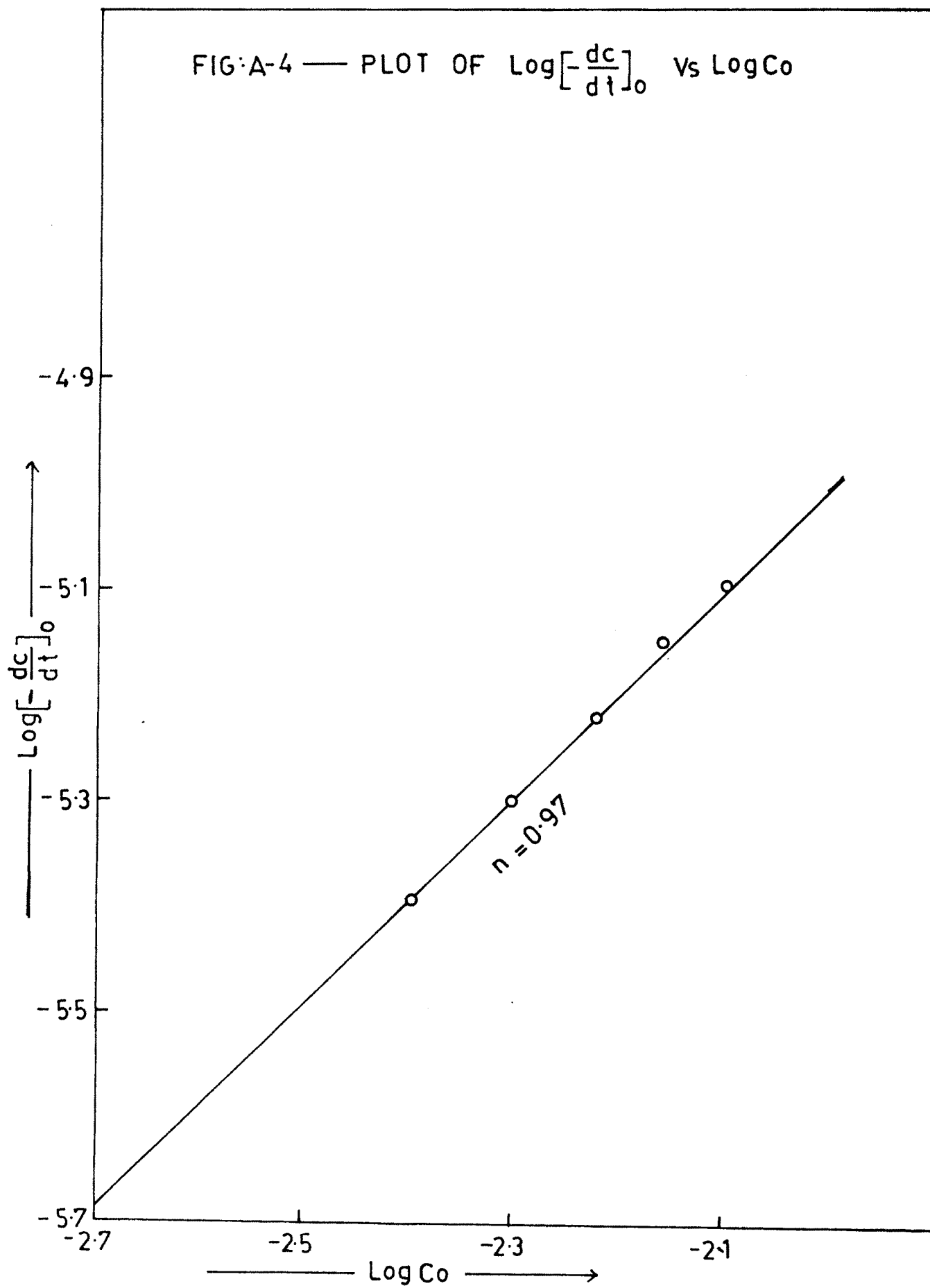


FIG:A-5 — EFFECT OF TEMPERATURE

$$[\text{HCF(III)}] = 50 \times 10^{-4} \text{ M}$$

$$[\text{n-BAH}] = 50 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 50 \times 10^{-4} \text{ M}$$

