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## **CHAPTER - I I I**

### **RESULTS**

**SECTION A :**

**Kinetic study of oxidation of o-Cl BAH**

**SECTION B :**

**Kinetic study of oxidation of p-Cl BAH**

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CHAPTER - IIIRESULTSKINETICS OF OXIDATION OF o-CHLORO AND  
p-CHLORO BENZOIC ACID HYDRAZIDES

This chapter deals with the detail kinetic study of oxidation of o-chloro and p-chloro benzoic acid hydrazides by alkaline hexacyanoferrate(III) in water-dioxane mixture (50% v/v).

To study the oxidation of hydrazide, the reaction mixture was prepared by using the requisite concentrations of hexacyanoferrate(III), hydrazide and NaOH. The progress of reaction was followed by measuring the optical density (O.D.) of unreacted hexacyanoferrate(III) at 420 nm spectrophotometrically as a function of time.

Experiments were set to include the following studies :

1. Overall order of reaction and order w.r.t. reactants.
2. Effect of hexacyanoferrate(III) concentration on the rate of 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 ionic strength.
7. Effect of dielectric constant of the medium.
8. End product analysis and free radical tests.

SECTION - A

KINETICS OF OXIDATION OF o-CHLORO BENZOIC ACID HYDRAZIDE

Standard Kinetic Run :

In the beginning, preliminary experiments were carried to decide suitable concentrations of substrate, oxidant and alkali, composition of water-dioxane mixture and temperature. It was found that in dioxane-water mixture (50% v/v) at 50°C and in the presence of  $5.0 \times 10^{-4}$  M hexacyanoferrate(III),  $5.0 \times 10^{-3}$  M hydrazide and  $1.0 \times 10^{-3}$  M NaOH reaction proceeds with measurable velocity.

The kinetic data of this standard run is given in the Table 3:A: 1.

TABLE 3:A: 1

$[\text{o-Cl-BAH}] = 5.0 \times 10^{-3} \text{M}$ 
 $[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{M}$   
 $[\bar{\text{O}}\text{H}] = 1.0 \times 10^{-3} \text{M}$ 
 $\lambda_{\text{max}} = 420 \text{ nm}$ 
Temp.  $50^{\circ}\text{C}$

Time in min	O.D.	$k \times 10^2 \text{ min}^{-1}$
0	0.480	-
5	0.445	1.51
10	0.415	1.46
15	0.390	1.38
20	0.365	1.36
30	0.320	1.35
40	0.285	1.30
50	0.255	1.26
60	0.230	1.22
80	0.180	1.22
100	0.150	1.16
Mean k	-	$1.32 \times 10^{-2} \text{ min}^{-1}$
k	by graphical method	$1.36 \times 10^{-2} \text{ min}^{-1}$

In this oxidation, the concentration of hydrazide is ten times greater than the concentration of hexacyanoferrate(III) hence it can be stated that the reaction is studied under pseudo first order condition.

The observed rate constant (k) of the reaction was evaluated by integration and graphical methods.

Integration method :

In this method the value of k at different intervals of time(t) was calculated by using the equation<sup>1</sup> for first order reaction

$$k = \frac{2.303}{t} \log \frac{D_o}{D_t}$$

where,

$D_o$  = optical density of hexacyanoferrate  
at time zero

$D_t$  = optical density of hexacyanoferrate  
at time 't'

Graphical Method :

The value of k is obtained from the slope of plot of log O.D. against time [Fig.3.A.1] by using the relation,

$$k = 2.303 \times \text{slope}$$

The results in the table 3:A:1 show that, the equation for first order reaction is quite valid as the values of k at different intervals of time calculated by using the same equation are almost constant. Again, the plot of log O.D. Vs time is linear with characteristic negative slope. This fact shows that the reaction follows first order

kinetics under the experimental conditions.

It has been observed that the pseudo first order rate constant goes on decreasing slightly with time. This shows that either the reaction follows an order greater than one or reaction may attend inhibition during the course of reaction. .

It is important to note that, the decrease in value of  $k$  is not in a particular region of reaction but it is gradual, i.e. first order rate constant of the reaction decreases with increase in time. Such a gradual decrease in first order rate constant with increase in time was observed by Patil and Patil<sup>2</sup> in silver catalysed oxidation of aliphatic acid hydrazides by peroxydisulphate ion. The authors suggested that, the slight decrease in rate constant with increase in time may be due to some inhibition as reaction progresses. Similar type of observation was observed by Hongekar and Patil.<sup>3</sup> Singh et al.<sup>4</sup> also observed similar gradual decrease in zero order rate constant with increase in time in oxidation of reducing sugars by alkaline hexacyanoferrate(III) and they attributed it to the gradual decrease in pH as the reaction progresses.

#### EFFECT OF HEXACYANOFERRATE(III) CONCENTRATION

In order to study the dependence of initial rate and also to determine the order w.r.t. hexacyanoferrate(III), the

reaction was performed by taking five different initial concentrations of hexacyanoferrate(III), keeping the concentrations of alkali and hydrazide constant.

The kinetic data of experiments is recorded in the Table 3:A:2. The value of first order rate constant  $k$  has been determined at different time intervals by integration method.

TABLE 3:A:2

[o-Cl BAH] = $5.0 \times 10^{-3} \text{M}$ Temp = $50^\circ \text{C}$		[OH] = $1.0 \times 10^{-3} \text{M}$ $\lambda_{\text{max}} = 420 \text{ nm}$			
[HCF(III)] $\text{M} \times 10^4$	3.0	4.0	5.0	6.0	7.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.280	0.390	0.480	0.590	0.680
5	0.260	0.360	0.445	0.545	0.625
10	0.240	0.335	0.415	0.505	0.580
15	0.225	0.315	0.390	0.470	0.540
20	0.210	0.295	0.365	0.440	0.510
30	0.185	0.260	0.320	0.385	0.450
40	0.165	0.230	0.285	0.335	0.400
50	0.145	0.205	0.255	0.295	0.355
60	0.130	0.185	0.230	0.260	0.315
80	0.105	0.145	0.180	0.200	0.265
100	0.085	0.115	0.150	0.160	0.215
Mean $k \times 10^2$ $\text{min}^{-1}$	1.37	1.36	1.32	1.43	1.38

From the data in Table 3:A:2 it is clear that, oxidation of hydrazide at different initial concentrations of hexacyanoferrate(III) follows first order kinetics because -

- (i) The values of  $k$  at different intervals of time calculated by using integrated equation of first order reaction are almost constant in any individual kinetic run.
- (ii) The plot of  $\log O.D.$  versus time in each kinetic run is linear with negative slope and intercept on  $\log O.D.$  axis.

The results in Table 3:A:2 indicate the constancy of mean  $k$  values at different  $[\text{Fe}(\text{CN})_6^{3-}]_0$ . Hence it can be inferred that the observed rate constant of the reaction under investigation is insensitive to initial concentration of hexacyanoferrate(III).

Kinetic data from Table 3:A:2 has been represented by plotting  $\log O.D.$  against time [Fig.3:A:1].

Determination of order of reaction with respect to hexacyanoferrate(III) :

The order of reaction 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.



By using van't Hoff differential method the order of reaction w.r.t. hexacyanoferrate(III) was determined. The initial rates were calculated by plotting O.D. versus time. Smooth curves were obtained for the plot of O.D. versus time. The tangent was drawn at the beginning of each curve and initial rate of each reaction was calculated from initial slope of the tangent using the relation

$$\left(-\frac{d_c}{d_t}\right)_0 = \frac{\left(-\frac{d_A}{d_t}\right)_0}{\epsilon}$$

where,

$\left(-\frac{d_c}{d_t}\right)_0$  = Initial rate of the reaction which gives decrease in concentration of hexacyanoferrate(III) per unit time.

$\left(-\frac{d_A}{d_t}\right)_0$  = Initial slope of tangent which gives decrease in absorbance per unit time.

$\epsilon$  = Molar extinction coefficient of  $K_3Fe(CN)_6$   
= 987 litres mole<sup>-1</sup>cm<sup>-1</sup>

The initial rates of reaction at different initial concentrations of hexacyanoferrate(III) are recorded in Table 3:A:3.

TABLE 3:A:3

$[\text{HCF(III)}]_0 \text{ M} \times 10^4$	$(-d_c/d_t)_0 \times 10^6 \text{ M min}^{-1}$
3.0	3.80
4.0	5.07
5.0	6.33
6.0	7.60
7.0	8.75

An examination of results in the above table shows that the initial rate of reaction depends on the initial concentration of hexacyanoferrate(III) and it increases with increase in concentration of HCF(III).

By using the data from Table 3:A:3, the order of reaction (n) w.r.t. hexacyanoferrate(III) was calculated with the help of van't Hoff equation<sup>5</sup> -

$$n = \frac{\log(-d_c/d_t)_{01} - \log(-d_c/d_t)_{02}}{\log C_1 - \log C_2}$$

The values of  $(-d_c/d_t)_0$  corresponding to the different initial concentrations of hexacyanoferrate(III) and values of 'n' calculated thereby are recorded in Table 3:A:4. The value of 'n' was found to be nearly one.

TABLE 3:A:4

$[\text{HCF(III)}]_0 \text{ M} \times 10^4$	$(-d_c/d_t)_0 \times 10^6 \text{ M min}^{-1}$	Order of reaction(n)
3.0	3.80	0.98
4.0	5.07	
4.0	5.07	1.00
5.0	6.33	
5.0	6.33	1.00
6.0	7.60	
6.0	7.60	0.91
7.0	8.75	

The order of reaction with respect to hexacyano-ferrate(III) was confirmed by plotting  $\log(-d_c/d_t)_0$  versus  $\log C_0$  [Fig. 3:A:2]. The slope of the straight line plot was found to be nearly one. This shows that order w.r.t. HCF(III) is one.

#### EFFECT OF HYDRAZIDE CONCENTRATION :

In order to investigate the effect of hydrazide concentration on the rate of reaction, the reaction was studied at different initial concentrations of hydrazide keeping the concentrations of hexacyanoferrate(III) and alkali constant. For this purpose the concentration of

hydrazide was varied from  $3.0 \times 10^{-3} \text{ M}$  to  $7.0 \times 10^{-3} \text{ M}$ . The results of these kinetic runs are recorded in Table 3:A:5 and depicted graphically in Fig. 3:A:3.

TABLE 3:A:5

[HCF(III)] = $5.0 \times 10^{-4} \text{ M}$		[OH] = $1.0 \times 10^{-3} \text{ M}$			
Temp = $50^\circ \text{C}$		$\lambda_{\text{max}} = 420 \text{ nm}$			
[o-Cl BAH] $\text{M} \times 10^3$	3.0	4.0	5.0	6.0	7.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.480	0.480	0.480	0.480	0.480
5	0.455	0.450	0.445	0.440	0.430
10	0.435	0.425	0.415	0.405	0.390
15	0.415	0.400	0.390	0.375	0.365
20	0.395	0.375	0.365	0.350	0.340
30	0.360	0.335	0.320	0.305	0.290
40	0.330	0.300	0.285	0.270	0.250
50	0.300	0.270	0.255	0.245	0.215
60	0.280	0.245	0.230	0.215	0.185
80	0.240	0.210	0.180	0.170	0.140
100	0.210	0.185	0.150	0.140	0.110
Mean $k \times 10^2$ $\text{min}^{-1}$	0.95	1.16	1.32	1.47	1.72

The plots of log O.D. against time (Fig.3:A:3) are linear, so the pseudo first order kinetic behaviour of the reaction is retained at different initial concentrations of

hydrazide that were used in the present study.

An examination of the results given in Table 3:A:5 indicates that the value of pseudo-first order rate constant ( $k$ ) depends on initial concentration of hydrazide and it increases with increase in  $[\text{hydrazide}]_0$ .

Order with respect to hydrazide :

It was found that the first order rate constant ( $k$ ) of the reaction increases with increase in concentration of hydrazide (Table 3:A:5) and consequently the second order rate constant remains nearly constant ( $2.60 \text{ mole}^{-1} \text{ min}^{-1}$ ). This shows first order rate dependence of reaction rate on concentration of hydrazide.

The second order rate constant is determined by using equation

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

where

$k_2$  = Second order rate constant,

$k_1$  = First order rate constant.

The order of reaction w.r.t. hydrazide has been determined by subjecting the kinetic data of the table 3:A:5 to van't Hoff's differential method. From the initial slopes of O.D. versus time plot, the initial rates  $(-d_c/d_t)_0$  of the

reaction at different initial concentrations of hydrazide were determined. These initial rates are recorded in table 3:A:6.

TABLE 3:A:6

[Hydrazide] <sub>0</sub> Mx10 <sup>3</sup>	(-d <sub>c</sub> /d <sub>t</sub> ) <sub>0</sub> x10 <sup>6</sup> M min <sup>-1</sup>
3.0	3.88
4.0	5.06
5.0	6.33
6.0	7.50
7.0	8.70

An examination of results in the Table 3:A:6 shows that the initial rate of reaction depends on the initial concentration of hydrazide and it increases with increase in initial concentration of hydrazide.

By using the data from Table 3:A:6, the order of reaction (n) w.r.t. hydrazide was calculated with the help of van't Hoff equation.

The values of  $(-d_c/d_t)_0$  corresponding to the different initial concentrations of hydrazide and values of

'n' calculated thereby are recorded in Table 3:A:7. The value of 'n' was found to be nearly one.

TABLE 3:A:7

$[o\text{-CIBAH}]_o \text{ M} \times 10^3$	$(-d_c/d_t)_o \times 10^6 \text{ M min}^{-1}$	Order of reaction(n)
3.0	3.88	0.92
4.0	5.06	
4.0	5.06	1.00
5.0	6.33	
5.0	6.33	0.93
6.0	7.50	
6.0	7.50	0.96
7.0	8.70	

The order of reaction w.r.t. hydrazide was confirmed by plotting  $\log (-d_c/d_t)_o$  versus  $\log C_o$  (Fig. 3:A:4) The slope of straight line plot was found to be one. This proves that order w.r.t. hydrazide is unity.

#### EFFECT OF SODIUM HYDROXIDE CONCENTRATION :

In order to study the effect of alkali concentration on the rate of oxidation of hydrazide the concentration of sodium hydroxide was varied from  $0.9 \times 10^{-3} \text{ M}$  to  $1.1 \times$

$10^{-3}M$  keeping all other parameters constant. The results of this investigation are embodied in Table 3:A:8.

TABLE 3:A:8

[HCF(III)] = $5.0 \times 10^{-4}M$		[o-Cl BAH] = $5.0 \times 10^{-3}M$			
Temp = $50^{\circ}C$		$\lambda_{max} = 420 \text{ nm}$			
[NaOH] $M \times 10^3$	0.90	0.95	1.0	1.05	1.10
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.485	0.480	0.480	0.480	0.475
5	0.460	0.445	0.440	0.440	0.430
10	0.440	0.420	0.415	0.410	0.395
15	0.420	0.395	0.390	0.380	0.365
20	0.400	0.375	0.365	0.355	0.335
30	0.365	0.340	0.320	0.310	0.285
40	0.335	0.310	0.285	0.270	0.245
50	0.310	0.285	0.255	0.240	0.215
60	0.280	0.275	0.230	0.210	0.195
80	0.235	0.235	0.180	0.170	0.140
100	0.200	0.210	0.150	0.140	0.110
Mean $k \times 10^2$ $\text{min}^{-1}$	0.94	1.13	1.32	1.46	1.70

Since the reaction is sensitive to NaOH, small span of concentration is used to study the effect.

