CHAPTER-V

Oxidation of P-Chloro aniline

Results :

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The results of the kinetics of the oxidation of P-chloro aniline by potassium bromate in sulphuric acid medium is reported here. All reactions are carried out in pseudo first order conditions. Appropriate concentration of bromate, P-chloro aniline and sulphuric acid were taken to prepare the reaction mixtures.

The 5 ml aliquot of the reaction mixtures was titrated periodically by usual iodometric method. Experiments were designed to study the following parameters.

1. Over all order of the reaction and order with respect to each of the reactants.
2. Effect of sulphuric acid concentration on the velocity of the reaction.
3. Effect of temperature and evaluation of thermodynamic parameters.
4. Effect of salt.
5. End product analysis and free radical test.
6. Stoichiometry.

5.3 Determination of the order of Reaction :

The order of reaction with respect to bromate was determined by isolation method.The concentration of potassium bromate was varied from 2.5. x 10^{-3}M To 12.5 x 10^{-3} M at constant concentration of P-chloro-aniline (5 x 10^{-2}M) The reaction was studied at $30^{o} \pm 0.1^{o}$ C.

However, order with respect to P-chloro aniline could not be determined by isolation method, because concentration of P-chloro aniline is higher than bromate. Hence comparable concentrations of bromate and P-chloro aniline were taken to determine the overall order of the reaction. For this purpose bromate concentration was kept constant (1 x 10^{-2}M) while concentration of P-chloro aniline was varied from 4 x 10^{-2}M to 7 x 10^{-2} M.

5.3.1 Effect of potassium bromate variation:

The results of the variation of bromate concentration at constant substrate concentration (5 x 10^{-2}M) at 30^{o} C are given in the table No.5.3.1. The plot of $\log_{10}(a-x)$ versus time (t) is straight line, shown in Fig.No.5.3.1. It is seen that values of k are fairly constant. This shows that there is no effect of variation of bromate concentration on the value of k therefore order with respect to oxidant is one.

5.3.2 Effect of variation of P-chloro aniline Concentration :

The concentration of P-chloro aniline was varied from 4×10^{-2} M to 7×10^{-2} M, keeping the concentration of bromate (1×10^{-2} M) constant. The results are included in the table No.5.3.2. A plot of $\log_{10}(a-x)$ versus time (t) is straight line (Fig. No.5.3.4). The values of k increase with the P-chloro aniline concentration. The ratio of k/[P-chloro aniline] is fairly constant which shows that first order with P-chloro aniline. It is also seen from calculation of order by differential method[22]. Table No.5.3.3. The order is one (Fig.No.5.3.3.).

It is also confirmed by the graph of $\log_{10}k$ versus $\log_{10}Co$. The results are given in the table No.5.3.4. The graph is straight line having slope approximately equal to one Fig. No.5.3.4. This indicates that order with respect to P-chloro aniline is one.

5.4 Effect of sulphuric Acid on Reaction Rate :

The reaction was studied in strong Acidic medium. The concentration of sulphuric acid was varied from 4 N to 8 N. It is seen that, as the concentration of Acid was increased, the rate constantincreases, while the P-chloro aniline and bromate concentrations were kept constant. The results are given in the table No.5.3.5. K values are given by the graph of $\log_{10}(a-x)$ versus time (t). Fig.5.3.5. The order with respect to acid is one. Plot of $\log_{10}k$ versus $\log_{10}Co$ gives slope equal to one (Table No .5.3.9. Fig.No.5.3.9).

5.5 Effect of temperature on Reaction rate and Calculation of thermodynamic parameters :

The reaction was studied at four different temperatures ($303^{o}K$, $308^{o}K$, $313^{o}K$ and $318^{o}K$). The results are given in the table No.5.3.6. The graph of $\log_{10}(a-x)$ versus time (t) is shown in the Fig.No.5.3.6. From the values of specific reaction rate Kr at different temperature, it is seen that the temperature coefficient of reaction is 2.013.

Arrhenius equation was used to calculate the energy of activation Ea and frequency factor A. For this $\log_{10}K$ versus $\frac{1}{T}$ was plotted Fig.No.5.3.7, Table No. 5.3.7 which is straight line. Ea was obtained. The graphical value was found to be 12.377 K cal $mole^{-1}$.

The value of Ea was used to calculate the frequency factor (A).

The graph of $\log_{10} K/T$ versus $\frac{1}{T}$ was straight line Fig. No.5.3.8. Table No.5.3.7, which was used to calculate $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ from the usual relations, given in Chapter No. 3.