TEMP-I = 30°C

II = 35°C

III = 40°C

IV = 45°C

V = 50°C

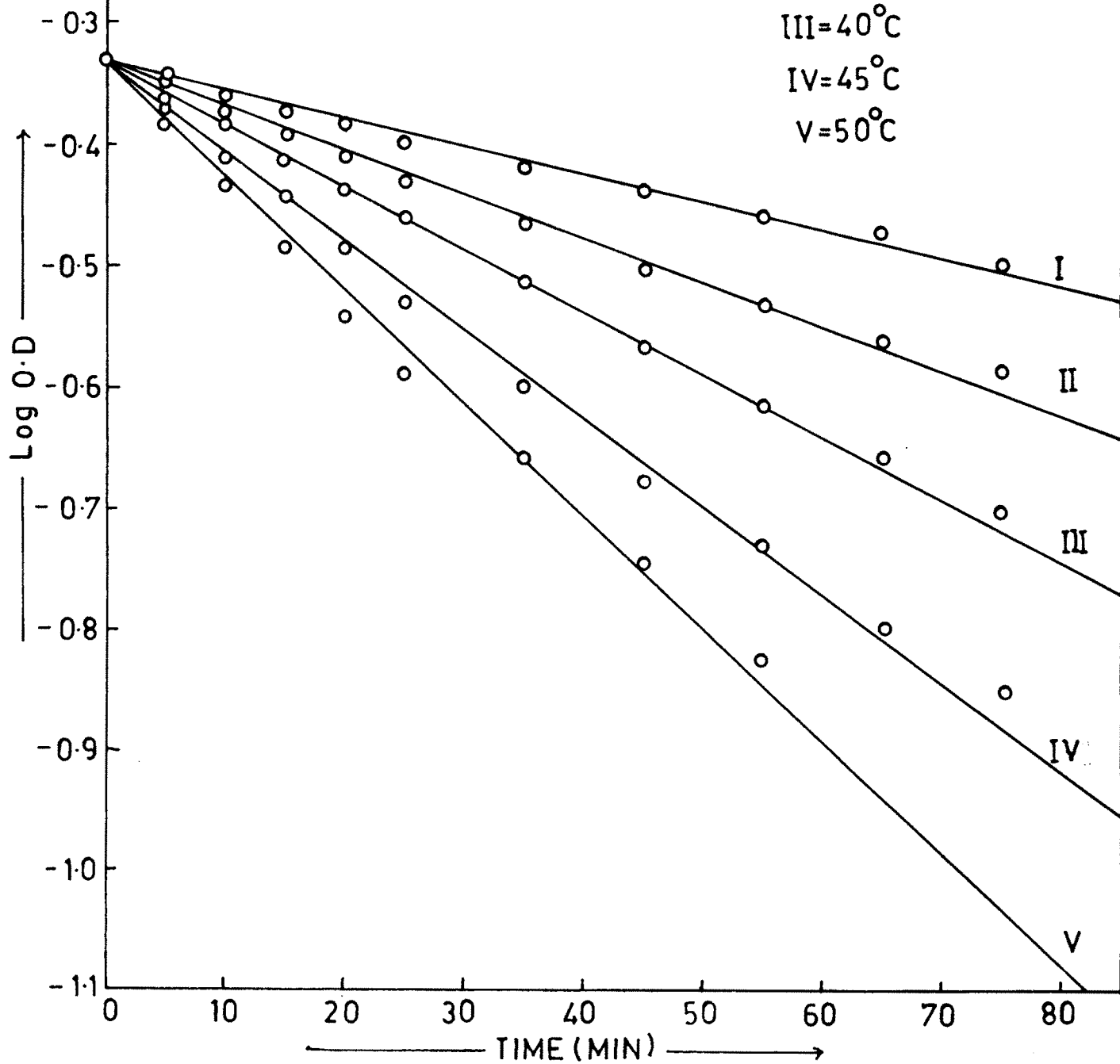




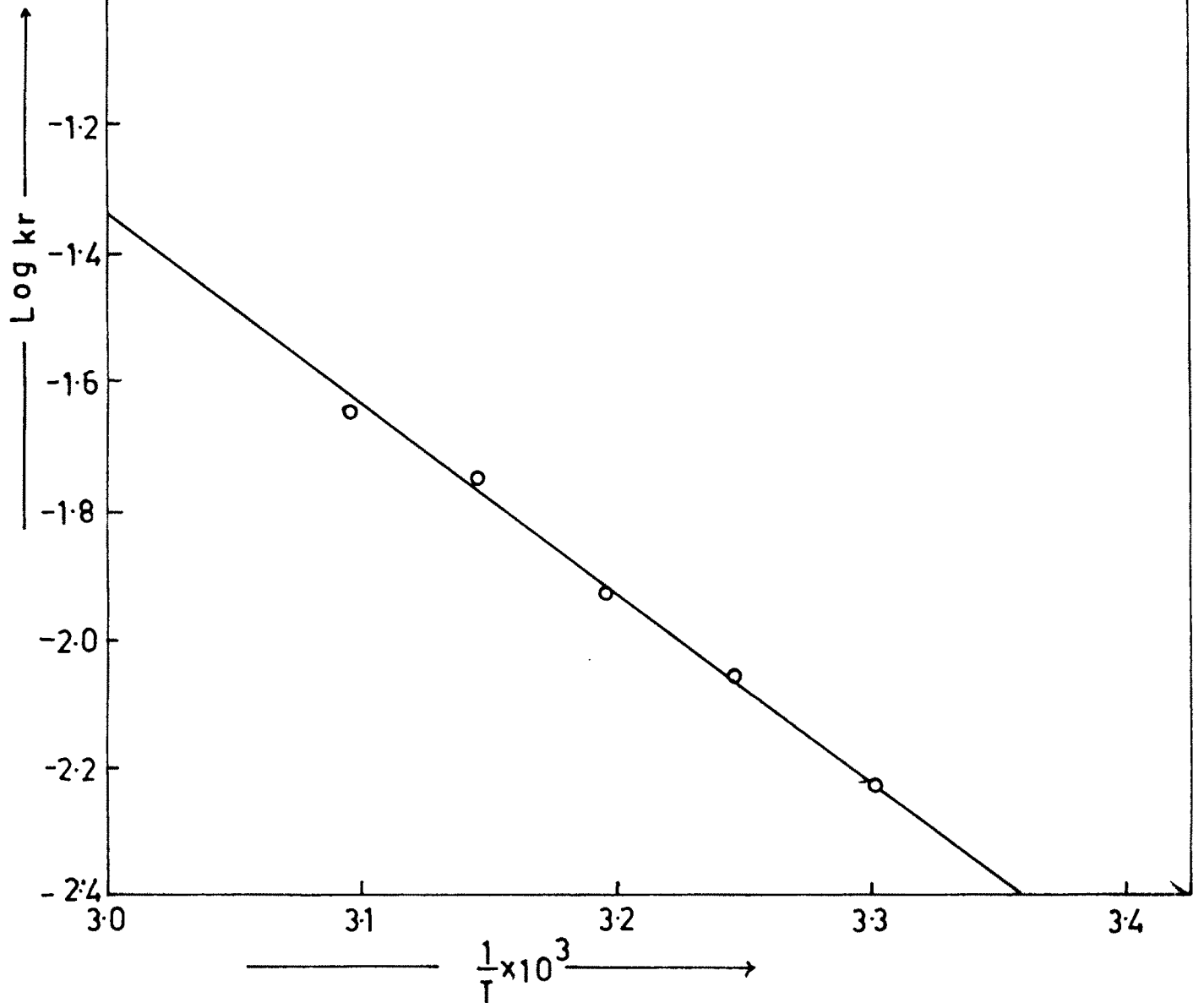
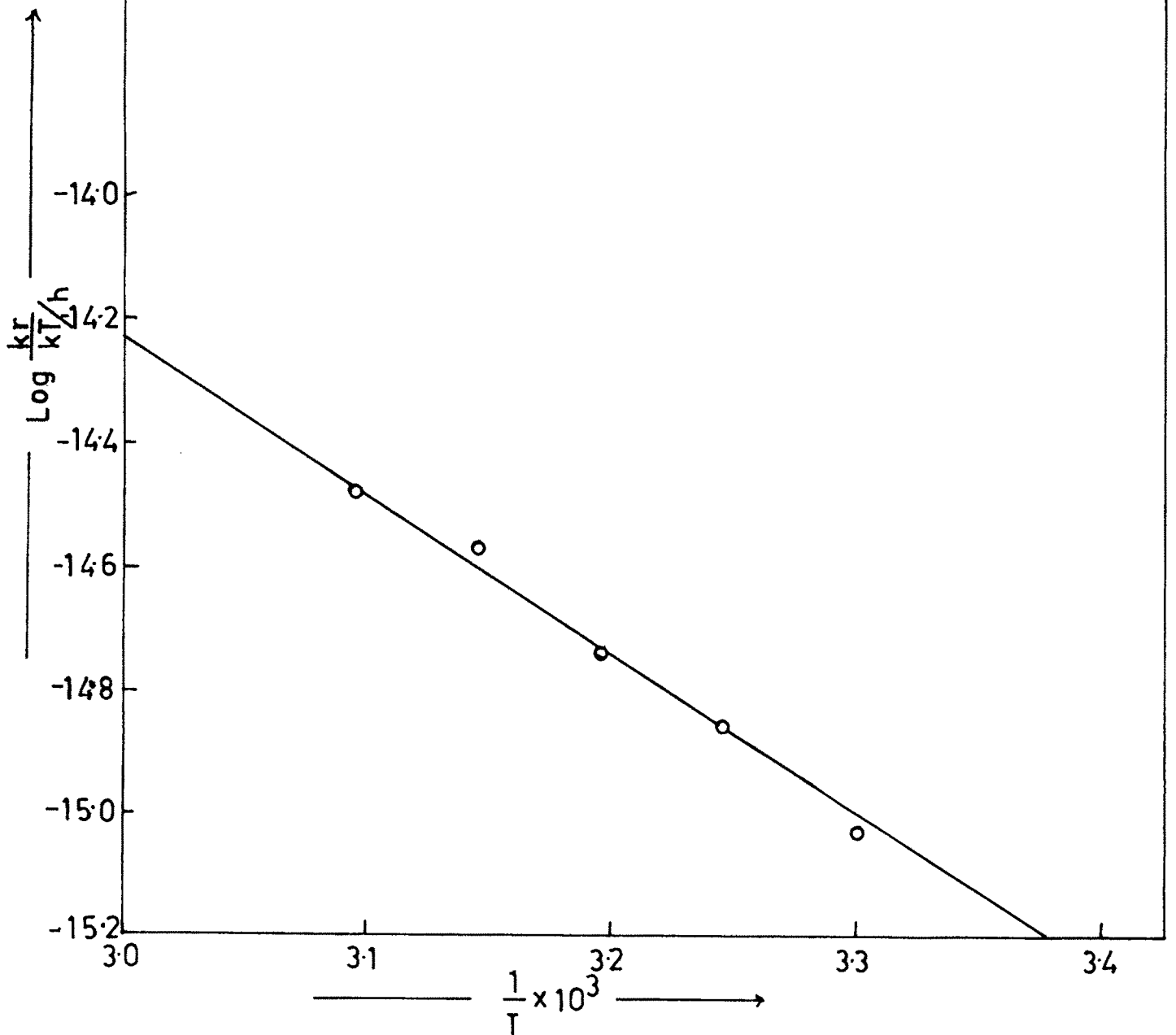
FIG:A-6 — PLOT OF  $\text{Log } kr$  Vs  $\frac{1}{T}$ 