The perusal of the data in table 3:A:8 shows that the increase in concentration of NaOH increases the rate of reaction. The kinetic study of o-Cl BAH by hexacyanoferrate



(III) was found to be directly proportional to concentration of sodium hydroxide.

#### EFFECT OF TEMPERATURE :

To study the effect of temperature and to evaluate energy parameters, the present oxidation reaction was carried out at five different temperatures, ranging from 40-60°C. The results of these experiments are recorded in Table 3:A:9 and represented graphically in Fig.3:A:5.

TABLE 3:A:9

	[HCF(III)] = $5.0 \times 10^{-4}$ M [OH <sup>-</sup> ] = $1.0 \times 10^{-3}$ M		[o-Cl BAH] = $5.0 \times 10^{-3}$ M $\lambda_{\max}$ = 420 nm		
Temperature	40°C	45°C	50°C	55°C	60°C
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.480	0.480	0.480	0.480	0.470
5	0.455	0.450	0.445	0.430	0.415
10	0.435	0.425	0.415	0.395	0.370
15	0.420	0.400	0.390	0.360	0.330
20	0.410	0.380	0.365	0.330	0.295
30	0.390	0.350	0.320	0.275	0.240
40	0.375	0.320	0.285	0.230	0.195
50	0.365	0.295	0.255	0.195	0.165
60	0.360	0.280	0.230	0.160	0.135
80	0.340	0.250	0.180	0.115	-
100	0.325	0.230	0.150	-	-
Mean $k \times 10^2$ $\text{min}^{-1}$	0.69	1.03	1.32	1.90	2.28

Results embodied in the above table show that the rate constants are approximately doubled for  $10^{\circ}\text{C}$  rise in temperature.

The plots of  $\log \text{O.D.}$  against time (Fig.3:A:5) at various temperatures are linear. This clearly shows that the pseudo first order kinetic behaviour of the reaction is not affected by change in temperature.

From the observed values of rate constants at different temperatures, thermodynamic parameters are determined.

Temperature Coefficient :

The ratio of first order rate constants for  $10^{\circ}\text{C}$  rise in temperature was calculated in 3 pairs of temperatures. The mean value of temperature coefficients of oxidation reaction for o-Cl BAlI was found to be 1.82.

Energy of Activation ( $E_a$ ) :

A plot of  $\log k$  vs  $1/T$  is found to be linear as shown in Fig. 3:A:6. This indicates that the reaction under study obeys Arrhenius relationship. The value of energy of activation ( $E_a$ ) was determined from the slope of this linear plot using the relation -

$$E_a = \text{slope} \times 2.303 R$$

It comes out to be  $12.11 \text{ K cal mole}^{-1}$

The same activation parameter was also determined by using temperature coefficient method,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 \times T_2} \right]$$

where,

$k_1$  : Rate constant at  $T_1^{\circ} \text{ K}$

$k_2$  : Rate constant at  $T_2^{\circ} \text{ K}$

$T_2 - T_1$  :  $10^{\circ} \text{ K}$

$R$  :  $1.987 \text{ cal/deg/mole}$

Values of  $E_a$  calculated for three pairs of temperatures are practically constant. Mean value of  $E_a$  for o-chloro benzoic acid hydrazide is  $12.47 \text{ K cal mole}^{-1}$ . This value is in good agreement with its value determined by graphical method.

Frequency Factor (A) :

With the help of calculated values of  $E_a$ , frequency factor (A) of the reaction was determined at different temperatures by applying Arrhenius law.

$$\log A = \log k + E_a / 2.303 RT$$

Mean value of A was found to be  $6.178 \times 10^4 \text{ sec}^{-1}$

The intercept of the plot  $\log k$  Vs  $(1/T)$  gives the value of  $\log A$ . The value of frequency factor ( $A$ ) obtained by this method is  $6.023 \times 10^4 \text{ sec}^{-1}$ . This value is in good agreement with calculated value  $6.178 \times 10^4 \text{ sec}^{-1}$

Free Energy of Activation ( $\Delta G^\ddagger$ ):

The free energy of activation is calculated by using the relation -

$$\log k = \log \left( \frac{KT}{h} \right) - \frac{\Delta G^\ddagger}{2.303RT}$$

This equation on rearranging,

$$\Delta G^\ddagger = [\log \left( \frac{KT}{h} \right) - \log k] 2.303 RT$$

The free energy was calculated at each temperature using above relationship and its mean value determined was :

$25.67 \text{ K cal mol}^{-1}$

These results were also confirmed by using equation,

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

Enthalpy of Activation ( $\Delta H$ ) :

The value of enthalpy change for the formation of an activated complex has been determined from the slope of

plot of  $\log \left( \frac{k}{KT/h} \right)$  Vs  $1/T$  [Fig.3:A:7] by using relation,

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

The value obtained was  $11.44 \text{ K cal mole}^{-1}$

Entropy of Activation ( $\Delta S^\ddagger$ ) :

The value of  $\Delta H^\ddagger$  obtained by graphical method was used to calculate entropy of activation at each temperature by applying the equation,

$$\log \left( \frac{k}{KT/h} \right) = \frac{\Delta S^\ddagger}{2.303R} - \frac{\Delta H^\ddagger}{2.303RT}$$

This equation on rearrangement gives,

$$\Delta S^\ddagger = \left[ \log \left( \frac{k}{KT/h} \right) + \frac{\Delta H^\ddagger}{2.303RT} \right] 2.303R$$

The mean value of  $\Delta S^\ddagger$  is found to be  $-26.66 \text{ e.u.}$

The value of  $\Delta S^\ddagger$  is also obtained from the graph of  $\log \left( \frac{k}{KT/h} \right)$  Vs  $\frac{1}{T}$  (Fig.3:A:7) by using the relation,

$$\text{Intercept} = \frac{\Delta S^\ddagger}{2.303R}$$

The value obtained by this method is  $-26.22 \text{ e.u.}$

This value is in good agreement with the calculated value.

The low value of frequency factor and high negative value of entropy of activation are suggestive of the formation of an activated complex involving two similarly charged ions or ion and a neutral molecule.<sup>6,7</sup>

To compare various thermodynamic parameters, they are summarized in Table 3:A:10.

TABLE 3:A:10

## THERMODYNAMIC PARAMETERS FOR o-Cl-BAH

Temp. T(K <sup>o</sup> )	kx10 <sup>4</sup> sec <sup>-1</sup>	Temp. E <sub>a</sub> coeff- icent	K cal <sub>s</sub> .mole <sup>-1</sup> Graph	Calcu- lated	ΔH <sup>‡</sup> K cal- mole <sup>-1</sup> (from graph)	Frequency factor A x 10 <sup>-4</sup> sec <sup>-1</sup>	ΔS <sup>‡</sup> e.u.	ΔG <sup>‡</sup> K.cals mole <sup>-1</sup>
313	1.15					6.03	-26.63	25.42
318	1.71	1.91		13.00		6.50	-26.55	25.58
323	2.20	1.84	12.11	12.74	11.44	6.03	-27.98	25.83
328	3.16	1.73		11.68		6.48	-26.14	25.22
333	3.80					5.85	-26.02	26.30
Mean		1.82		12.48		6.178x10 <sup>-4</sup>	-26.66	25.67

## EFFECT OF CHANGE IN IONIC STRENGTH

In order to study the effect of ionic strength on specific rate of reaction, the reaction was studied by varying the concentration of sodium chloride from  $2.00 \times 10^{-3}$  to  $6.00 \times 10^{-3}$  M. NaCl was not expected to give any secondary reaction and assumed that it is completely dissociated. The results of this kinetic study are tabulated in Table 3:A:11.

TABLE 3:A:11

[HCF(III)] = $5.0 \times 10^{-4}$ M		[o-Cl BAH] = $5.0 \times 10^{-3}$ M		
[OH] = $1.0 \times 10^{-3}$ M		Temp = $50^{\circ}\text{C}$		$\lambda_{\text{max}} = 420 \text{ nm}$
[NaCl] M $\times 10^3$	0.00	2.0	4.0	6.0
Time in min.	O.D.	O.D.	O.D.	O.D.
0	0.480	0.485	0.480	0.470
5	0.445	0.445	0.435	0.425
10	0.415	0.410	0.400	0.385
15	0.390	0.380	0.370	0.355
20	0.365	0.355	0.345	0.325
30	0.320	0.310	0.305	0.280
40	0.285	0.275	0.265	0.245
50	0.255	0.250	0.230	0.215
60	0.230	0.225	0.205	0.190
80	0.180	0.185	0.160	0.150
100	0.150	0.150	0.130	0.120
Mean $k \times 10^2$ $\text{min}^{-1}$	1.32	1.44	1.57	1.67

An examination of the results in the above table shows that the value of  $k$  increases with increase in ionic strength i.e. salt effect is positive.

If the values of  $k$  at different ionic strength are observed carefully it is observed that the acceleration of reaction rate is marginal; hence it was essential to investigate the nature of observed positive salt effect. For this purpose graphs :  $\log k$  Vs  $\mu$  (Fig.3:A:8) and  $\log k$  Vs  $\sqrt{\mu}$  (Fig. 3:A:9) have been plotted.

Perusal of the same plots shows that, the plot of  $\log k$  against  $\mu$  and plot of  $\log k$  against  $\sqrt{\mu}$  are linear. This straight line nature of the  $\log k$  Vs  $\mu$  plot is suggestive of validity of standard equation -

$$\begin{aligned} \ln k &= \ln k_0 + (b_A + b_B - b)\mu \\ &= \ln k_0 + b'\mu \end{aligned}$$

Hence positive salt effect observed in the study is primary exponential type and it suggests the reaction to be between neutral molecule and ion<sup>8,9</sup>.

#### EFFECT OF DIELECTRIC CONSTANT OF SOLVENT :

Effect of solvent on the rate of reaction is one of the important factors to elucidate mechanism. The effect of dielectric constant ( $D$ ) of the solvent was investigated at



different composition of water-dioxane mixture [v/v]. The data is collected in Table 3:A:12.

TABLE 3:A:12

[HCF(III)] = $5.0 \times 10^{-4} \text{M}$		[o-Cl BAH] = $5.0 \times 10^{-3} \text{M}$			
[OH] = $1.0 \times 10^{-3} \text{M}$		Temp = $50^\circ \text{C}$		$\lambda_{\text{max}} = 420 \text{ nm}$	
Dioxane % V/V	30	40	50	60	70
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.470	0.480	0.480	0.480	0.485
5	0.415	0.435	0.445	0.450	0.465
10	0.370	0.395	0.415	0.425	0.450
15	0.325	0.360	0.390	0.405	0.435
20	0.290	0.330	0.365	0.385	0.420
30	0.230	0.280	0.320	0.350	0.395
40	0.185	0.240	0.285	0.325	0.375
50	0.150	0.210	0.255	0.330	0.360
60	0.120	0.180	0.230	0.280	0.340
80	-	0.135	0.180	0.245	0.315
100	-	-	0.150	0.210	0.290
Mean $k \times 10^2$ $\text{min}^{-1}$	2.37	1.78	1.32	1.025	0.66

It is observed that the increase in % of dioxane decreases the rate of oxidation reaction.

The dielectric constants of water-dioxane mixture were calculated from the dielectric constants of the pure solvents using an equation:

$$D = D_1 + W (D_2 - D_1)$$

where,

- D : Dielectric constant of binary solvent  
(water+dioxane)
- D<sub>1</sub> : Dielectric constant of water (78.55)<sup>10</sup>
- D<sub>2</sub> : Dielectric constant of dioxane (2.209)<sup>10</sup>
- W : Weight of dioxane per ml. of the binary  
solvent

The calculated values of dielectric constant of different composition of water-dioxane mixtures are incorporated in Table 3:A:13. The results contained in this table show that the specific rate of the reaction increases with increase in dielectric constant of the solvent i.e. the reaction is favoured in polar solvent having high dielectric constant.

The positive dielectric effect observed in the present case is suggestive of negative ion-dipole interaction in rate determining step as per Amis equation.<sup>11</sup>

TABLE 3:A:13

% Dioxane v/v	D	Mean k x 10 <sup>2</sup> min <sup>-1</sup>
30	50.89	2.37
40	47.16	1.78
50	39.23	1.32
60	31.47	1.025
70	23.62	0.66

concluding Remarks ?

FIG. 3:A:1 — EFFECT OF [HCF(III)].