The values of energy of activation frequency factor, enthalpy of Activation, entropy of Activation and free energy of activation are given in the table No.5.3.8.

5.6 Free radical detection and End product Analysis :

The absence of free radical was shown by acrylonitrile test, which gives no precipitate. In a reaction mixture one ml of acrylonitrile was added, but there is no formation of precipitate which indicate absence of free radical formation.

The end product identified was to be chloroderivative of quinone [40,10] .

5.7 Salt effect :

It is observed that there is no salt effect on the reaction rate. The salts used were sodium sulphate, potassium sulphate, and Mangnesium sulphate.

5.8 Stiochiometry :

To determine the stoichiometry of bromate and P-chloro aniline, the reaction mixture was taken to be 2.5×10^{-2} M Bromate and 1×10^{-2} M P-chloro aniline. The blank and back reading were taken and the difference of these two were used to find out the stochiometry. The stoichometry is found to be 1:1 for Bromate and P-chloro aniline.

Table No. 5.3.1

Variation of Oxidant Concentration ($KBrO_3$)

[P.Chloro Aniline] = 5 x 10^{-2} Mole dm^{-3}

[Sodium thiosulphate] = 2 x 10^{-3} Mole dm^{-3}

[Sulphuric Acid] = 5 N

Temperature = $30^{o}C$

[Potassium Bromate] 10^{-3} M	2.5	5	7.5	10	12.5
Time (min)	(a-x)	(a-x)	(a-x)	(a-x)	(a-x)
0	9.5	18.5	26.6	36.2	45.1
5	--	17.3	25.1	34.2	42.5
10	8.5	16.2	23.6	32.2	40.0
15	--	15.3	22.2	30.2	37.8
20	7.5	14.4	20.9	28.6	35.8
25	--	13.7	19.9	27.2	34.3
30	6.7	13.0	19.0	26.0	32.8
35	--	12.3	18.1	24.9	31.3
40	6.1	11.8	17.2	23.8	29.8
45	--	11.41	16.4	22.7	28.3
50	5.5	11.0	15.7	21.6	27.0
55	--	10.6	15.1	20.6	25.7
60	5.0	10.2	14.6	19.7	24.5
K graphically (per min.)	1.02×10^{-2}	1.042×10^{-2}	1.096×10^{-2}	1.091×10^{-2}	1.097×10^{-2}
K Sec^{-1}	1.705×10^{-4}	1.736×10^{-4}	1.826×10^{-4}	1.818×10^{-4}	1.828×10^{-4}

Table No. 5.3.2

Variation of Substrate Concentration (P-Chloro Aniline)

[Potassium Bromate] = 1×10^{-2} mole dm^{-3}

[sulphuric Acid] = 5 N

[sodium Thiosulphate] = 2×10^{-3} Mole dm^{-3}

Temperature = $30^{o}C$

[P-Chloro Aniline] 10^{-2} M	4	5	6	7
Time (min)	(a-x)	(a-x)	(a-x)	(a-x)
00	38.5	38.4	38.5	38.5
05	36.6	36.0	35.2	34.8
10	34.8	33.8	33.0	32.0
15	33.0	31.8	31.0	29.5
20	31.5	30.0	28.2	27.0
25	30.0	28.2	27.2	25.0
30	28.5	26.4	24.6	23.1
35	27.1	24.8	23.0	21.5
40	25.9	23.4	21.4	20.1
45	24.9	22.0	20.1	18.5
50	23.9	21.0	18.2	17.0
55	22.0	20.0	17.1	15.1
60	21.2	19.0	16.2	13.3
K graphically per min	1.00×10^{-2}	1.228×10^{-2}	1.402×10^{-2}	1.645×10^{-2}
K Sec^{-1}	$1.668\ 10^{-4}$	2.046×10^{-4}	2.336×10^{-4}	2.741×10^{-4}

Table No 5.3.3

Order with respect to P-Chloro Aniline

[P-Cloro Aniline] 10^{-2}	$\frac{-dc}{dt}$	$\log_{10} Co$	$\log_{10} (\frac{-dc}{dt})$
4.0	0.2934	- 1.3979	- 0.5325
5.0	0.3620	- 1.3010	- 0.4416
6.0	0.4340	- 1.2219	- 0.3625
7.0	0.5090	- 1.1549	- 0.2932

Table No 5.3.4

Order with respect to P.Chloro Aniline

[P-Chloro Aniline]$_0$ 10^{-2} M	K	$\log_{10}K$	$\log_{10}Co$
4.0	1.001×10^{-2}	- 1.9995	- 1.3979
5.0	1.228×10^{-2}	- 1.9108	- 1.3010
6.0	1.402×10^{-2}	- 1.8532	- 1.2219
7.0	1.645×10^{-2}	- 1.7838	- 1.549