FIG:A-7 — PLOT OF  $\text{Log } \frac{kr}{kT/h}$  Vs  $\frac{1}{T}$ 

CHAPTER - III SECTION - B  
KINETICS OF OXIDATION OF  
iso-BUTYRIC ACID HYDRAZIDE

## SECTION-B

3.2 KINETICS OF OXIDATION OF iso-BUTYRIC ACID HYDRAZIDE [Iso-BAH]:

Preliminary experiments were performed in order to decide the suitable temperature and concentration range of the reactants. It was observed that the reaction proceeds with measurable velocity at 40°C and at a concentration of iso-butyric acid hydrazide of  $5.0 \times 10^{-3}M$ , that of hexacyanoferrate(III)  $5.0 \times 10^{-4}M$ , sodium hydroxide  $5.0 \times 10^{-4}M$  and potassium chloride  $5.0 \times 10^{-4}M$ . In this experiment the hydrazide concentration is in excess over that of hexacyanoferrate (III) concentration.

EFFECT OF HEXACYANOFERRATE(III) CONCENTRATION :

In order to investigate the effect of concentration of hexacyanoferrate(III) on the reaction, the kinetic runs were performed in which concentration of the Hexacyanoferrate(III) was varied, whereas that of hydrazide and NaOH concentrations were kept constant. Using these experimental data, the value of k was determined. Table B-1 embodied the results of these kinetic runs, and the first order rate constant has been obtained from the initial slope of the curves shown in Fig. B-1, as well as calculated at different times by integration method, which are in good agreement with each other.

A perusal of the data shows that when the hydrazide concentration is in excess, the pseudo first order specific rate increases with increase in hexacyanoferrate concentration, indicating that the rate of disappearance of hexacyanoferrate(III) obeys the first order kinetics.

TABLE B - 1

$$[\text{iso-BAH}] = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp} = 40^\circ\text{C}$$

$$\lambda_{\text{max}} = 420 \text{ nm}$$

[HCF(III)] M x 10 <sup>4</sup>	3.0	4.0	5.0	6.0	7.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.270	0.365	0.465	0.560	0.660
5	0.265	0.355	0.440	0.535	0.620
10	0.260	0.333	0.415	0.505	0.585
15	0.250	0.325	0.395	0.475	0.550
20	0.245	0.315	0.375	0.455	0.515
25	0.240	0.305	0.365	0.430	0.490
35	0.230	0.280	0.335	0.390	0.435
45	0.215	0.260	0.310	0.345	0.390
55	0.205	0.245	0.280	0.310	0.335
65	0.200	0.220	0.255	0.275	0.300
75	0.190	0.205	0.235	0.250	0.265
90	0.180	0.185	0.210	0.225	0.230
Mean <sub>min</sub> $\times 10^2$	0.46	0.67	1.00	1.05	1.21

To confirm the order of reaction w.r.t. hexacyanoferrate(III) the values of  $(-\frac{dA}{dt})$  were determined by plotting the optical density against time for different initial concentrations of oxidant. These values are tabulated in Table B-2.

TABLE B-2

[HCF(III)] M x 10 <sup>4</sup>	(-dc/dt) x 10 <sup>6</sup>	Log C <sub>o</sub>	Log (-dc/dt) <sub>o</sub>
3.0	3.0520	- 3.5229	- 5.515
4.0	4.0710	- 3.3979	- 5.390
5.0	5.0850	- 3.3010	- 5.294
6.0	6.1041	- 3.2218	- 5.214
7.0	7.1215	- 3.1549	- 5.147

TABLE B-3

[HCF(III)] M x 10 <sup>4</sup>	(-dc/dt) x 10 <sup>6</sup>	Order of reaction 'n'
3.0	3.0520	] ----- 1.00
4.0	4.071	
4.0	4.071	] ----- 0.99
5.0	5.085	
5.0	5.085	] ----- 1.00
6.0	6.1041	
6.0	6.1041	] ----- 1.00
7.0	7.1215	

The order w.r.t. hexacyanoferrate(III) has been determined from the plot of  $\text{Log} \left( -\frac{dc}{dt} \right)$  vs  $\text{log } C_0$ , tabulated in the Table B-3 and graphically represented in the Fig. B-2. The order comes out to be 1.0. This establishes the first order behaviour of the reaction w.r.t. hexacyanoferrate(III).

#### EFFECT OF HYDRAZIDE CONCENTRATION :

In order to study the effect of hydrazide concentration on the rate of oxidation of iso-butyric acid hydrazide, the hydrazide concentration was varied from  $4.0 \times 10^{-3}$  M to  $8.0 \times 10^{-3}$  M, keeping the concentrations of hexacyanoferrate(III) and NaOH constant. The results of these kinetic runs are recorded in Table B-4 and depicted graphically in Fig. B-3.

The results in the table B-4 show that the first order rate constant increases with increase in hydrazide concentration. The plots of  $\text{log O.D.}$  vs time (Fig. B-3) are found to be linear.

The second order rate constant  $k_2$ .

$$k_2 = \frac{k_1}{[\text{Hydrazide}]_0}$$

where  $k_2$  = second order rate constant, and

$k_1$  = first order rate constant

is found to be nearly constant (Table B-5), indicating the first order dependence of the rate on hydrazide concentration.

TABLE B - 4

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp} = 40^\circ\text{C}$$

[iso-BAH] M x 10 <sup>3</sup>	4.0	5.0	6.0	7.0	8.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.470	0.465	0.465	0.465	0.460
5	0.450	0.440	0.435	0.430	0.420
10	0.430	0.415	0.410	0.400	0.390
15	0.415	0.395	0.390	0.375	0.365
20	0.395	0.375	0.370	0.350	0.340
25	0.380	0.365	0.350	0.330	0.315
35	0.345	0.335	0.310	0.290	0.270
45	0.320	0.310	0.275	0.255	0.235
55	0.300	0.280	0.255	0.225	0.205
65	0.290	0.255	0.240	0.200	0.180
75	0.275	0.235	0.220	0.185	0.155
90	0.250	0.210	0.190	0.160	0.130
Mean <sub>1</sub> min	0.83	1.00	1.15	1.30	1.46



TABLE B-5

[iso-BAH] =M x 10 <sup>3</sup>	k <sub>1</sub> x 10 <sup>2</sup> min <sup>-1</sup>	k <sub>2</sub> min <sup>-1</sup> mole <sup>-1</sup>
4.0	0.83	2.07
5.0	1.00	2.00
6.0	1.15	1.91
7.0	1.30	1.86
8.0	1.46	1.83

The order w.r.t. iso-butyric acid hydrazide was also determined by Van't Hoff differential method. The values of  $(-\frac{dc}{dt})$  and initial concentration of hydrazide ( $C_o$ ) are given in the Table B-6, and these values are substituted in the Van't Hoff's equation i.e.

$$n = \frac{\log(-\frac{dC_{o1}}{dt}) - \log(\frac{dC_{o2}}{dt})}{\log C_{o1} - \log C_{o2}}$$

The order of reaction was calculated, which is found to be almost one.