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

$$[\text{NaOH}] = 1.0 \times 10^{-3} \text{ M}$$

$$\text{TEMP.} = 50^\circ \text{C}$$

$$[\text{HCF(III)}] = \text{I} = 3.0 \times 10^{-4} \text{ M}$$

$$\text{II} = 4.0 \times 10^{-4} \text{ M}$$

$$\text{III} = 5.0 \times 10^{-4} \text{ M}$$

$$\text{IV} = 6.0 \times 10^{-4} \text{ M}$$

$$\text{V} = 7.0 \times 10^{-4} \text{ M}$$

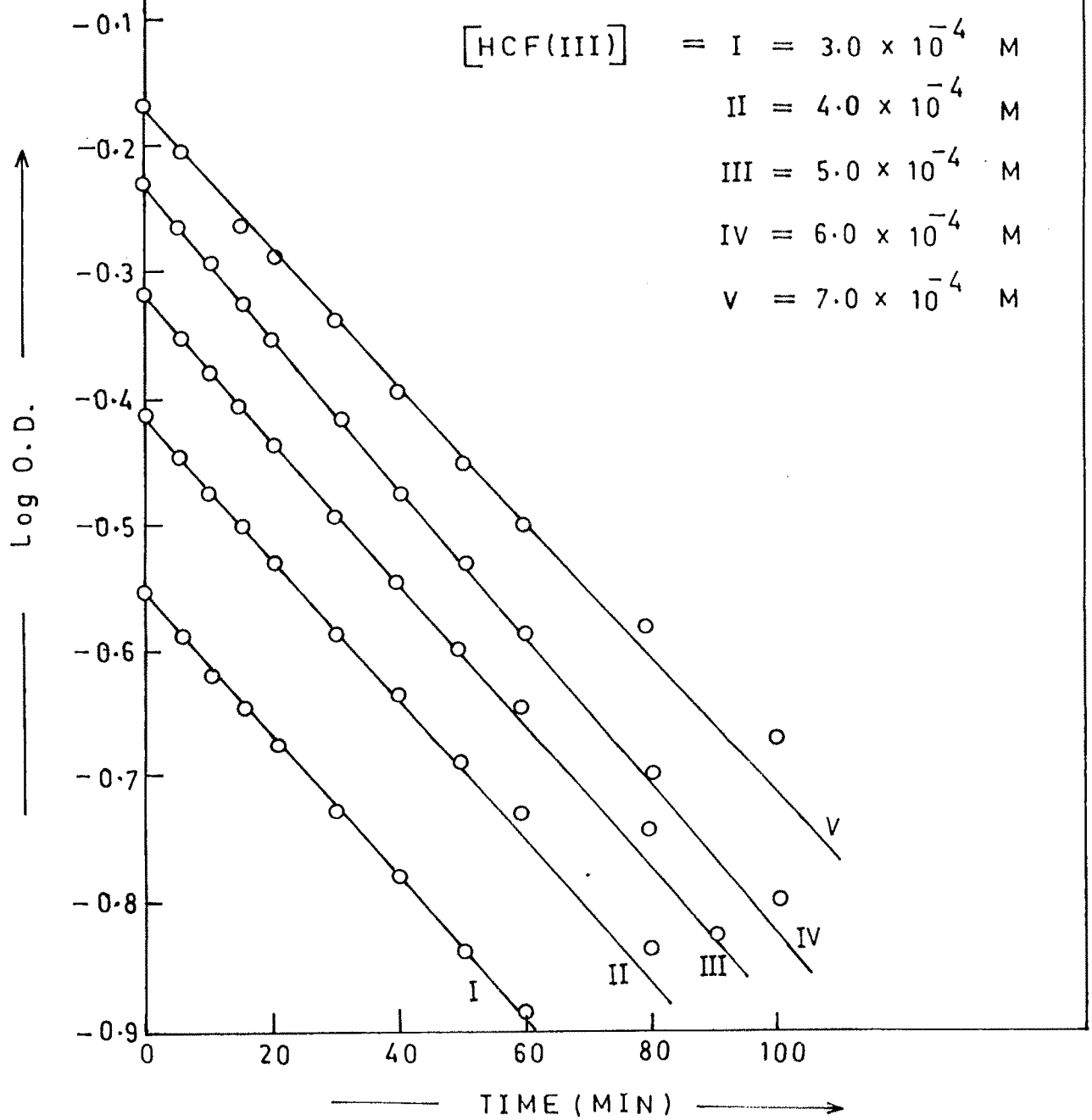
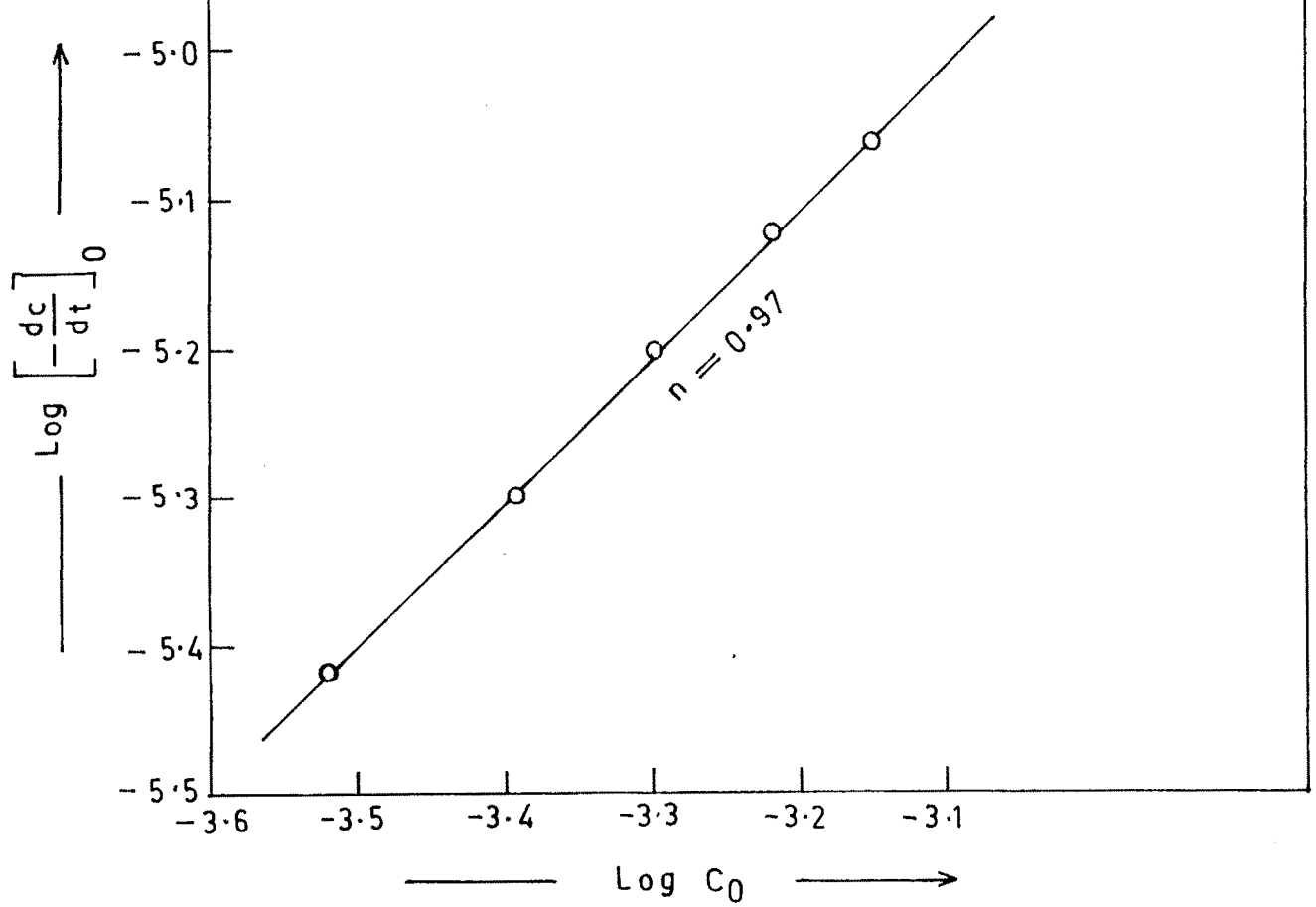


FIG. 3:A:2 — PLOT OF  $\text{Log} \left[ \frac{dc}{dt} \right]_0$  Vs  $\text{Log} C_0$  .



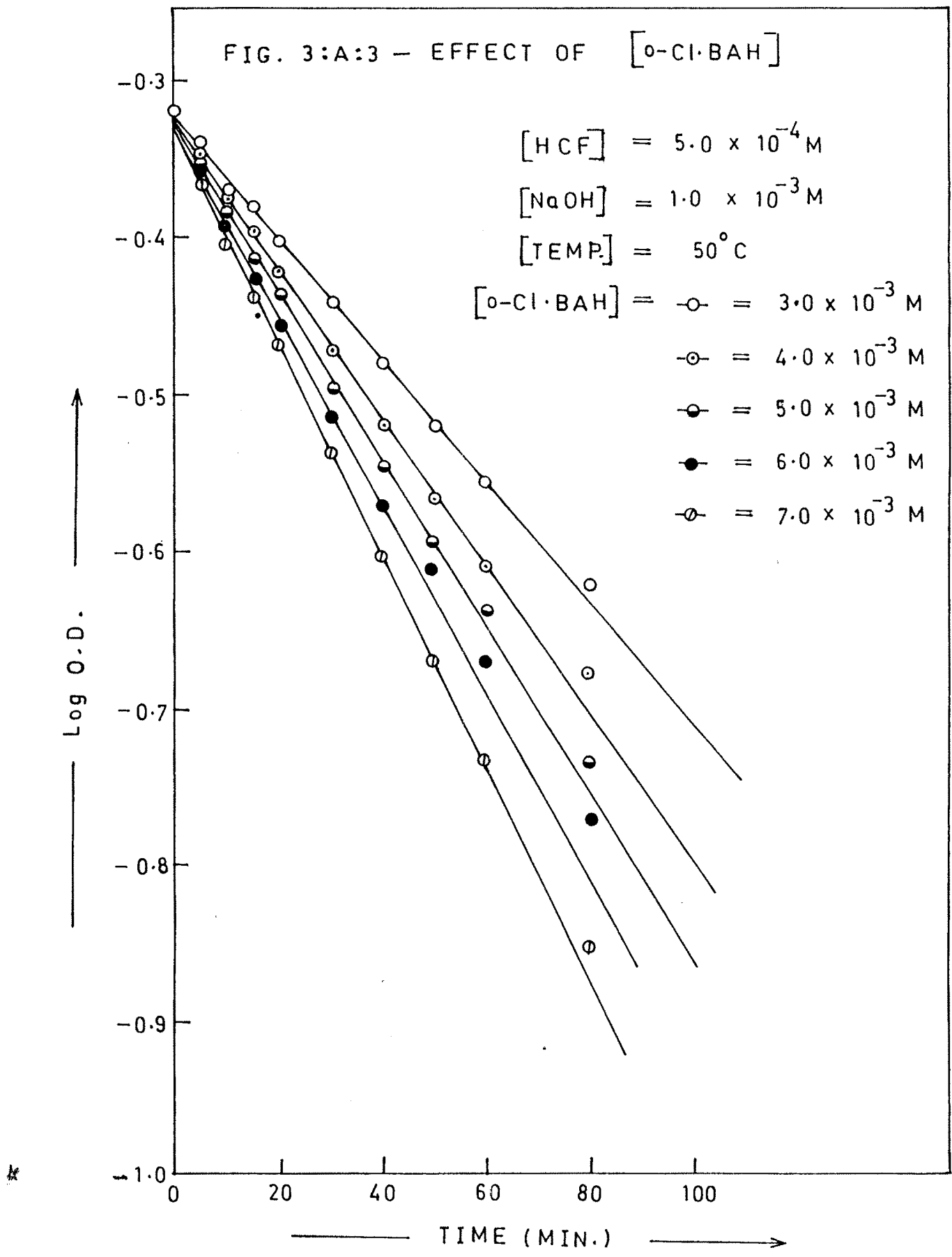


FIG. 3:A:4 — PLOT OF  $\text{Log}\left(-\frac{dc}{dt}\right)_0$  Vs  $\text{Log } C_0$ .

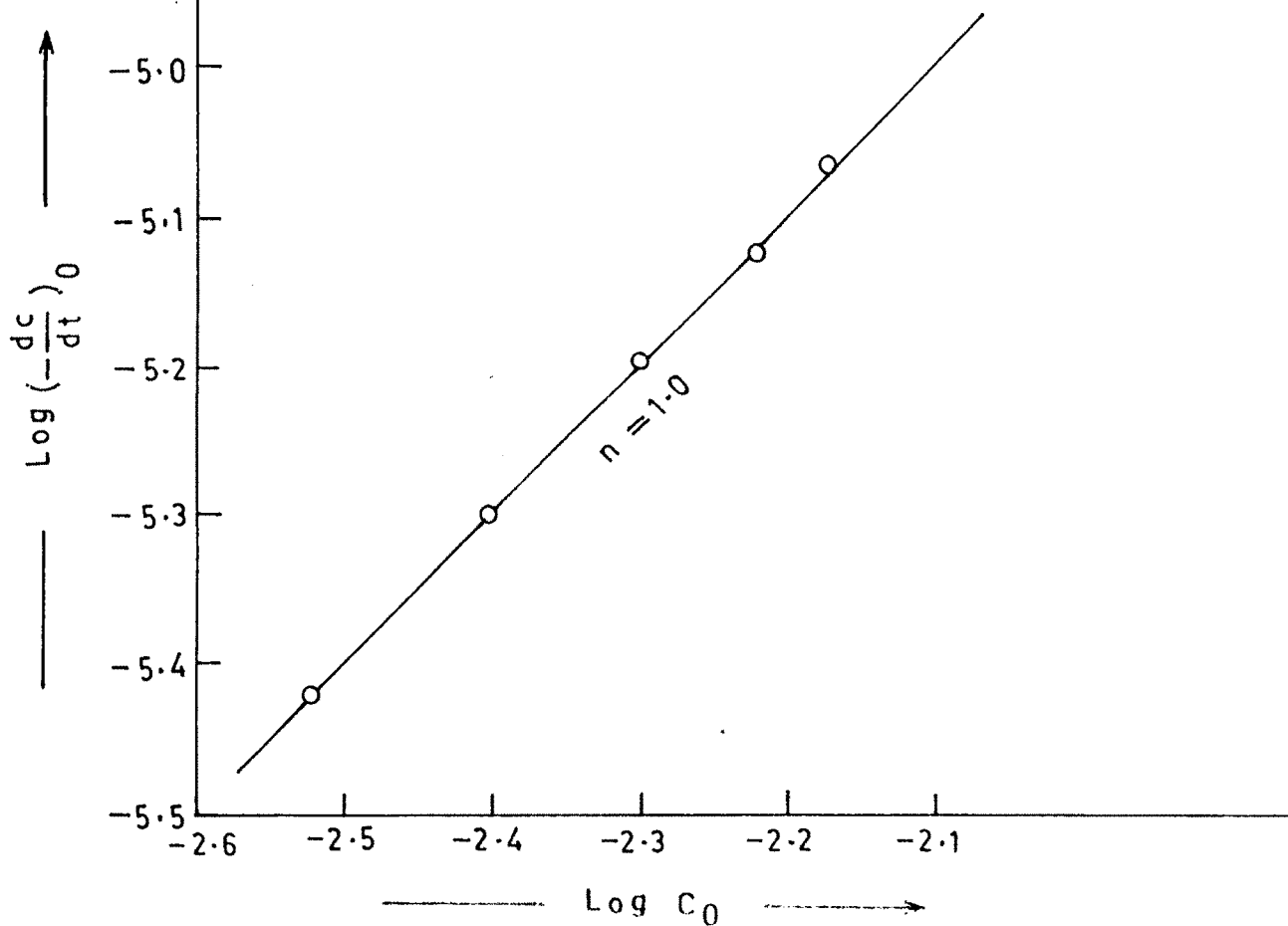


FIG. 3:A:5 - EFFECT OF TEMPERATURE .