Table No.5.3.5

Effect of Sulphuric Acid Concentration

[Potassium Bromate] = $1x10^{-2}$ Mole dm^{-3}

[P-Chloro Aniline] = 0.05 Mole dm^{-3}

[Sodium Thiosulphate]= 0.002 Mole dm^{-3}

Temperature = $30^{o}C$

[Sulphuric Acid] N	4	5	6	7	8
Time (min)	(a-x)	(a-x)	(a-x)	(a-x)	(a-x)
0	36.2	36.2	36.2	36.3	36.0
5	34.4	34.2	33.3	33.0	32.0
10	32.5	32.2	30.2	29.7	28.2
15	30.7	30.2	28.0	26.8	25.1
20	29.2	28.5	25.9	25.0	22.6
25	27.9	27.0	24.0	23.0	20.5
30	26.7	25.5	22.2	21.2	19.0
35	25.4	24.0	20.8	19.5	17.5
40	24.1	22.7	19.6	18.4	16.0
45	22.9	21.7	18.4	17.3	14.6
50	21.9	20.2	17.3	16.3	13.5
55	20.9	19.1	16.3	15.3	12.5
60	20.0	18.0	15.2	14.5	11.8
K graphically (Permin)	$1.023x10^{-2}$	$1.223x10^{-2}$	$1.536x10^{-2}$	$1.87x10^{-2}$	$2.303x10^{-2}$
K Sec^{-1}	$1.705x10^{-4}$	$2.038x10^{-4}$	$2.56x10^{-4}$	$3.128x10^{-4}$	$3.83x10^{-4}$

Table No. 5.3.6

Effect of Temperature

[Potassium Bromate] = 1 x 10^{-2} Mole dm^{-3}

[P-Chloro Aniline] = 5 x 10^{-2} Mole dm^{-3}

[Sodium Thiosulphate] = 2 x10^{-3} Mole dm^{-3}

[Sulphuric Acid] = 5 N

Temperature °C	30	35	40	45
Time (min)	(a-x)	(a-x)	(a-x)	(a-x)
0	36.5	36.3	36.4	36.5
5	34.3	33.0	32.1	31.6
10	32.3	30.0	28.5	27.0
15	30.3	27.8	25.0	22.5
20	28.6	25.7	22.0	19.5
25	27.0	23.7	19.5	17.0
30	25.5	21.7	17.5	14.5
35	24.0	19.6	15.5	12.0
40	22.5	18.0	14.0	9.5
45	21.4	16.5	12.5	8.4
50	20.3	15.5	11.0	7.0
55	19.2	14.5	9.5	-
60	18.1	13.6	8.2	-
K.graphically Permin)	1.152×10^{-2}	1.706×10^{-2}	2.377×10^{-2}	3.350×10^{-2}
$KSec^{-1}$	1.92×10^{-4}	2.843×10^{-4}	3.961×10^{-4}	5.583×10^{-4}

Table No. 5.3.7

Temp T (^{O}K)	$\frac{1}{T} \times 10^{3}$	K	$\log_{10}k$	$\log_{10}k/T$
303	3.301	1.152×10^{-2}	- 1.9383	- 4.4199
308	3.246	1.706×10^{-2}	- 1.7680	- 4.2565
313	3.195	2.377×10^{-2}	- 1.6239	- 4.1195
318	3.144	3.350×10^{-2}	- 1.4743	- 3.9773

Table No.5.3.8

Temperature T (O_{KK})	K permin	Temperature co-efficient	Energy of activation E_aK, $Calmol^{-1}$	Enthalpy of Activation $\Delta H^{\neq}$	Frequency factor (A)Sec^{-1}	Entropy of Activation $\Delta S^{\neq}$ e.u.	Free energy of activation $\Delta G^{\neq}$ K $calmol^{-1}$
303	1.152×10^{-2}						
308	1.706×10^{-2}	2.06335	13.2945	12.377	6.0394×10^{-7}	- 27.0093	20.763
313	2.377×10^{-2}	1.9636					
318	3.350×10^{-2}						

Table No. 5.3.9.