The values of  $(-\frac{dc}{dt})$  for different initial concentrations of hydrazide and the values of 'n' calculated, thereby are recorded in Table B-6 and B-7 respectively.

In order to confirm the order of reaction with respect to iso-butyric acid hydrazide, from the plot of  $\log(-\frac{dc}{dt})$  vs  $\log C_o$  (represented in Fig. B-4), the value of the order with respect to

TABLE B-6

[iso-BAH] M x 10 <sup>3</sup>	(-dc/dt) x 10 <sup>6</sup>	Log C <sub>o</sub>	Log (-dc/dt) <sub>o</sub>
4.0	4.0682	- 2.3979	- 5.3906
5.0	5.0850	- 2.3010	- 5.2937
6.0	6.1021	- 2.2218	- 5.2145
7.0	7.1190	- 2.1549	- 5.1476
8.0	8.1362	- 2.0969	- 5.0896

TABLE B-7

[iso-BAH] M x 10 <sup>3</sup>	(-dc/dt) x 10 <sup>6</sup>	Order of reaction 'n'
4.0	4.0682	] --- 0.99
5.0	5.0850	
5.0	5.0850	] --- 1.00
6.0	6.1021	
6.0	6.1021	] --- 0.99
7.0	7.1190	
7.0	7.1190	] --- 1.00
8.0	8.1362	



iso-butyric acid hydrazide has been evaluated which comes out to be 0.96. This confirms the first order behaviour of the reaction with respect to iso-butyric acid hydrazide.

#### EFFECT OF SODIUM HYDROXIDE CONCENTRATION :

In order to investigate the effect of sodium hydroxide concentration on the oxidation of iso-butyric acid hydrazide, the concentration of NaOH was varied from  $2.0 \times 10^{-4} \text{M}$  to  $6.0 \times 10^{-4} \text{M}$  by keeping the concentrations of other reactants constant. The results of these kinetic runs are given in Table B-8.

The results contained in Table B-8 show that first order rate constant increases with increase in the initial concentration of alkali. The kinetics of oxidation of iso-butyric acid hydrazide is found to be alkali concentration dependence.

#### EFFECT OF TEMPERATURE :

To determine the temperature coefficient, energy of activation ( $E_a$ ), 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  $30^\circ\text{C}$  to  $50^\circ\text{C}$ . The results of these kinetic runs have been tabulated in Table B-9, and graphically represented in Fig. B-5.

It is seen from the above results that the specific rate has approximately doubled for  $10^\circ\text{C}$  rise in temperature. A plot of  $\log k$  vs  $\frac{1}{T}$  as shown in Fig. B-6, is found to be linear, showing that the reaction obeys the Arrhenius relationship. The value of energy

TABLE B - 8

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{iso-BAH}] = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp} = 40^\circ\text{C}$$

[NaOH] M x 10 <sup>4</sup>	2.0	3.0	4.0	5.0	6.0
Time in min.	0.D.	0.D.	0.D.	0.D.	0.D.
0	0.465	0.465	0.465	0.465	0.465
5	-	-	0.445	0.440	0.435
10	0.435	0.430	0.425	0.415	0.405
15	0.420	0.410	0.405	0.395	0.385
20	0.405	0.395	0.385	0.375	0.360
25	0.395	0.385	0.370	0.365	0.345
35	0.375	0.355	0.340	0.335	0.310
45	0.360	0.325	0.315	0.310	0.285
55	0.350	0.305	0.285	0.280	0.260
65	0.340	0.295	0.265	0.255	0.220
75	0.330	0.285	0.255	0.235	0.200
90	0.310	0.260	0.225	0.210	0.175
Mean <sub>min</sub> kx10 <sup>2</sup>	0.59	0.64	0.83	1.00	1.21

TABLE B - 9

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{iso-BAH}] = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{Cl}^-] = 5.0 \times 10^{-4} \text{ M}$$

Temperature	30°C	35°C	40°C	45°C	50°C
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.465	0.465	0.465	0.465	0.465
5	0.450	0.445	0.440	0.425	0.420
10	0.440	0.425	0.415	0.395	0.380
15	0.430	0.410	0.395	0.365	0.345
20	0.420	0.390	0.375	0.340	0.315
25	0.410	0.380	0.365	0.315	0.285
35	0.390	0.350	0.335	0.270	0.235
45	0.370	0.325	0.310	0.235	0.195
55	0.355	0.300	0.280	0.205	0.160
65	0.340	0.275	0.255	0.175	0.140
75	0.325	0.260	0.235	0.160	0.125
90	0.305	0.235	0.210	0.130	0.100
Mean <sub>1</sub> / min $\times 10^2$	0.52	0.81	1.00	1.49	1.77

of activation ( $E_a$ ) evaluated from the slope of this curve comes out to be 11.28 k cal mole<sup>-1</sup>.

TABLE B-10

Temp. T (k°)	$\frac{1}{T} \times 10^3$	$k_r \times 10^2$ min <sup>-1</sup>	Log $k_r$	Log $\frac{k_r}{kT/h}$
303	3.3003	0.5200	- 2.2839	- 15.0840
308	3.2467	0.8130	- 2.0899	- 14.8970
313	3.1948	1.0000	- 2.0000	- 14.8141
318	3.1446	1.4900	- 1.8268	- 14.6478
323	3.0959	1.7700	1.7520	- 14.5798

The Arrhenius equation has been used directly to calculate energy of activation, which comes out to be 11.86 k cal mole<sup>-1</sup>. On the basis of this calculated value, the frequency factor (A), free energy of activation ( $\Delta G^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ) have been calculated by the application of the following equations :

$$\begin{aligned} \text{i)} \quad k_r &= A e^{-E/RT} \\ \text{ii)} \quad k_r &= (kT/h) e^{-\Delta G^\ddagger / RT} \\ \text{iii)} \quad A &= e (kT/h) e^{\Delta S^\ddagger / R} \end{aligned}$$

Where equation (iii) is applicable to the reactions taking place in solutions. In the above equation " $k_r$ " is the specific rate,  $k$  is the Boltzmann constant,  $h$  is Plank's constant and 'e' is a constant (2.178) to be introduced in the equation. When the reaction takes place in solution, other symbols carry their usual meanings.

TABLE B-11

## THERMODYNAMIC - PARAMETERS

Temp. $T$ ( K° )	$k_r \times 10^2$	Temp. coeffi- cient per 10°C	$E_a$ k cal/mole <sup>-1</sup>		$\Delta H^\ddagger$ k cal/mole <sup>-1</sup>	$A \times 10^{-4}$ sec <sup>-1</sup>	$\Delta S^\ddagger$ e.U.	$\Delta G^\ddagger$ k cal/mole <sup>-1</sup>
			Graph	Calculated				
303	0.5200				Graph	1.189	- 39.87	24.773
308	0.8130	1.92		12.325		1.372	- 39.62	24.895
313	1.000		11.283		12.692	1.257	- 39.83	25.158
318	1.4900	1.83		11.791		1.408	- 39.64	25.297
323	1.7700	1.77		11.472		1.269	- 39.87	25.570
Mean		1.84	11.28	11.86	12.69	1.30	- 39.76	25.137

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

$$\text{iv) } k_r = \frac{kT}{h} e^{-\Delta G^\ddagger / RT}$$

equation (ii) can be expressed in terms of enthalpy changes as

$$k_r = \left[ \frac{kT}{h} \right] e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R}$$

OR

$$\log \frac{k_r}{kT/h} = \frac{-\Delta H^\ddagger}{2.303 RT} + \frac{\Delta S^\ddagger}{2.303 R}$$

The values of  $\log \left[ \frac{k_r}{kT/h} \right]$  have been plotted against  $\frac{1}{T}$  in Fig. B-7 from the slope of which the enthalpy change for the formation of activated complex ( $\Delta H^\ddagger$ ) has been calculated. The value of the  $\Delta H^\ddagger$  [ $12.69 \text{ k cal/mole}^{-1}$ ] obtained from the graph has been used to calculate  $\Delta S^\ddagger$  from above equation. The various energy parameters obtained, have been recorded in Table B-11.