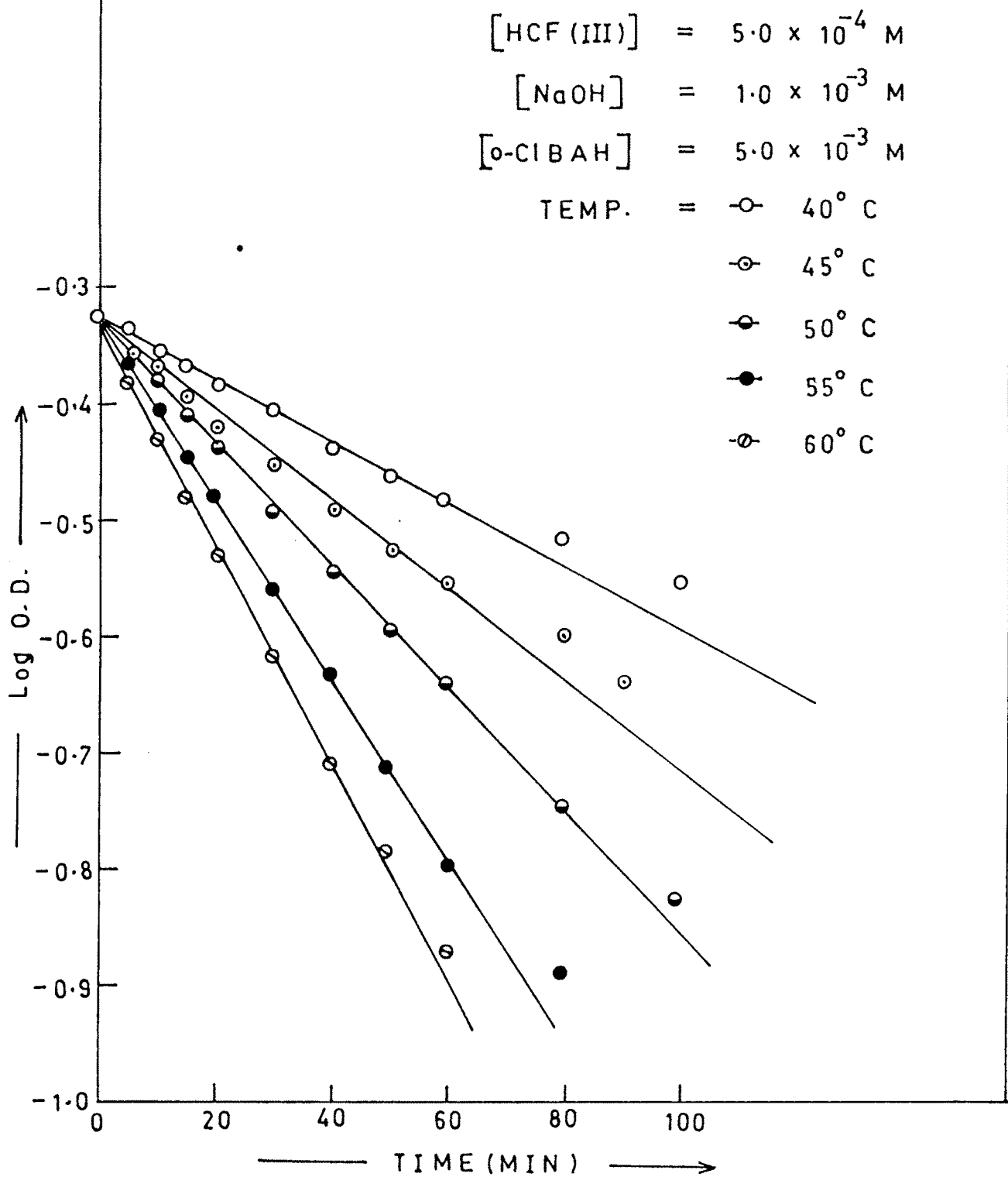
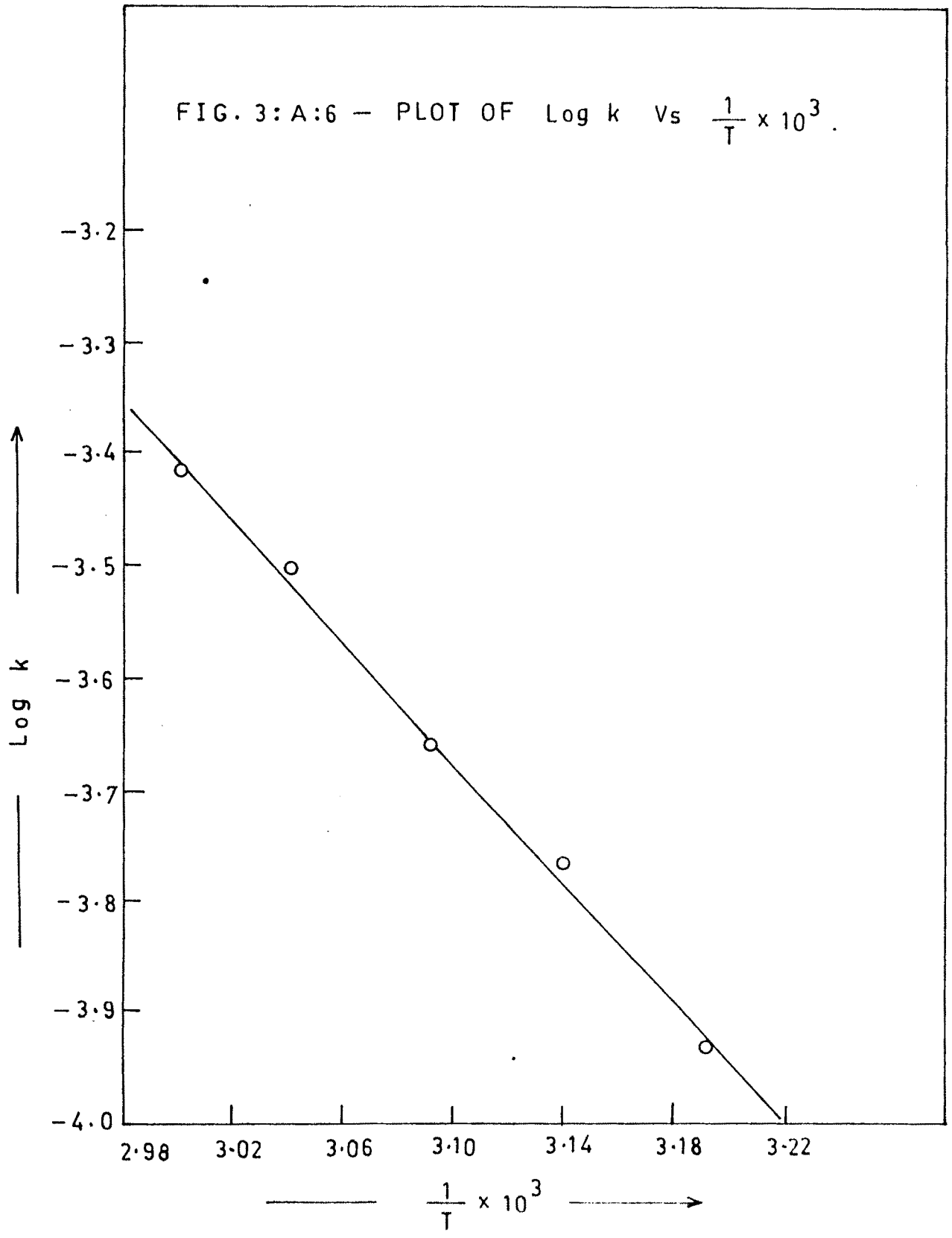


FIG. 3:A:6 - PLOT OF Log k Vs  $\frac{1}{T} \times 10^3$ .





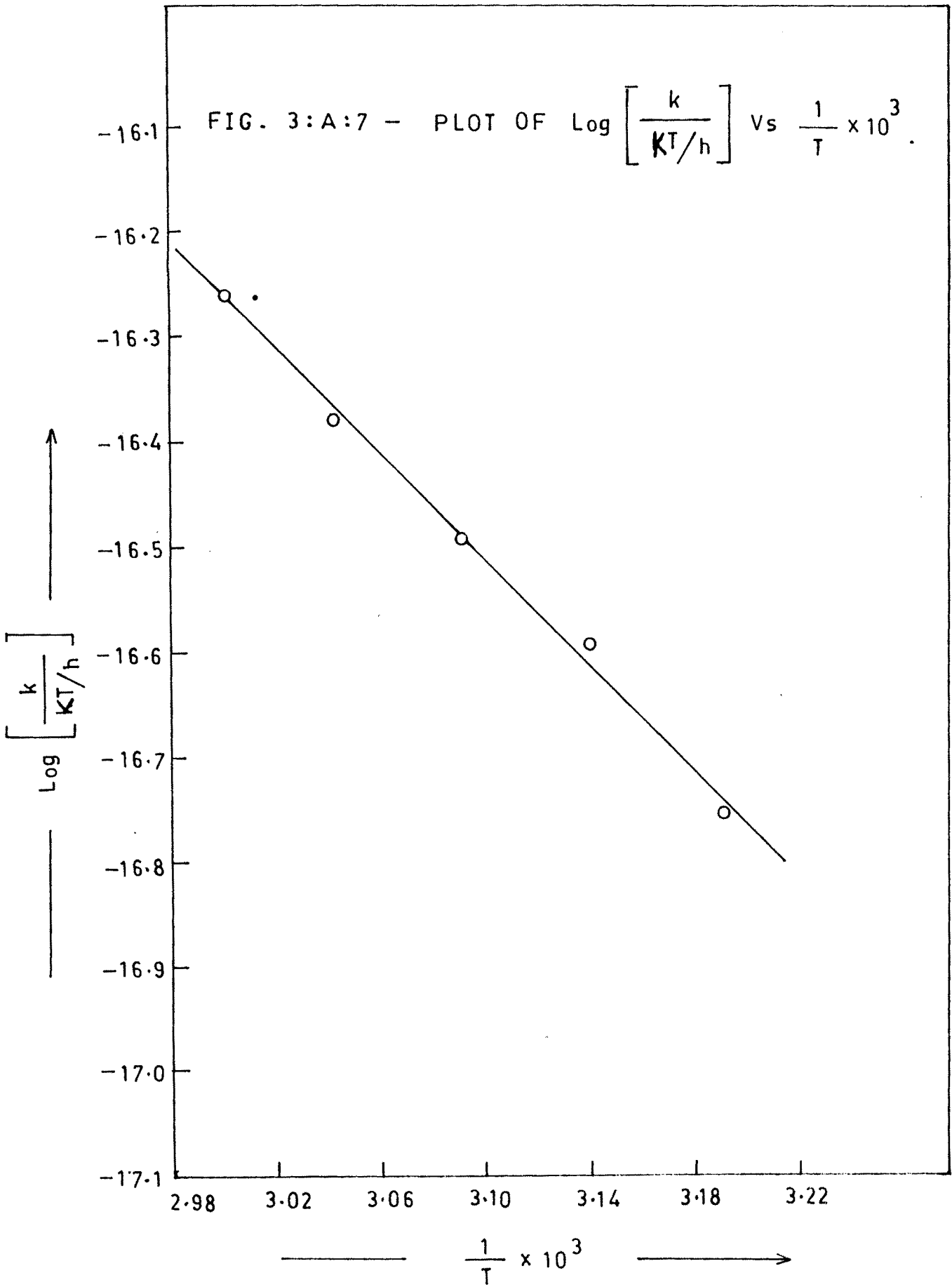


FIG. 3:A:8 - PLOT OF Log k Vs  $\mu$  .

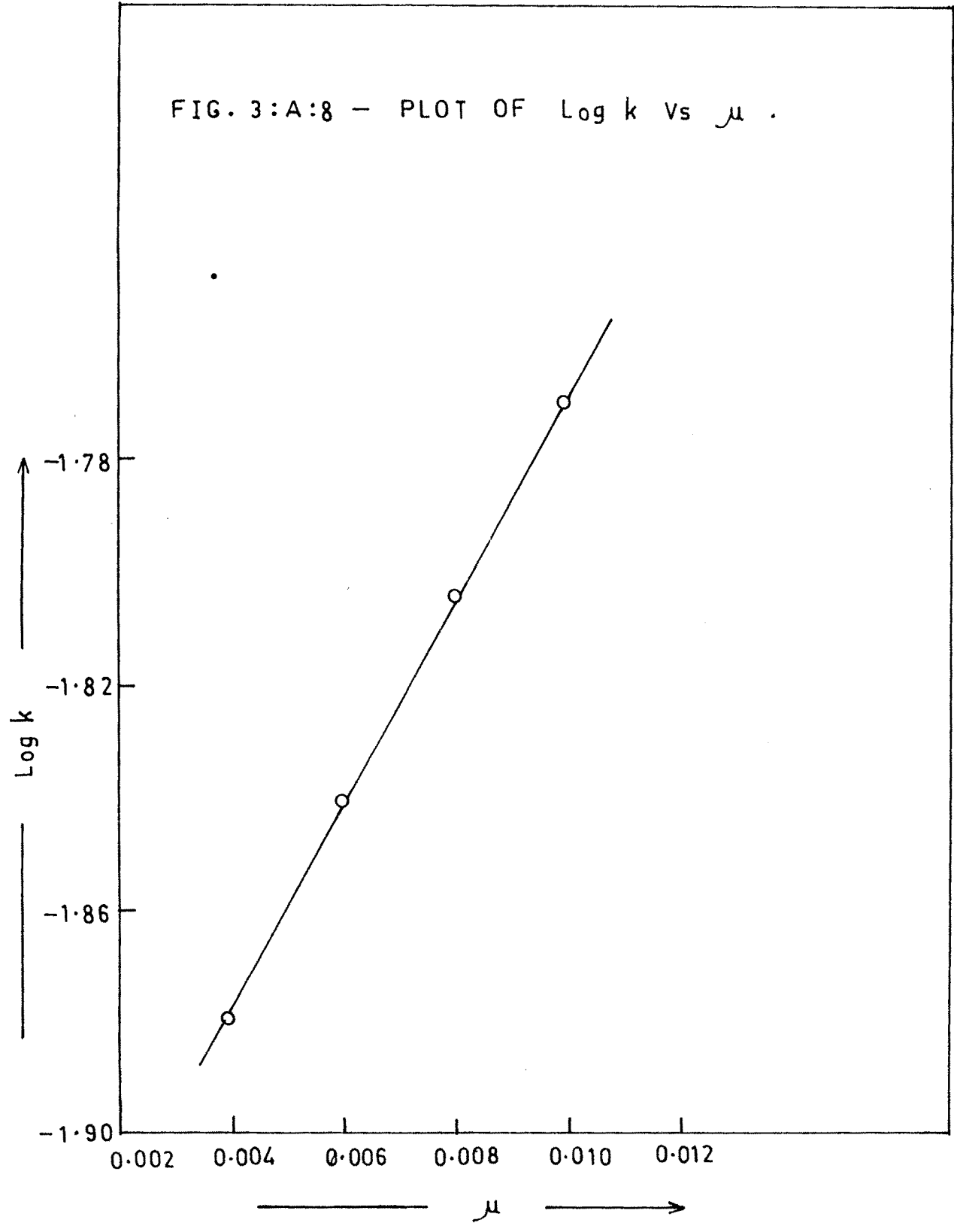
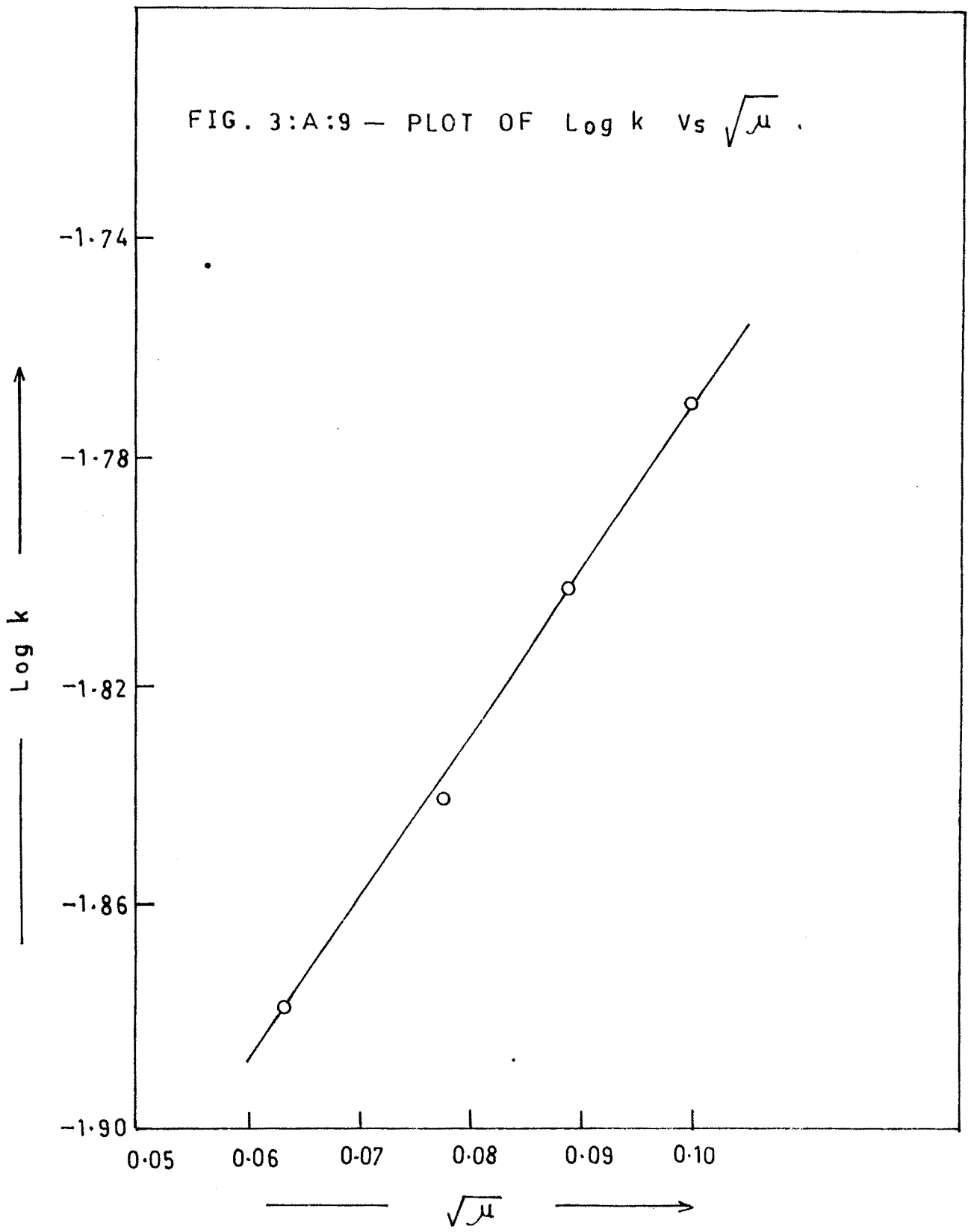


FIG. 3:A:9 — PLOT OF Log k Vs  $\sqrt{\mu}$  .