A large negative value of entropy of activation is indicative of the formation of an activated complex involving two oppositely charged ions.

#### EFFECT OF CHLORIDE ION CONCENTRATION :

To study the effect of addition of chloride ion on the rate of oxidation of hydrazide, the concentration of potassium chloride was varied from 0.0 M to  $6.0 \times 10^{-4}$  M, keeping all the other concentrations constant. An examination of the results contained in the Table B-12 shows that the increase in chloride ion concentration increases the specific rate slightly.



TABLE B - 12

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{iso-BAH}] = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp.} = 40^\circ\text{C}$$

[KCl]= Mx10 <sup>4</sup>	0.0	2.0	4.0	6.00
Time in min.	O.D.	O.D.	O.D.	O.D.
0	0.465	0.465	0.465	0.465
5	0.440	0.435	0.430	0.425
10	0.415	0.410	0.405	0.400
15	0.395	0.390	0.385	0.380
20	0.375	0.370	0.365	0.360
25	0.365	0.350	0.345	0.340
35	0.335	0.330	0.325	0.315
45	0.310	0.300	0.295	0.290
55	0.280	0.275	0.270	0.265
65	0.255	0.250	0.245	0.240
75	0.235	0.230	0.225	0.220
90	0.210	0.200	0.195	0.195
Mean <sub>min</sub> <sup>-1</sup> kx10 <sup>2</sup>	1.00	1.03	1.16	1.23

TABLE B - 13

$$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$$

$$[\text{iso-BAH}] = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 5.0 \times 10^{-4} \text{ M}$$

$$\text{Temp.} = 40^\circ\text{C}$$

Ethanol % (v/v)	0.0	10.0	20.0	30.00
Time in min.	O.D.	O.D.	O.D.	O.D.
0	0.465	0.465	0.465	0.465
5	0.440	0.435	0.430	0.425
10	0.415	0.410	0.405	0.400
15	0.395	0.380	0.375	0.365
20	0.375	0.365	0.355	0.345
25	0.365	0.355	0.340	0.330
35	0.355	0.325	0.315	0.305
45	0.310	0.290	0.285	0.270
55	0.280	0.275	0.270	0.265
65	0.255	0.250	0.245	0.240
75	0.235	0.230	0.220	0.215
90	0.210	0.200	0.100	0.185
Mean <sub>min</sub> <sup>-1</sup> kx10 <sup>2</sup>	1.00	1.06	1.20	1.33

EFFECT OF DIELECTRIC CONSTANT OF MEDIUM :

To investigate the effect of change in dielectric constant of the medium on the rate of oxidation of hydrazide, the percentage (v/v) of ethanol is varied from 0.0 to 30.0% keeping all other concentrations unchanged. The results are recorded in Table B-13.

It is observed from the Table B-13 that the rate of oxidation of hydrazide was found to be increased with increase dielectric constant of the medium. The values of dielectric constant (D) recorded in Table B-14 were obtained from investigation of GOSTA-AKEROLF<sup>1</sup>.

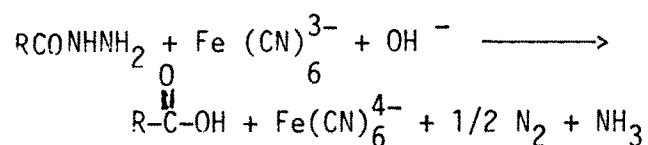
TABLE B-14

Ethanol % (v/v)	Dielectric constant(D)	$k \times 10^{-2}$ $\text{min}^{-1}$	$\frac{10^2}{D}$	$2 + \log k$
0.0	73.12	1.00	1.367	2.000
10.0	67.86	1.06	1.473	2.0253
20.0	62.41	1.20	1.602	2.0791
30.0	56.73	1.33	1.763	2.1238

Results recorded in the above table clearly show that, decrease in dielectric constant increases the specific rate of the reaction which may be due to the fact that, the rate determining step may have involved between the ions of similar charges.

STOICHIOMETRY

The ratio of hexacyanoferrate(III) to hydrazide was varied in presence of sodium hydroxide and equilibrated at 40°C. The different sets of reaction mixtures containing known excess of hexacyanoferrate(III) over hydrazides were kept in presence of the  $5.0 \times 10^{-4}$  M sodium hydroxide for 40 hours. The amount of HCF(III) concentration left in all cases were consistent with a stoichiometric equation



It was found that one mole of the oxidant required to oxidise one mole of substrate completely. The stoichiometry was found to be 1:1 which can be represented as above.

PRODUCT ANALYSIS :

The knowledge of 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 considered necessary to identify the products formed in the reaction.

The existence of an intermediate may be deduced from the nature of the product. Identification of the intermediate is one of the important goals of mechanistic investigation. Detection of n-butyric and iso-butyric acids were carried by thin layer chromatographic (TLC) method.

Ethanol water mixture was used as a solvent and chromatographic plate was placed in iodine chamber. The oxidation products obtained were identified by TLC with the authentic samples.

- i) R.F. value for n-butyric acid - hydrazide = 0.422
- ii) R.F. value for iso-butyric acid - hydrazide = 0.416
- iii) Nitrogen is detected by lime test<sup>2</sup>
- iv) Free radicals are detected by addition of acrylonitrile<sup>3</sup>.
- v) Ammonia is detected by Nessler's reagent.

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Elsevier Publishing Co. New York, 2nd Ed. (1972).
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FIG:B-1 — EFFECT OF HCF(III) CONCENTRATION

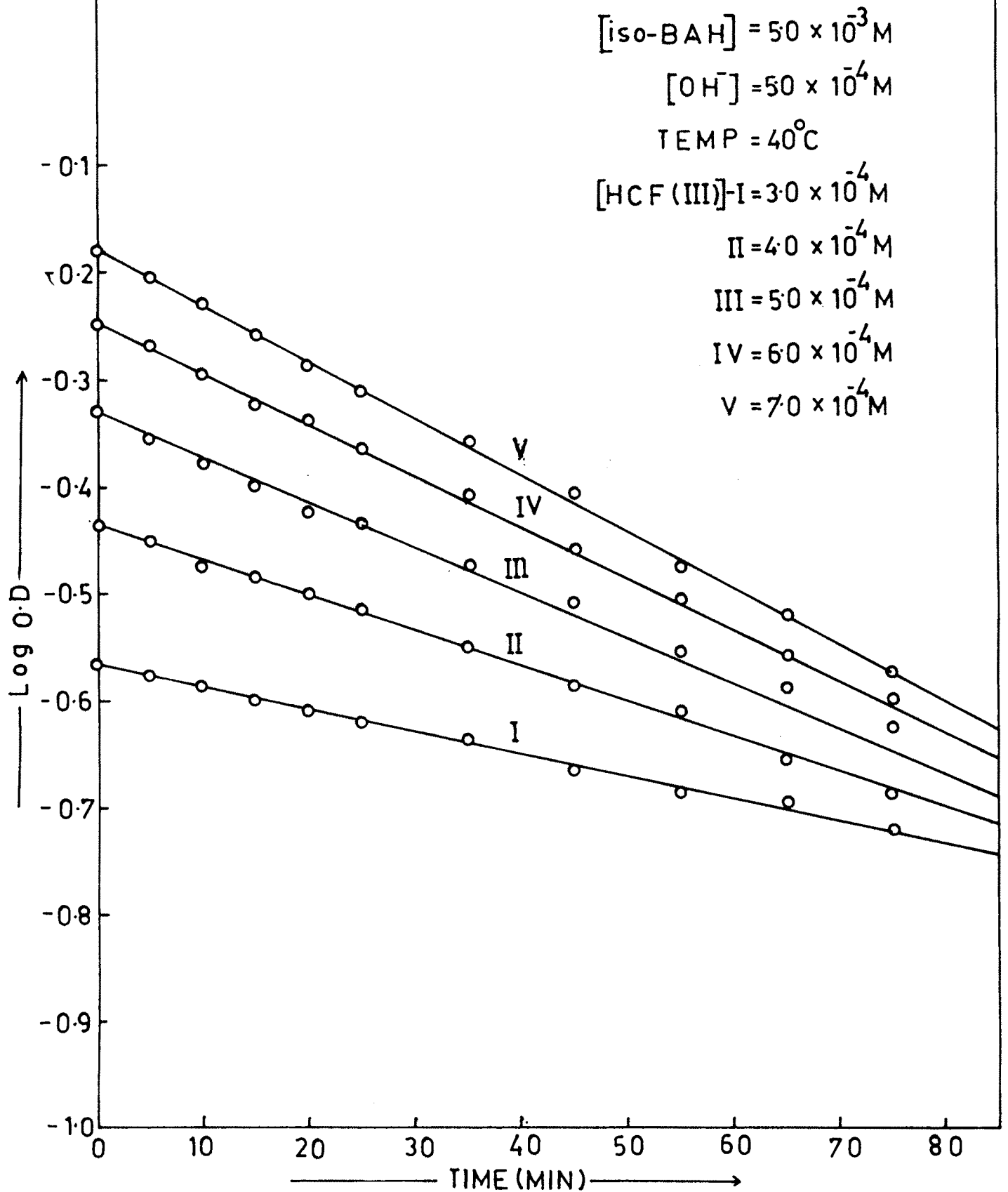


FIG:B-2 — PLOT OF  $\text{Log}[-\frac{dc}{dt}]_0$  Vs  $\text{Log } C_0$

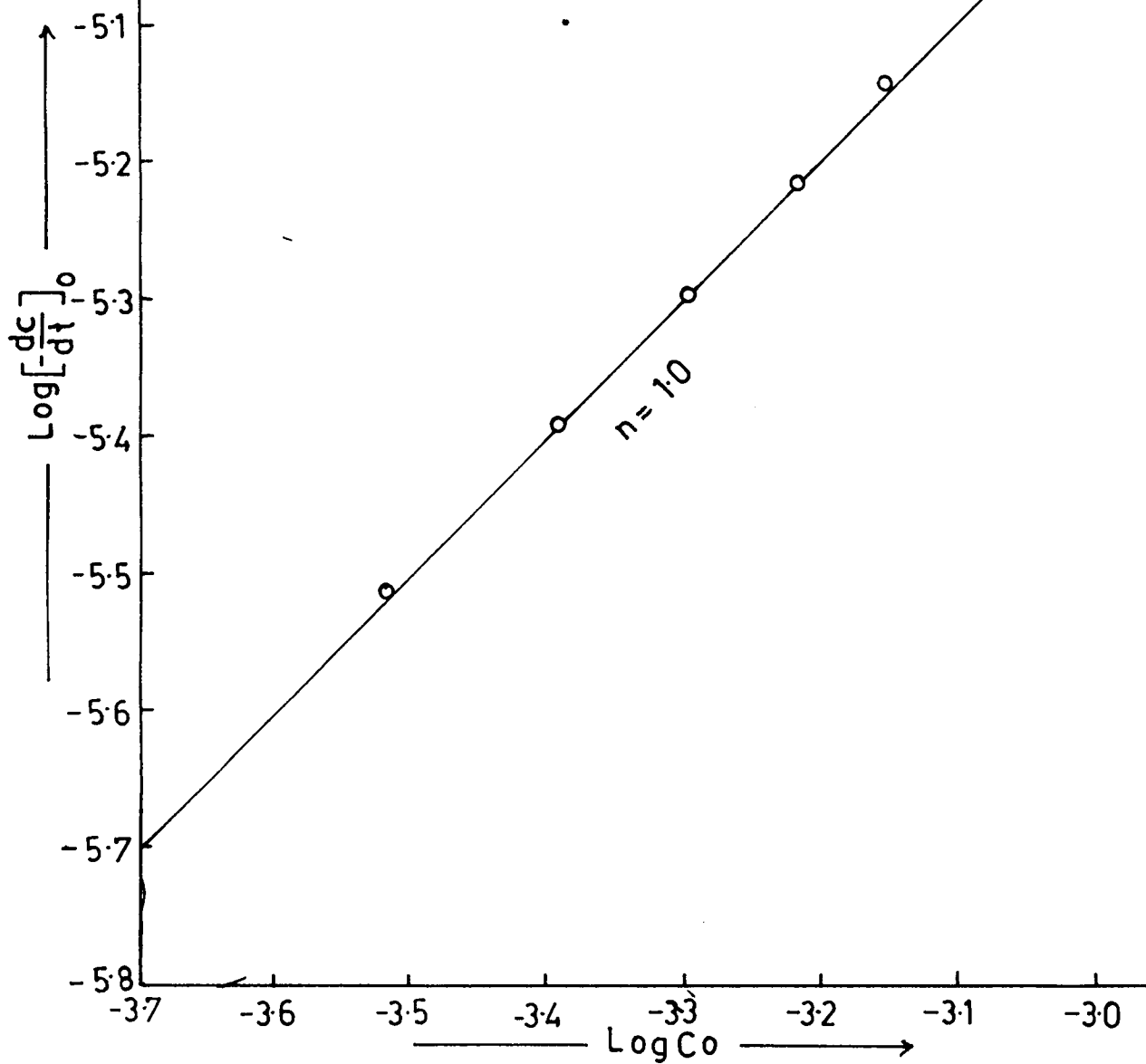




FIG:B-3 — EFFECT OF iso-BAH CONCENTRATION

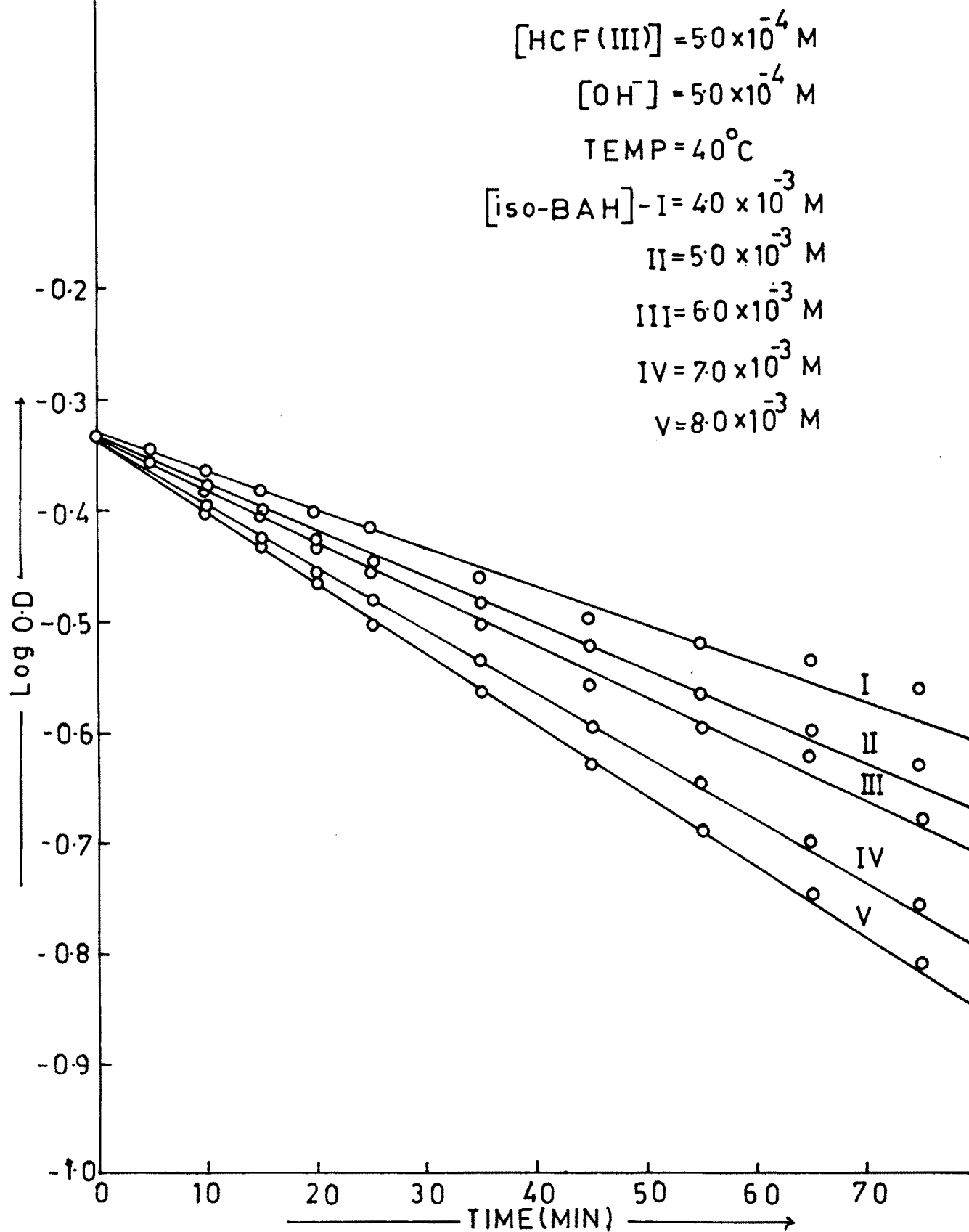


FIG:B-4 — PLOT OF  $\text{Log}\left[-\frac{dc}{dt}\right]_0$  Vs  $\text{Log } C_0$