SECTION - BKINETICS OF OXIDATION OF p-CHLORO  
BENZOIC ACID HYDRAZIDESTANDARD KINETIC RUN :

The preliminary experiments showed that the oxidation reaction under investigation proceeds with measurable velocity at 50°C in water-dioxane mixture (50% v/v) when concentrations of hexacyanoferrate(III), hydrazide and NaOH were  $5.0 \times 10^{-4} \text{M}$ ,  $5 \times 10^{-3} \text{M}$  and  $1.0 \times 10^{-3} \text{M}$  respectively.

The kinetic data of this typical experiment is recorded in the Table 3:B:1.

TABLE 3:B: 1

$[p\text{-Cl-BAH}] = 5.0 \times 10^{-3} \text{ M}$                        $[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{ M}$   
 $[\bar{\text{O}}\text{H}] = 1.0 \times 10^{-3} \text{ M}$                        $\lambda_{\text{max}} = 420 \text{ nm}$                       Temp.  $50^{\circ}\text{C}$

Time in min	O.D.	$k \times 10^2 \text{ min}^{-1}$
0	0.480	-
5	0.435	1.97
10	0.410	1.82
15	0.370	1.73
20	0.340	1.72
30	0.290	1.68
40	0.250	1.63
50	0.220	1.55
60	0.190	1.54
80	0.150	1.45
100	0.120	1.38
Mean k	-	$1.64 \times 10^{-2} \text{ min}^{-1}$
k by graph		$1.56 \times 10^{-2} \text{ min}^{-1}$

In this oxidation reaction, the concentration of hydrazide is ten times greater than the concentration of hexacyanoferrate(III) hence it can be stated that the

reaction is studied under pseudo first order condition.

The observed rate constant ( $k$ ) at different intervals of time was calculated by integration method. The value of  $k$  was also determined by graphical method from slope of linear plot of  $\log O.D.$  against time (Fig.3:B:1). These two values of  $k$  are practically <sup>the</sup> same.

The perusal of the data in Table 3:B:1 reveals that the equation for first order reaction is quite valid as the values of  $k$  at different intervals of time calculated by using same integrated equation are almost constant. In addition, the plot of  $\log O.D.$  versus time (Fig.3:B:1) is linear with negative slope. Hence it is concluded that reaction follows first order kinetics under experimental conditions.

Further an examination of the figures in Table 3:B:1 indicates that the first order rate constant goes on slightly decreasing with the time. This fact leads to conclude that either the reaction follows an order greater than one or reaction is attended with inhibition during the course of reaction.

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

The reaction was carried out by using different initial concentrations of hexacyanoferrate(III) while concentration of hydrazide and NaOH was kept fixed. The kinetic

data of this set of experiments is recorded in Table 3:B:2 and represented graphically by log O.D. Vs time plots (Fig. 3:B:1).

TABLE 3:B:2

[p-Cl BAH] = $5.0 \times 10^{-3} \text{M}$		[OH] = $1.0 \times 10^{-3} \text{M}$			
Temp = $50^\circ \text{C}$		$\lambda_{\text{max}} = 420 \text{ nm}$			
[HCF(III)] $\text{M} \times 10^4$	3.0	4.0	5.0	6.0	7.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.285	0.390	0.480	0.590	0.670
5	0.260	0.355	0.435	0.535	0.605
10	0.235	0.325	0.400	0.490	0.555
15	0.220	0.300	0.370	0.450	0.515
20	0.205	0.275	0.340	0.415	0.475
30	0.175	0.235	0.290	0.355	0.410
40	0.150	0.200	0.250	0.315	0.350
50	0.130	0.170	0.220	0.280	0.300
60	0.110	0.150	0.190	0.245	0.260
80	0.090	0.120	0.150	0.190	0.200
100	—	—	0.120	—	—
Mean $k \times 10^2$ $\text{min}^{-1}$	1.63	1.71	1.64	1.66	1.70

From the data in Table 3:B:2 it is clear that oxidation of p-chloro benzoic acid hydrazide at different initial concentrations of hexacyanoferrate(III) obeys first order kinetic.

The data in Table 3:B:2 reflects that the values of  $k$  at various initial concentrations of ferricyanide are fairly constant indicating independence of  $k$  on initial concentration of hexacyanoferrate(III).

Determination of order with respect to HCF(III) :

To determine the order of reaction with respect to hexacyanoferrate(III) by van't Hoff differential method, initial rates of reaction at different  $[\text{HCF(III)}]_0$  were determined from the initial slopes of corresponding O.D. against time curves using the relation -

$$\left(-\frac{d_c}{d_t}\right)_0 = \frac{\left(-\frac{d_A}{d_t}\right)_0}{\epsilon}$$

The values of initial rates of oxidation of p-Cl BAH at different initial concentrations of hexacyanoferrate(III) are tabulated in Table 3:B:3.

TABLE 3:B:3

$[\text{HCF(III)}]_0 \times 10^4$	$\left(-\frac{d_c}{d_t}\right)_0 \times 10^6 \text{ M min}^{-1}$
3.0	4.48
4.0	5.91
5.0	7.47
6.0	8.98
7.0	10.44



The results reported in the above table indicate that the initial rate of oxidation depends on the initial concentration of hexacyanoferrate(III) and it increases with increase in concentration of hexacyanoferrate(III)

The order of reaction w.r.t. HCF(III) was then calculated by substituting the values of initial rates  $(-d_c/d_t)_0$  and corresponding  $[HCF(III)]_0$  in van't Hoff equation -

$$n = \frac{\log(-d_c/d_t)_{01} - \log(-d_c/d_t)_{02}}{\log C_1 - \log C_2}$$

Initial rates and order of reaction obtained thereby are listed in Table 3:B:4.

TABLE 3:B:4

$[HCF(III)]_0 \text{ M} \times 10^4$	$(-d_c/d_t)_0 \times 10^6 \text{ M min}^{-1}$	Order of reaction(n)
3.0	4.48	0.96
4.0	5.91	
4.0	5.91	1.04
5.0	7.47	
5.0	7.47	1.00
6.0	8.98	
6.0	8.98	0.97
7.0	10.44	

The graph of  $\log (-d_e/d_t)_0$  Vs  $\log [\text{HCF(III)}]_0$  is plotted in order to confirm the order of reaction [Fig.3:B:2] The slope of straight line plot was found to be one. This confirms that order w.r.t. HCF(III) is unity.

#### EFFECT OF HYDRAZIDE CONCENTRATION :

To observe the effect of hydrazide concentration on the rate of reaction and also for determination of order of reaction w.r.t. hydrazide, the oxidation reaction was studied at different initial concentrations of p-Cl BAH at 50°C, keeping concentrations of  $\text{K}_3\text{Fe}(\text{CN})_6$  and NaOH unchanged. Table 3:B:5 gives the results of these experiments. These results are represented graphically in Fig.3:B:3.

TABLE 3:B:5

[HCF(III)] = $5.0 \times 10^{-4} \text{M}$		[OH] = $1.0 \times 10^{-3} \text{M}$			
Temp = $50^\circ \text{C}$		$\lambda_{\text{max}} = 420 \text{ nm}$			
[p-Cl BAH] $\text{M} \times 10^3$	3.0	4.0	5.0	6.0	7.0
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.480	0.480	0.480	0.480	0.475
5	0.445	0.440	0.435	0.430	0.420
10	0.425	0.405	0.400	0.395	0.375
15	0.395	0.375	0.370	0.360	0.345
20	0.375	0.355	0.340	0.330	0.315
30	0.330	0.310	0.290	0.285	0.270
40	0.295	0.270	0.250	0.245	0.215
50	0.265	0.240	0.220	0.210	0.180
60	0.240	0.215	0.190	0.180	0.150
80	0.195	0.170	0.150	0.140	-
100	0.160	0.140	0.120	0.115	-
Mean $k \times 10^2$ $\text{min}^{-1}$	1.25	1.47	1.64	1.78	2.05

As the plots of log O.D. Vs time (Fig.3:B:3) are linear, the pseudo first order behaviour of reaction at different initial concentrations of hydrazide is retained.

From the results embodied in Table 3:B:5 it is evident that specific rate of reaction is sensitive to the concentration of hydrazide and it increases proportionally

with increase in concentration of hydrazide.

Order with respect to hydrazide :

The specific rate of the reaction increases with increase in initial concentration of hydrazide. However ratio  $\frac{k_1}{[\text{hydrazide}]_0}$  which gives a second order constant ( $k_2$ ) remains almost constant ( $3.18 \text{ mole}^{-1} \text{ min}^{-1}$ ). This indicates first order dependence of reaction rate on concentration of hydrazide.

The investigation of order of reaction w.r.t. hydrazide is done by subjecting the kinetic data from Table 3:B:5 to van't Hoff's differential method. The initial rates  $(-d_c/d_t)_0$  of the reaction at different initial concentrations of hydrazide were determined from the initial slopes of O.D. Vs time plots. These initial rates are given in Table 3:B:6.

TABLE 3:B:6

$[\text{Hydrazide}]_0 \text{ M} \times 10^3$	$(-d_c/d_t)_0 \times 10^6 \text{ M min}^{-1}$
3.0	4.66
4.0	6.10
5.0	7.47
6.0	9.10
7.0	10.70

An examination of the results in above table shows that the initial rate of the reaction depends on the initial concentration of hydrazide.

Initial rates and corresponding initial concentrations of hydrazide were employed to calculate the order of reaction w.r.t. hydrazide by using van't Hoff equation. The  $(-d_c/d_t)_0$  value at different  $[\text{hydrazide}]_0$  and values of 'n' determined thereby are recorded in Table 3:B:7. The value of 'n' was found to be nearly one.

TABLE 3:B:7

$[\text{o-CIBAH}]_0 \text{ M} \times 10^3$	$(-d_c/d_t)_0 \times 10^6 \text{ M min}^{-1}$	Order of reaction(n)
3.0	4.66	0.93
4.0	6.10	
4.0	6.10	0.90
5.0	7.47	
5.0	7.47	1.08
6.0	9.10	
6.0	9.10	1.06
7.0	10.70	

The data in Table 3:B:7 has also been represented by  $\log [-d_c/d_t]_0$  against  $\log [\text{hydrazide}]_0$  plot which is shown in Fig.3:B:4. This plot is straight line with positive slope nearly equal to one. This value of slope is quite in good agreement with the results presented in Table 3:B:7. This proves that order w.r.t. hydrazide is one.

#### EFFECT OF SODIUM HYDROXIDE CONCENTRATION :

To observe the effect of NaOH concentration on the rate of the oxidation of p-Cl BAH, the reaction was studied using different initial concentrations of NaOH whereas all other parameters of reaction such as temperature, concentration of hexacyanoferrate(III) and hydrazide were kept constant. The experimental conditions and results of this investigation are given in Table 3:B:8.

TABLE 3:B:8

[HCF(III)] = $5.0 \times 10^{-4}$ M		[p-Cl BAH] = $5.0 \times 10^{-3}$ M			
Temp = 50°C		$\lambda_{\max}$ = 420 nm			
[NaOH] M $\times 10^3$	0.90	0.95	1.0	1.05	1.10
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.480	0.480	0.480	0.475	0.470
5	0.440	0.440	0.435	0.425	0.415
10	0.410	0.405	0.400	0.385	0.370
15	0.385	0.375	0.370	0.350	0.330
20	0.360	0.350	0.340	0.320	0.295
30	0.315	0.300	0.290	0.270	0.235
40	0.280	0.265	0.250	0.230	0.180
50	0.260	0.235	0.220	0.195	0.155
60	0.235	0.210	0.190	0.170	0.125
80	0.200	0.170	0.150	0.125	—
100	0.175	0.150	0.120	—	—
Mean $k \times 10^2$ $\text{min}^{-1}$	1.35	1.50	1.64	1.91	2.32

From the results in Table 3:B:8 it is seen that increase in the concentration of NaOH enhances the rate of reaction. The kinetic study of present oxidation reaction by alkaline hexacyanoferrate(III) was found to be directly proportional to the concentration of sodium hydroxide.

## EFFECT OF TEMPERATURE :

To investigate the effect of temperature and to determine thermodynamic parameters, the reaction was studied at five different temperatures ranging from 40-60°C keeping concentrations of hydrazide, hexacyanoferrate(III) and NaOH constant.

The results of these experiments are tabulated in Table 3:B:9 and represented graphically in Fig.3:B:5.

TABLE 3:B:9

	$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{M}$		$[\text{p-Cl BAH}] = 5.0 \times 10^{-3} \text{M}$		
	$[\text{OH}^-] = 1.0 \times 10^{-3} \text{M}$		$\lambda_{\text{max}} = 420 \text{ nm}$		
Temperature	40°C	45°C	50°C	55°C	60°C
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.480	0.480	0.480	0.480	0.470
5	0.450	0.445	0.435	0.420	0.400
10	0.430	0.415	0.400	0.370	0.345
15	0.415	0.390	0.370	0.330	0.295
20	0.405	0.365	0.340	0.295	0.255
30	0.380	0.320	0.290	0.235	0.190
40	0.360	0.280	0.250	0.190	0.145
50	0.340	0.250	0.220	0.155	0.110
60	0.320	0.225	0.190	0.125	-
80	0.285	0.185	0.150	-	-
100	0.250	0.150	0.120	-	-
Mean $k \times 10^2$ $\text{min}^{-1}$	0.83	1.32	1.64	2.42	3.06



It is clear from the results in the above table that the rate constant is approximately doubled for 10°C rise in temperature.

The kinetic data from Table 3:B:9 is represented graphically as log O.D. vs time plots, <sup>[Fig 3:B:5]</sup> at various temperatures. These plots are linear. This proves that the pseudo first order kinetic behaviour of the reaction is not affected by change in temperature.

Reaction under investigation obeys Arrhenius law as log k vs (1/T) plot is linear with negative slope (Fig. 3:B:6). The plot of  $\log \left( \frac{k}{KT/h} \right)$  Vs  $\frac{1}{T}$  depicted in Fig. 3:B:7 is also linear indicating validity of Eyring equation

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

The various thermodynamic parameters obtained by using values of k from Table 3:B:9 are summarized in Table 3:B:10.

TABLE 3:B:10

## THERMODYNAMIC PARAMETERS FOR p-Cl-BAH

Temp. T(K <sup>o</sup> )	kx10 <sup>4</sup> sec <sup>-1</sup>	Temp. E <sub>a</sub> coeff- icent	E <sub>a</sub> K Graph	K cal <sub>2</sub> .mole <sup>-1</sup> Calcu- lated	ΔH <sup>‡</sup> K cal <sub>2</sub> - mole <sup>-1</sup> (from graph)	Frequency factor A x 10 <sup>-5</sup> sec <sup>-1</sup>	ΔS <sup>‡</sup> e.u.	ΔG <sup>‡</sup> K.cals mole <sup>-1</sup>
313	1.38					1.80	-26.68	23.88
318	2.20	1.97		13.68		2.10	-26.37	23.96
323	2.73	1.83	13.51	12.54	13.23	1.86	-26.11	24.22
328	4.03	1.86		12.95		2.03	-25.96	24.35
333	5.10					1.90	-25.82	24.58
Mean		1.88		13.05		1.94	-26.19	24.19

From the figures in Table 3:B:10 it is observed that -

- i) Temperature coefficient and energy of activation are practically constant.
- ii) Values of frequency factor (A), entropy of activation ( $\Delta S^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) at different temperatures are fairly constant.
- iii) Energy of activation obtained by temperature coefficient method is in good agreement with its value determined by graphical method.

The low value of frequency factor and high negative value of entropy of activation suggest the formation of an activated complex involving two similarly charged ions or ion and a neutral molecule.

#### EFFECT OF CHANGE IN IONIC STRENGTH :

The oxidation of p-Cl BAH was carried using different quantities of NaCl keeping all other concentrations of reactants and temperature unchanged. The reaction conditions and results of these kinetic experiments are listed in Table 3:B:11.

TABLE 3:B:11

$[\text{HCF(III)}] = 5.0 \times 10^{-4} \text{M}$                        $[\text{p-Cl BAH}] = 5.0 \times 10^{-3} \text{M}$   
 $[\text{OH}^-] = 1.0 \times 10^{-3} \text{M}$                       Temp =  $50^\circ\text{C}$                        $\lambda_{\text{max}} = 420 \text{ nm}$

$[\text{NaCl}] \text{M} \times 10^3$	0.00	2.0	4.0	6.0
Time in min.	O.D.	O.D.	O.D.	O.D.
0	0.480	0.485	0.475	0.470
5	0.435	0.435	0.425	0.415
10	0.400	0.400	0.385	0.375
15	0.370	0.365	0.350	0.340
20	0.340	0.335	0.320	0.310
30	0.290	0.280	0.270	0.255
40	0.250	0.240	0.230	0.215
50	0.220	0.205	0.195	0.180
60	0.190	0.175	0.165	0.150
80	0.150	0.135	0.120	0.105
100	0.120	-	-	-
Mean $k \times 10^2$ $\text{min}^{-1}$	1.64	1.81	1.94	2.10

From the above data, it is evident that the rate of oxidation of hydrazide increases with increase in concentration of salt i.e. the salt effect is positive.

A close examination of k values at different ionic strengths reveals that the acceleration of reaction rate is marginal; hence it was essential to analyse the observed salt

effect. For this purpose plots of  $\log k$  against  $\mu$  and  $\log k$  versus  $\sqrt{\mu}$  have been plotted which are represented in Fig. 3:B:8 and 3:B:9.

It is observed that, the plot of  $\log k$  against  $\mu$  and plot of  $\log k$  versus  $\sqrt{\mu}$  are linear. This straight line nature of the  $\log k$  Vs  $\mu$  plot is indicative of validity of standard equation -

$$\begin{aligned} \ln k &= \ln k_0 + (b_A + b_B - b)\mu \\ &= \ln k_0 + b'\mu \end{aligned}$$

Thus, positive salt effect observed in the present oxidation reaction is primary exponential type and it suggests that the reaction is between neutral molecule and ion.

#### EFFECT OF DIELECTRIC CONSTANT OF SOLVENT :

The effect of dielectric constant of solvent was observed by studying the reaction in different compositions of water-dioxane mixture (v/v) keeping all other parameters fixed.

The kinetic data of these runs is given in Table 3:B:12.

TABLE 3:B:12

[HCF(III)] =  $5.0 \times 10^{-4} \text{M}$                       [p-Cl BAH] =  $5.0 \times 10^{-3} \text{M}$   
 $[\bar{\text{O}}\text{H}] = 1.0 \times 10^{-3} \text{M}$                       Temp =  $50^\circ\text{C}$                        $\lambda_{\text{max}} = 420 \text{ nm}$

Dioxane % V/V	30	40	50	60	70
Time in min.	O.D.	O.D.	O.D.	O.D.	O.D.
0	0.470	0.470	0.480	0.480	0.480
5	0.400	0.415	0.435	0.445	0.455
10	0.350	0.370	0.400	0.420	0.430
15	0.305	0.330	0.370	0.395	0.415
20	0.265	0.295	0.340	0.370	0.400
30	0.205	0.240	0.290	0.330	0.370
40	0.160	0.195	0.250	0.290	0.345
50	0.125	0.160	0.220	0.260	0.320
60	0.100	0.135	0.190	0.240	0.300
80	-	-	0.150	0.200	0.270
100	-	-	0.120	0.160	0.250
Mean $k \times 10^2$ $\text{min}^{-1}$	2.85	2.28	1.64	1.24	0.86

From the results obtained in the above table it is clear that the value of  $k$  decreases with increase in dioxane content of the solvent. Thus reaction is favoured in polar solvent having high dielectric constant.

The calculated values of dielectric constants of different compositions of water-dioxane mixtures and values of rate constants are summarized in Table 3:B:13.

TABLE 3:B:13

% Dioxane v/v	D	Mean $k \times 10^2 \text{ min}^{-1}$
30	50.89	2.85
40	47.16	2.28
50	39.23	1.64
60	31.47	1.24
70	23.62	0.86

The positive dielectric effect observed in the present oxidation reaction is indicative of negative ion-dipole interaction in rate determining step.

#### FREE RADICAL TEST AND PRODUCT ANALYSIS :

It is already seen that in oxidation of o- and p- chloro benzoic acid hydrazides, the order of reaction w.r.t. HCF(III) is one. This first order dependence of reaction rate on concentration of  $\text{Fe}(\text{CN})_6^{3-}$  itself indicates the possibility of free radical formation during the course of reaction.<sup>12</sup> To confirm the same, tests were carried out with acrylonitrile and mercuric chloride solutions.

i) Test with acrylonitrile :

The reaction mixture of  $\text{Fe}(\text{CN})_6^{3-}$  and hydrazide becomes turbid in the presence of 10% acrylonitrile and white suspension is formed in both the cases. The formation of white suspension is indicative of polymerisation of acrylonitrile. This proves that the oxidation of hydrazide by alkaline hexacyanoferrate involves the formation of free radical as reactive species.

ii) Test with  $\text{HgCl}_2$  :

When the solution of mercuric chloride was added to reaction mixture, white turbidity of mercurous chloride was formed spontaneously. Here mixture reduces  $\text{HgCl}_2$  to  $\text{Hg}_2\text{Cl}_2$ . However, there was no polymerisation of acrylonitrile or reduction of  $\text{HgCl}_2$  in the absence of hydrazide.

Thus polymerisation of acrylonitrile<sup>13</sup> and reduction of  $\text{HgCl}_2$ <sup>14</sup> by the reaction mixture in both oxidation reactions prove that the reaction involves the formation of free radicals or radical ions during the course of oxidation.

Identification of Oxidation Products :

The knowledge of oxidation products of the substrate under investigation is an important step in the elucidation of mechanism of reaction. Hence identification of the



products formed in the present reaction was undertaken.

For identification of products the reaction was carried out by using aqueous solution of o-Cl BAH ( $1.0 \times 10^{-2} \text{M}$ ),  $\text{K}_3\text{Fe}(\text{CN})_6$  ( $5.0 \times 10^{-2} \text{M}$ ) and alkali ( $1.0 \times 10^{-3} \text{M}$ ). The flask containing reaction mixture was kept in thermostated water bath maintained at  $50^\circ\text{C}$  for 24 hours to complete the reaction. After completion of reaction, the reaction mixture was acidified with dil HCl and extracted with ether. The residue obtained after evaporation of ether was analysed for acid as follows :

- i) The presence of carboxylic acid group was detected by testing with bicarbonate.
- ii) The formation of o-chlorobenzoic acid as main end product was confirmed by its physical constant.

o-chlorobenzoic acid : M.P. =  $140^\circ\text{C}$  [ $138-140^\circ\text{C}$ ]

Detection of  $\text{N}_2$  :

Nitrogen was detected by lime test.<sup>15</sup> A mixture of lime and manganese dioxide in 10:1 proportion was ignited in a small hard glass tube. A test portion of concentrated filtrate was rendered neutral with NaOH solution and it was added to the ignited mixture. The tube was heated slowly and the liberated gas was tested with filter paper moistened with manganese nitrate and silver nitrate solutions. This

indicator paper held at the mouth of the tube shows gray fleck which turns blue immediately on treatment with a drop of benzidine solution. This shows the formation of  $N_2$  as one of the end products.

Detection of  $NH_3$  :

Formation of  $NH_3$  was tested by Nessler's reagent. When 5 ml reaction was added to 2 ml of Nessler's reagent the formation of brown colouration indicated the presence of  $NH_4^+$  radical and the formation of  $NH_3$  in the reaction mixture was detected.

The same method was followed for identification of end products in the oxidation of p-chloro benzoic acid hydrazide. The end products were found to be p-chloro benzoic acid,  $N_2$  and ammonia.

p-chlorobenzoic acid : M.P. =  $238^{\circ}C$  [ $239-241^{\circ}C$ ]

FIG. 3:B:1 — EFFECT OF [HCF (III)] .

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

$$[\text{NaOH}] = 1.0 \times 10^{-3} \text{ M}$$

$$\text{TEMP.} = 50^\circ \text{ C}$$

$$[\text{HCF}]_0 = \text{I} = 3.0 \times 10^{-4} \text{ M}$$

$$\text{II} = 4.0 \times 10^{-4} \text{ M}$$

$$\text{III} = 5.0 \times 10^{-4} \text{ M}$$

$$\text{IV} = 6.0 \times 10^{-4} \text{ M}$$

$$\text{V} = 7.0 \times 10^{-4} \text{ M}$$

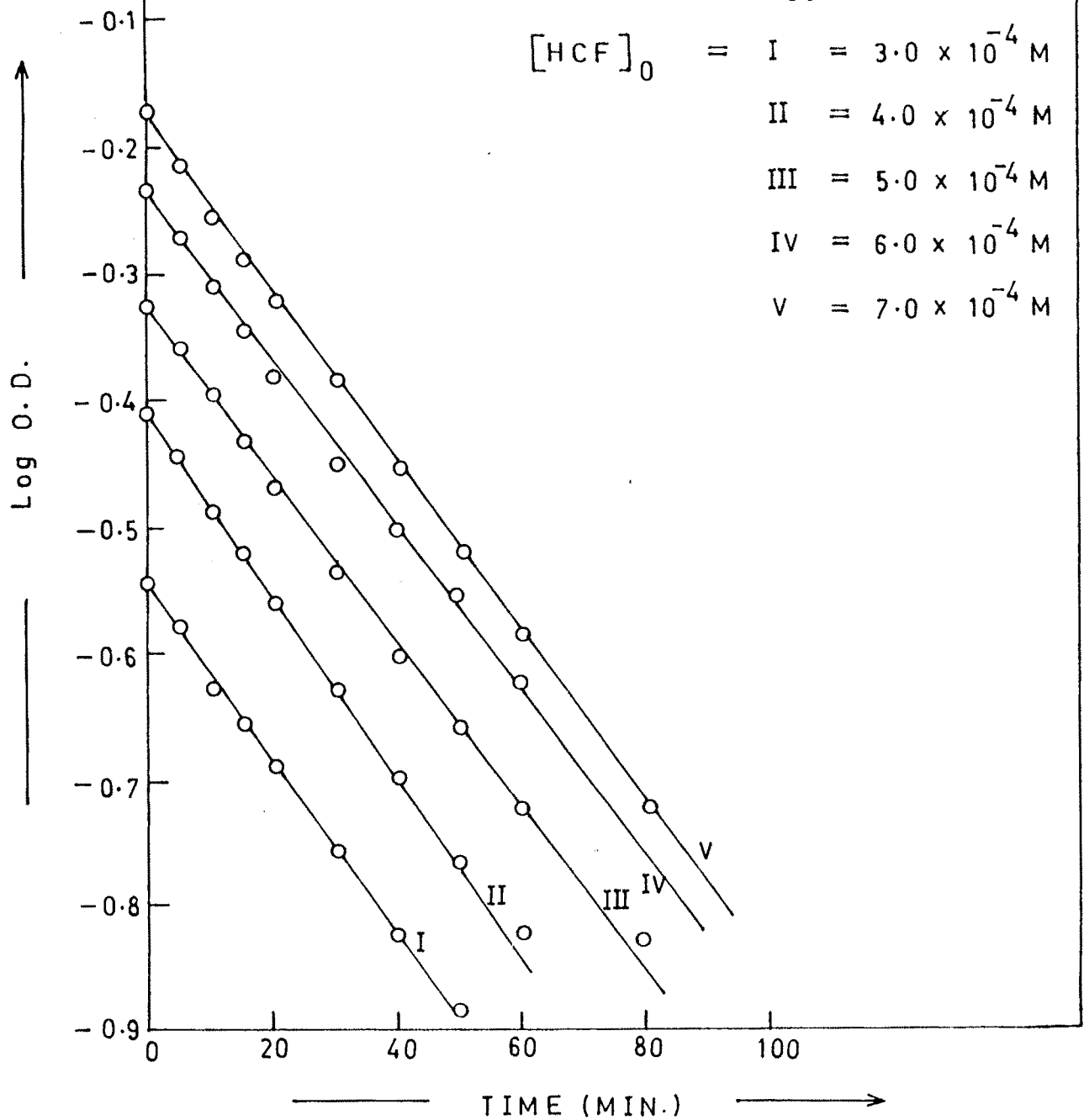
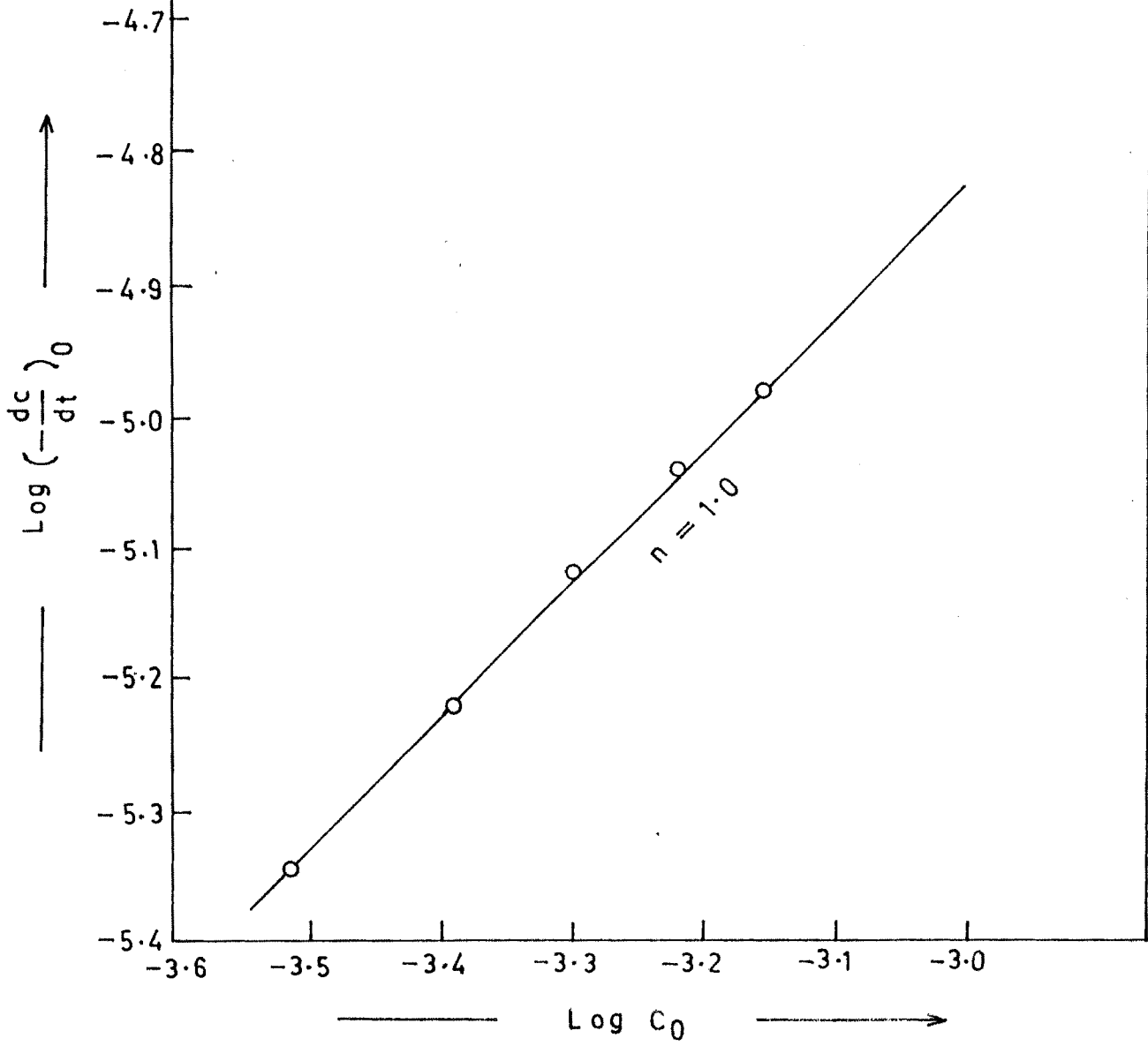