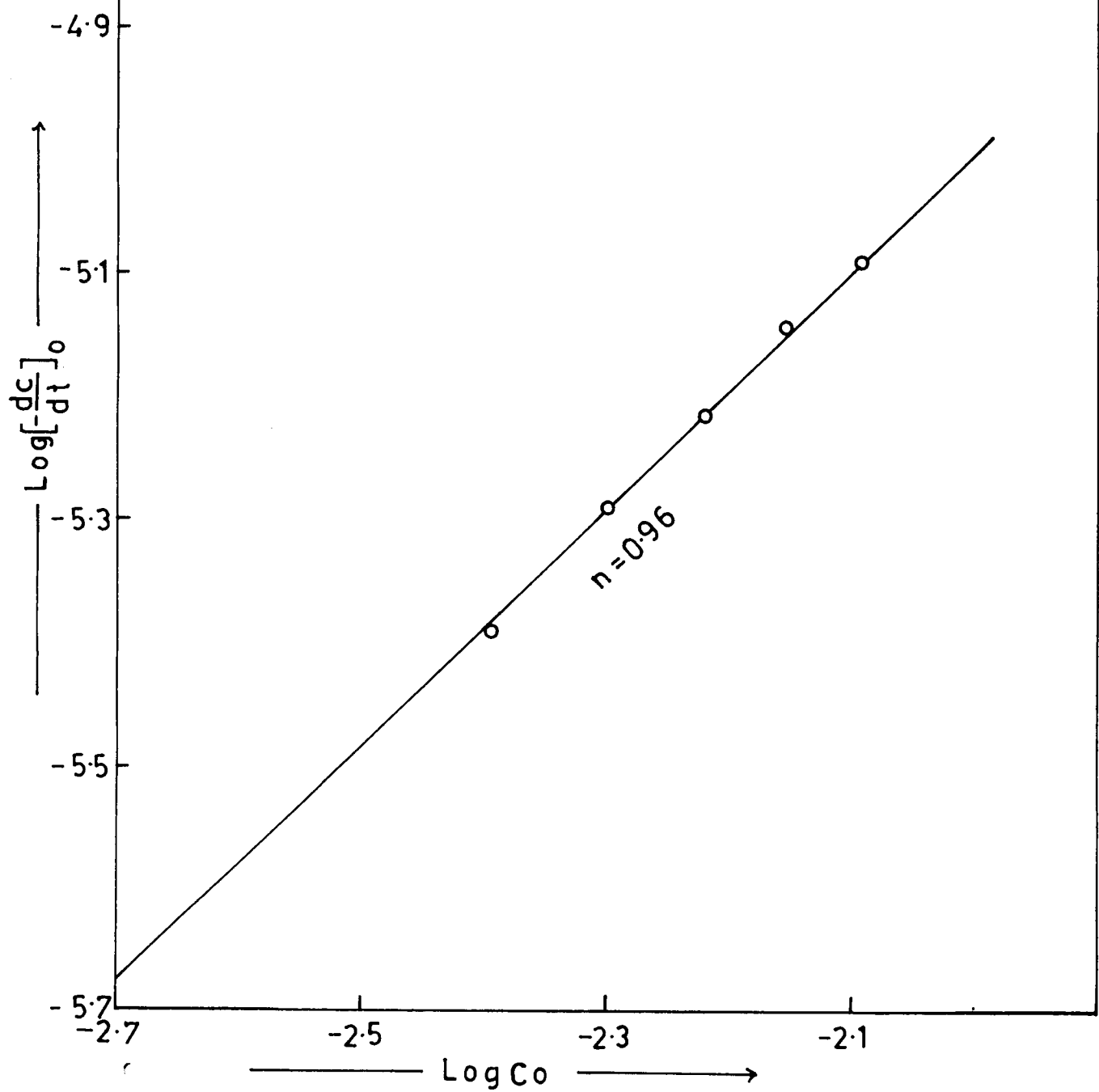


FIG: B-5 — EFFECT OF TEMPERATURE

$[HCF(III)] = 5.0 \times 10^{-4} M$

$[iso-BAH] = 5.0 \times 10^{-3} M$

$[OH^-] = 5.0 \times 10^{-4} M$