FIG. 3:B:2 — A PLOT OF  $\text{Log}\left(-\frac{dc}{dt}\right)_0$  Vs  $\text{Log } C_0$  .



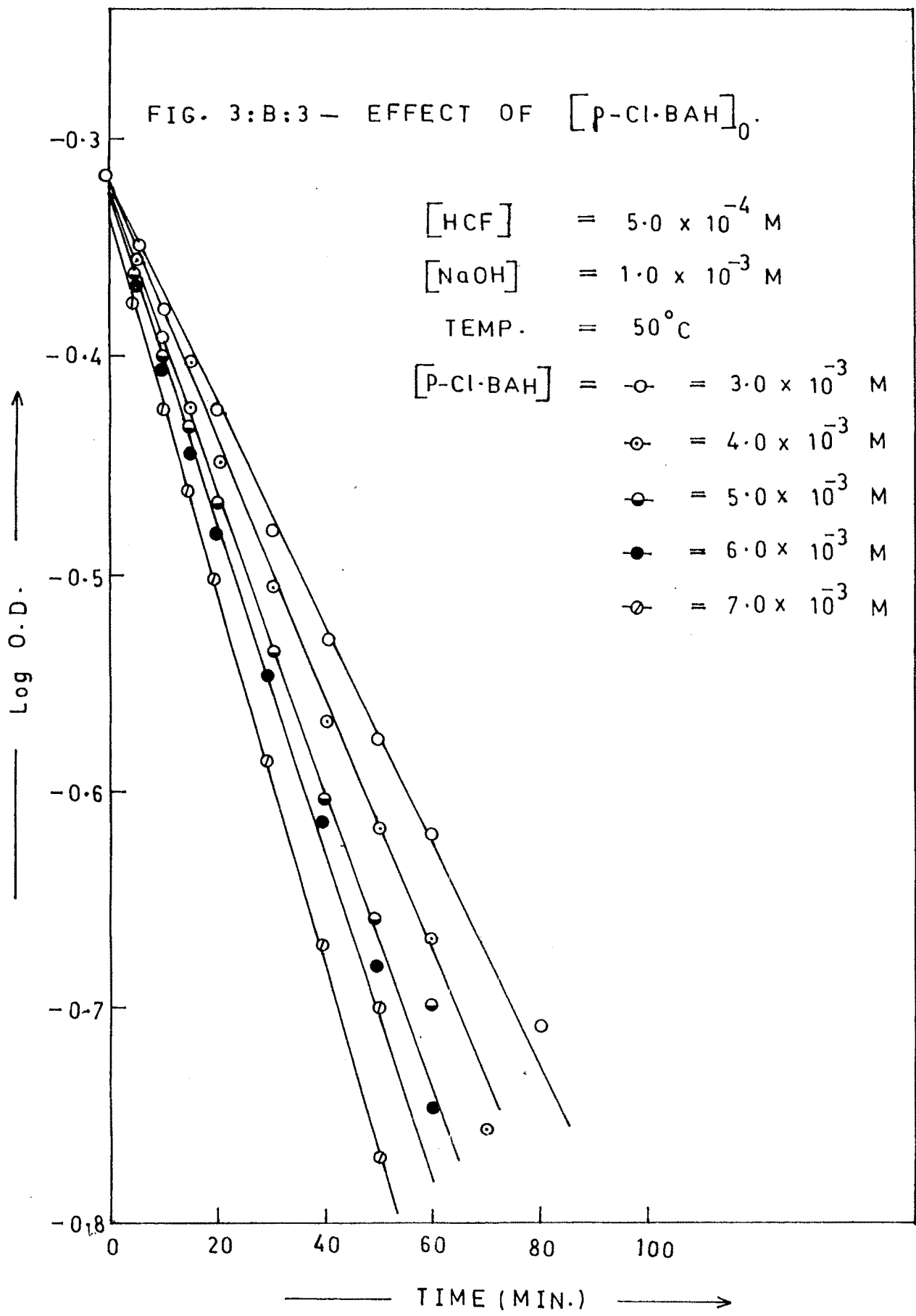


FIG. 3:B:4 - PLOT OF  $\text{Log} \left( -\frac{dc}{dt} \right)_0$  Vs  $\text{Log } C_0$  .

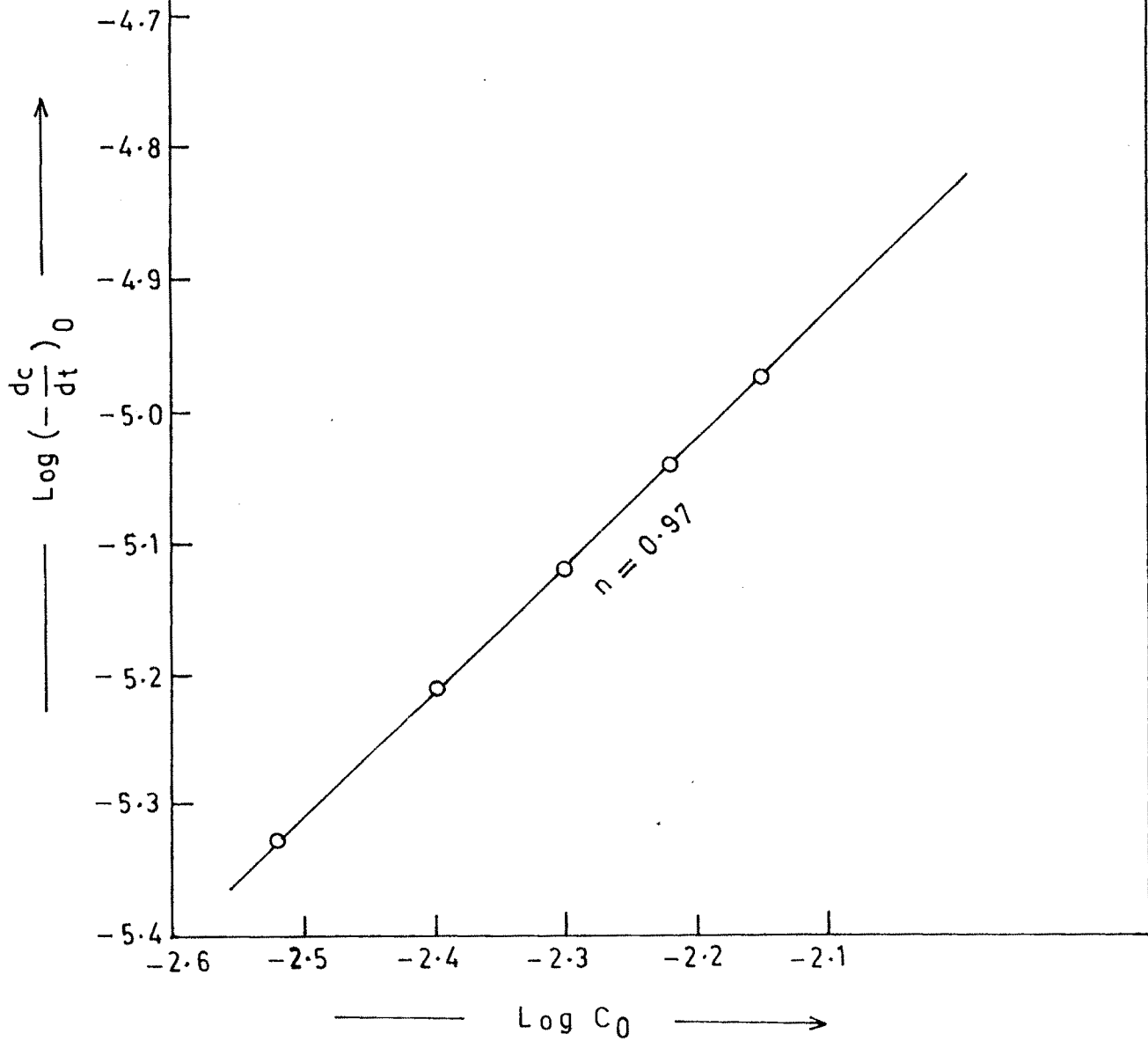
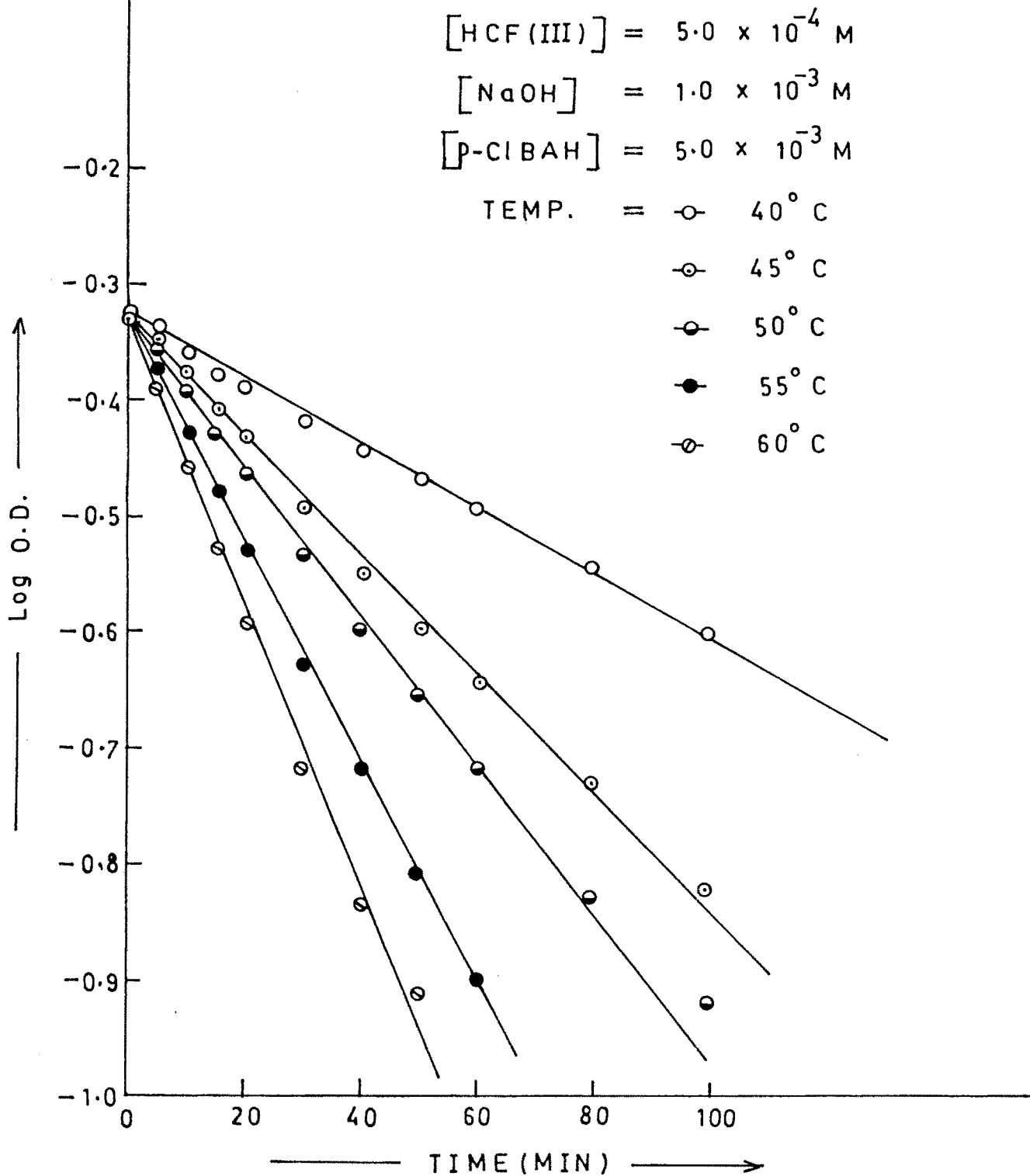
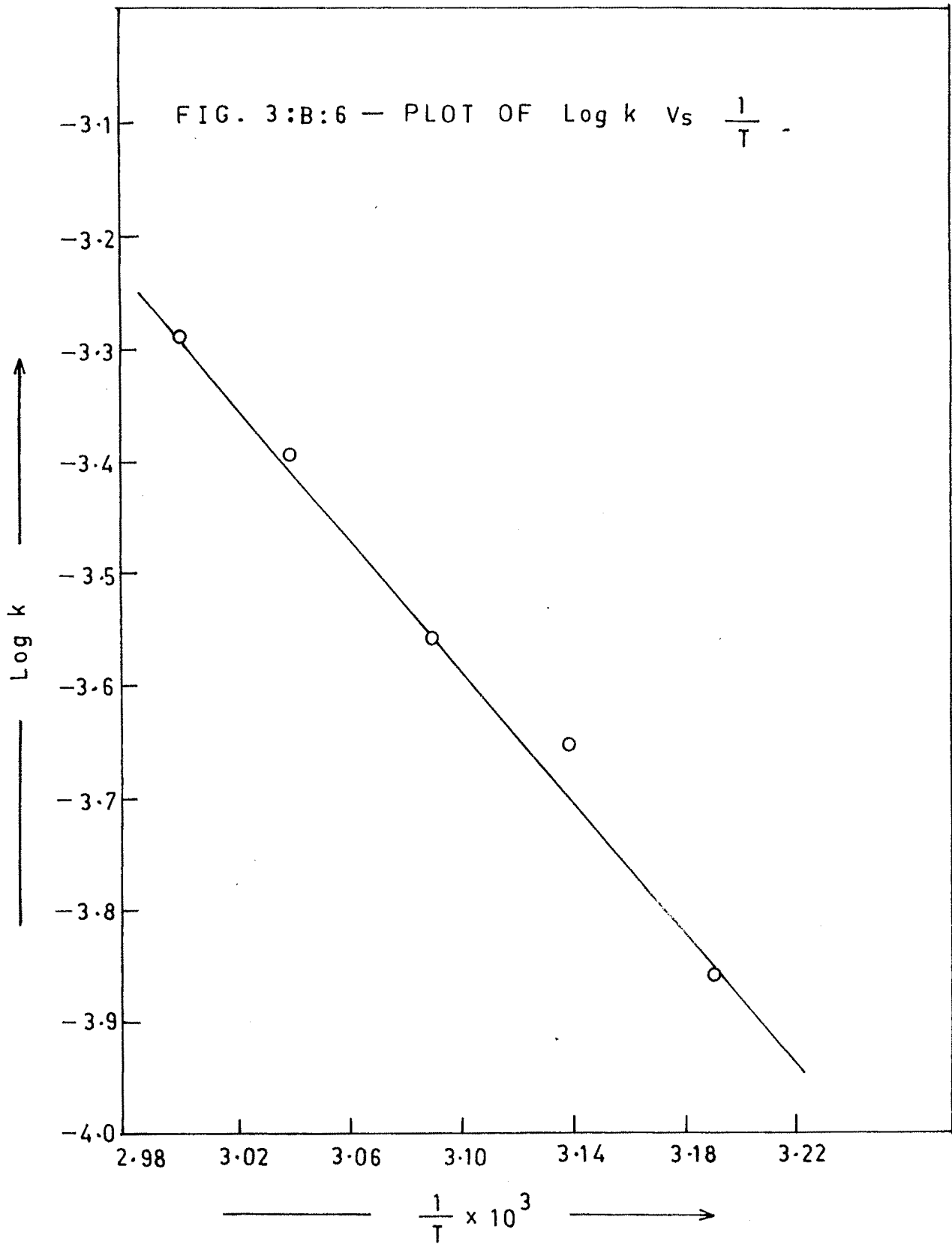


FIG. 3:B:5 — EFFECT OF TEMPERATURE .







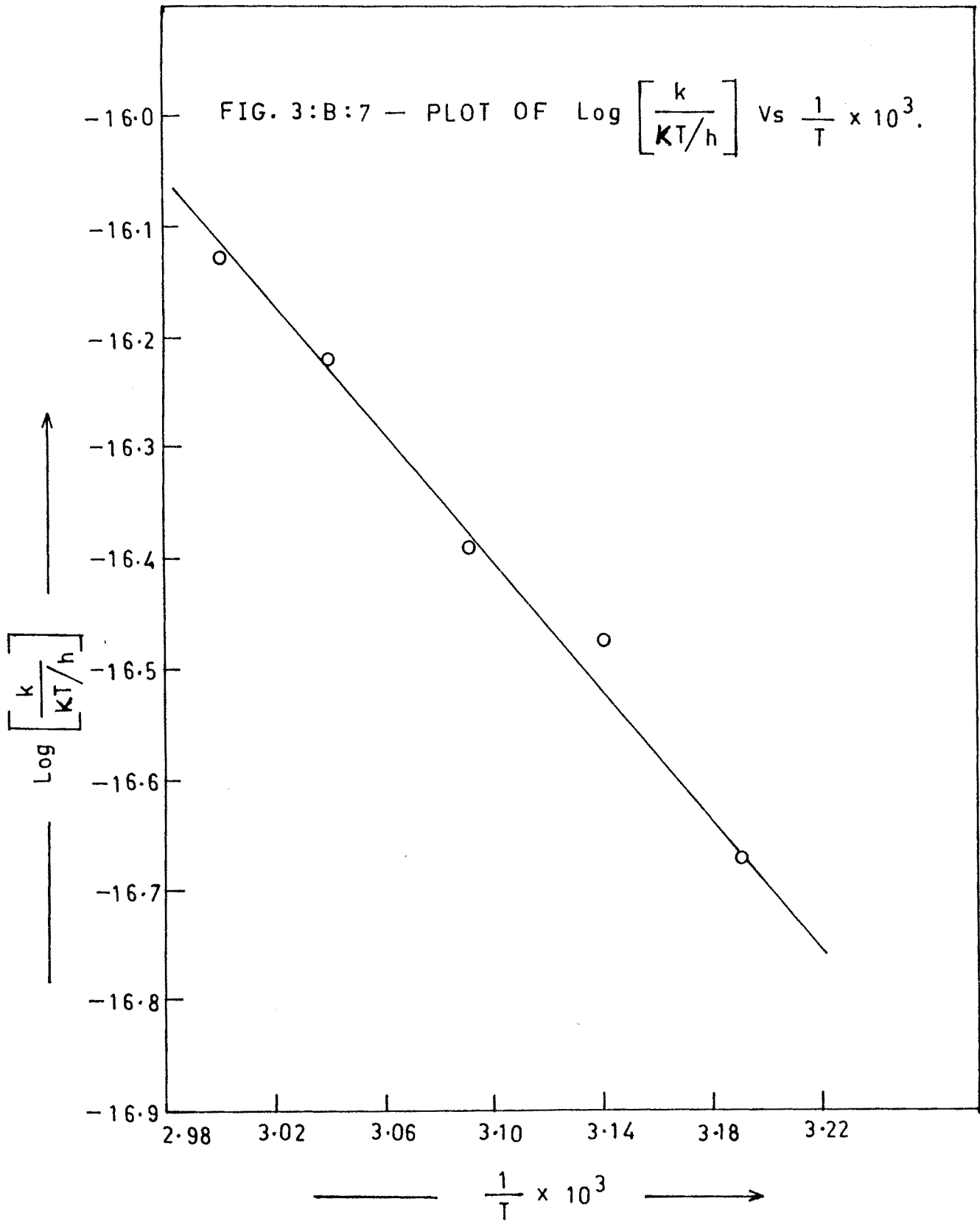


FIG. 3:B:8 — PLOT OF Log k Vs  $\mu$  .

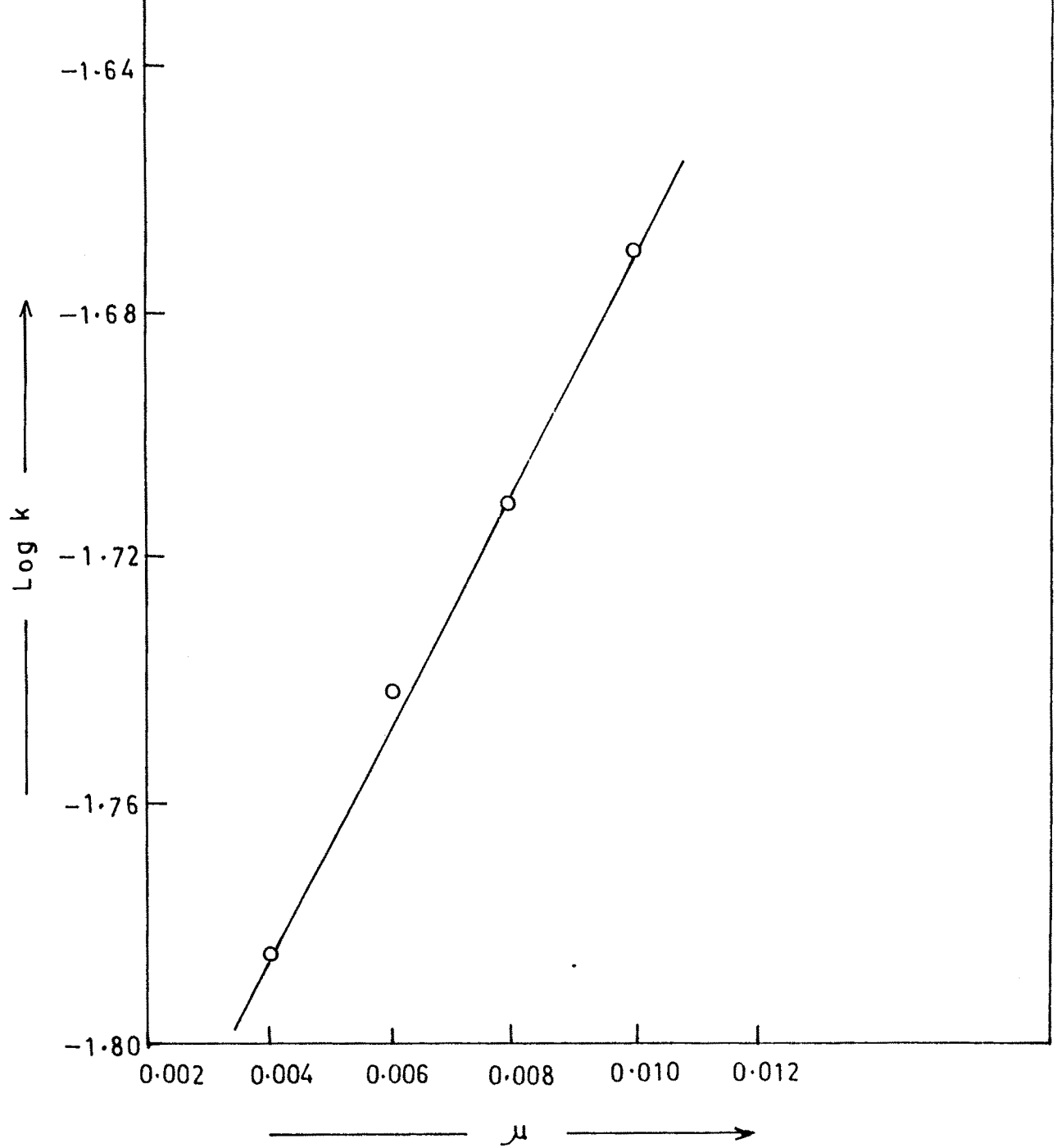
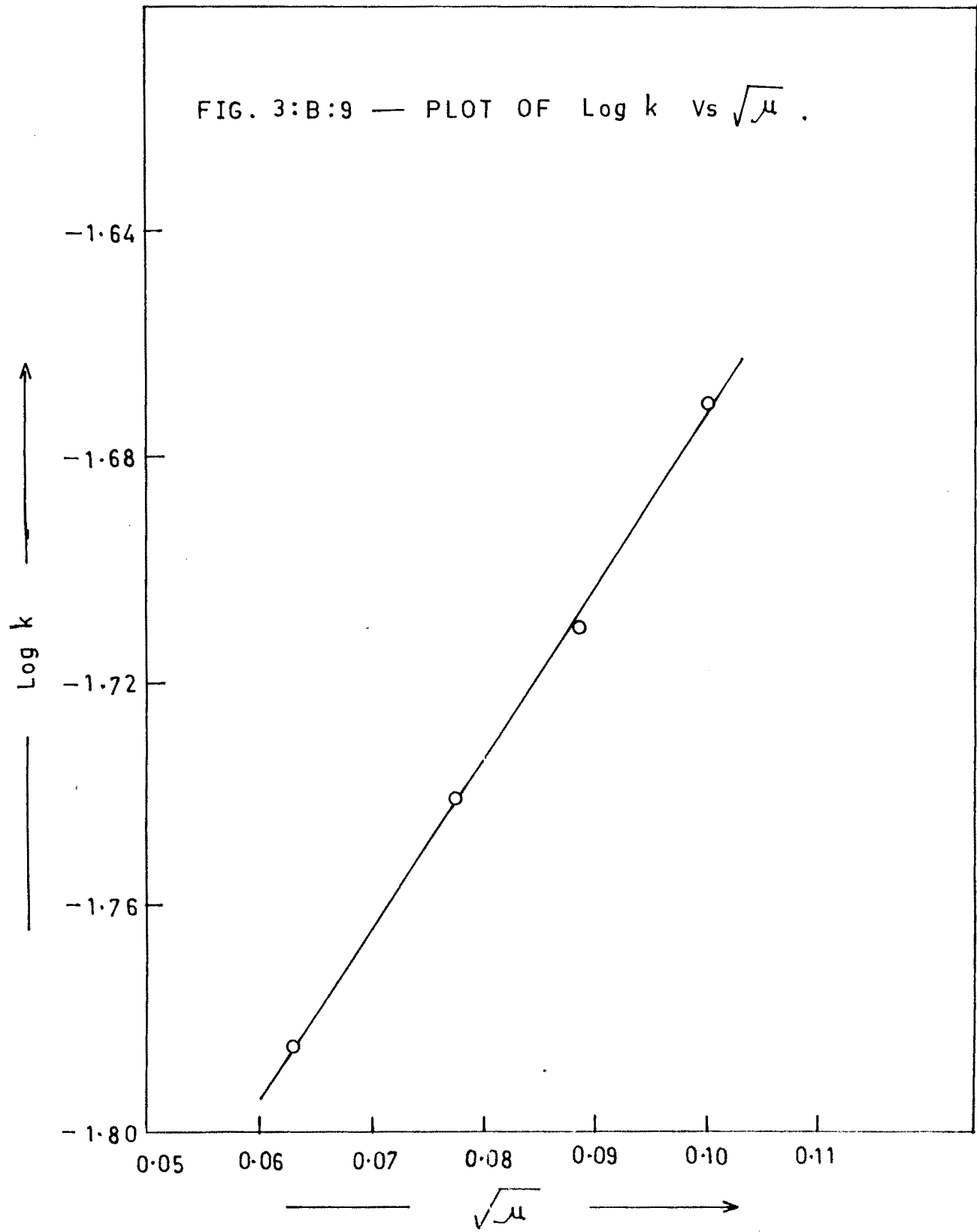


FIG. 3:B:9 — PLOT OF  $\text{Log } k$  Vs  $\sqrt{\mu}$  .



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