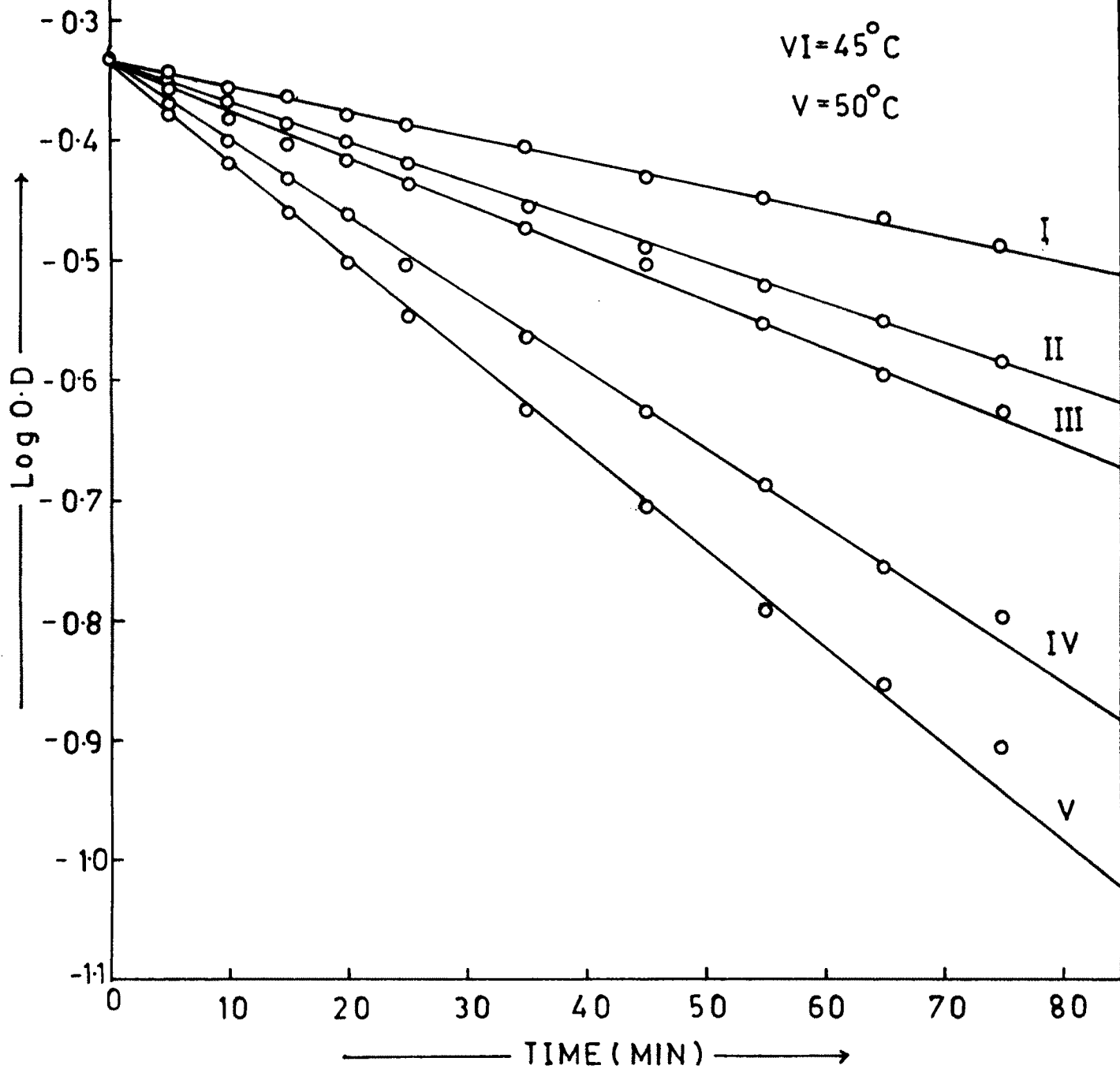
[TEMP] = I = 30°C

II = 35°C

III = 40°C

VI = 45°C

V = 50°C



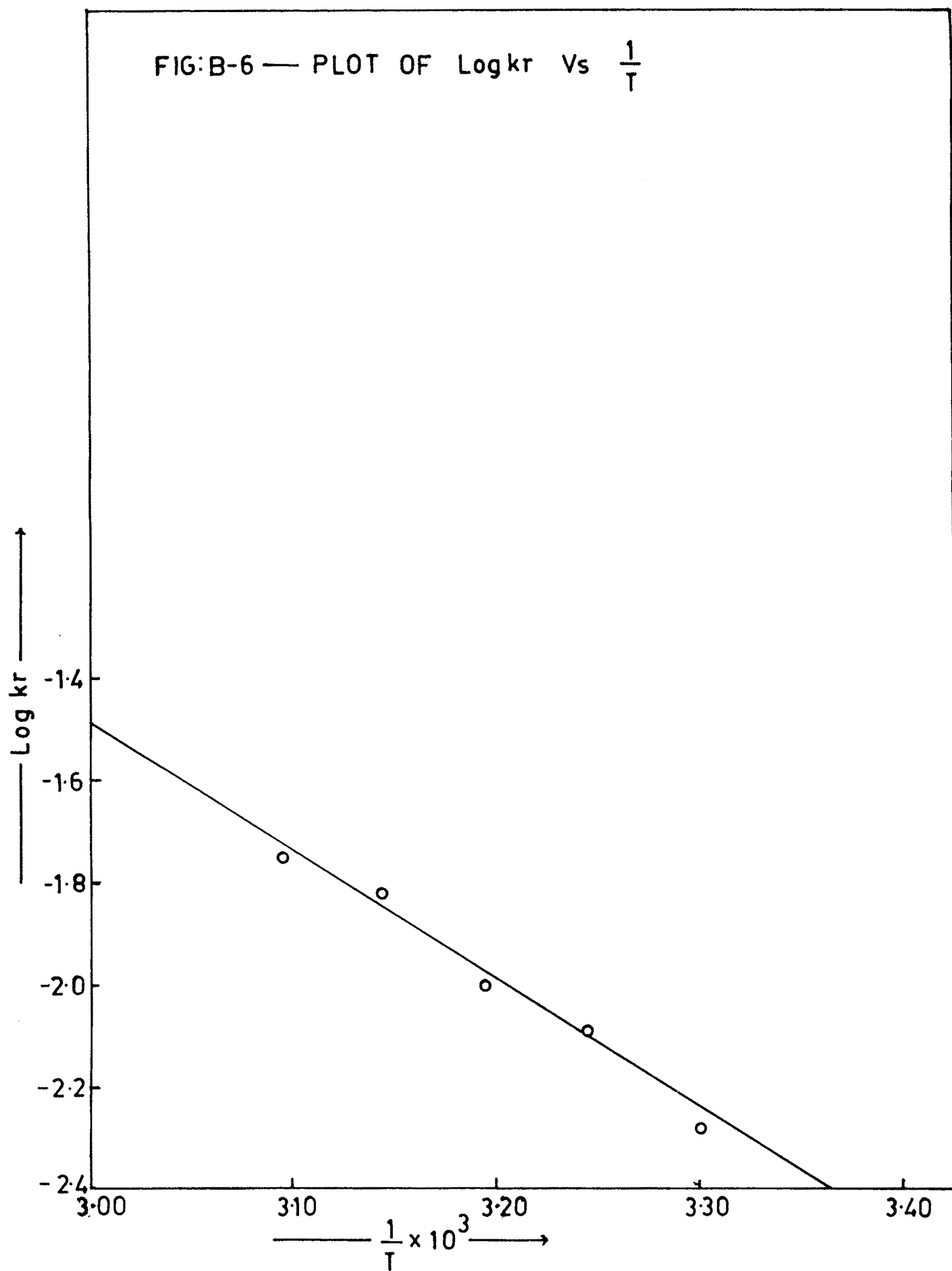


FIG: B-7 — PLOT OF  $\text{Log } \frac{kr}{kT/h}$  Vs  $\frac{1}{T}$