Order with respect to Acid

[Sulphurc Acid] M	k	$\log_{10}K$	$\log_{10}Co$
4	1.023x10	- 1.9901	0.6020
5	1.223x10	- 1.9125	0.6990
6	1.536x10	- 1.8136	0.7782
7	1.877x10	- 1.7265	0.8450
8	2.303x10	- 1.6377	0.9031

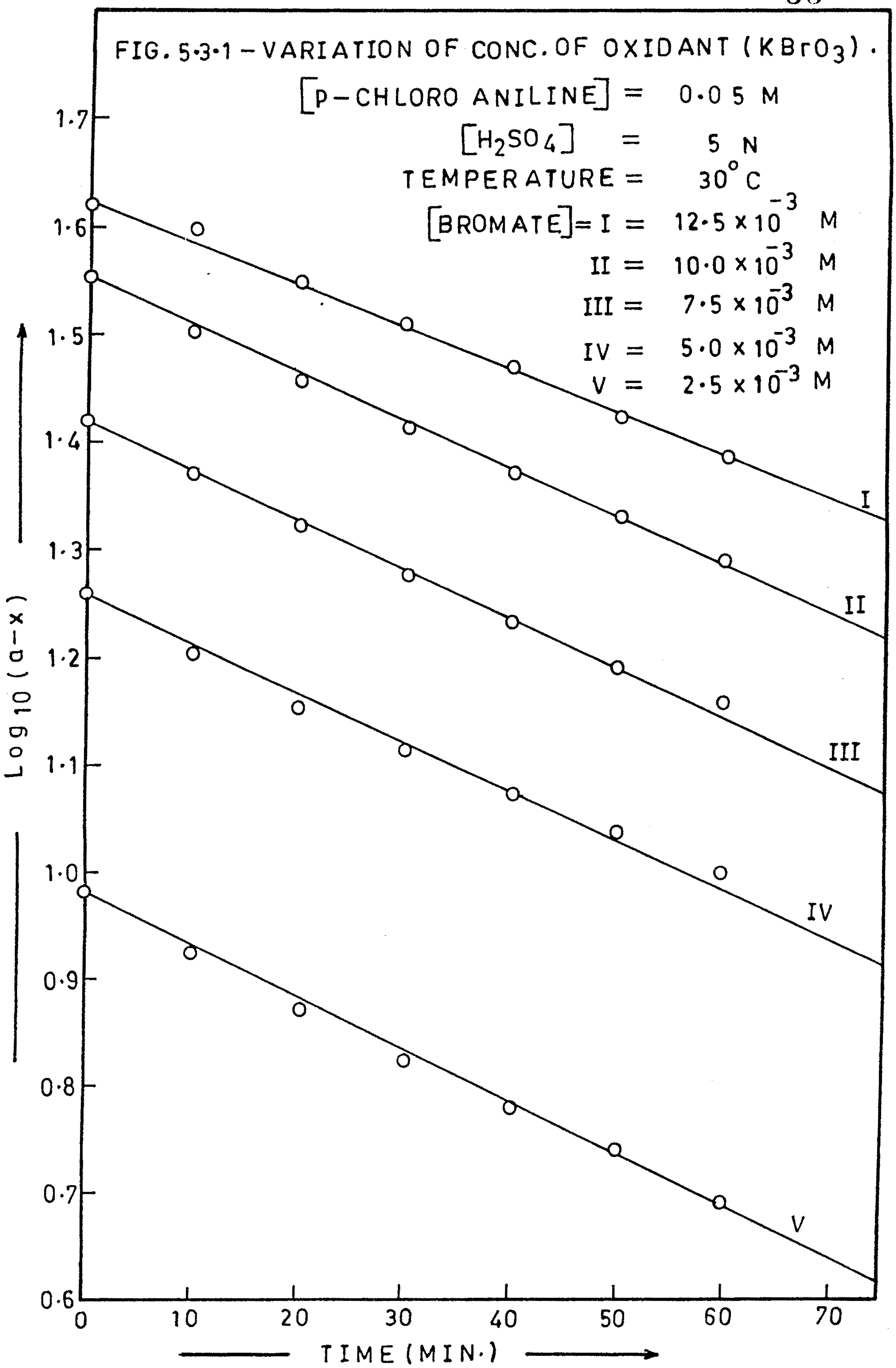


FIG. 5·3·1 – VARIATION OF CONC. OF OXIDANT (KBrO3).
[P-CHLORO ANILINE] = 0·05 M
[H2SO4] = 5 N
TEMPERATURE = 30°C
[BROMATE] = I = 12·5 × 10-3 M
II = 10·0 × 10-3 M
III = 7·5 × 10-3 M
IV = 5·0 × 10-3 M
V = 2·5 × 10-3 M
I
II
III
IV
V
Log10 (a–x)
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0
10
20
30
40
50
60
70
TIME (MIN.)

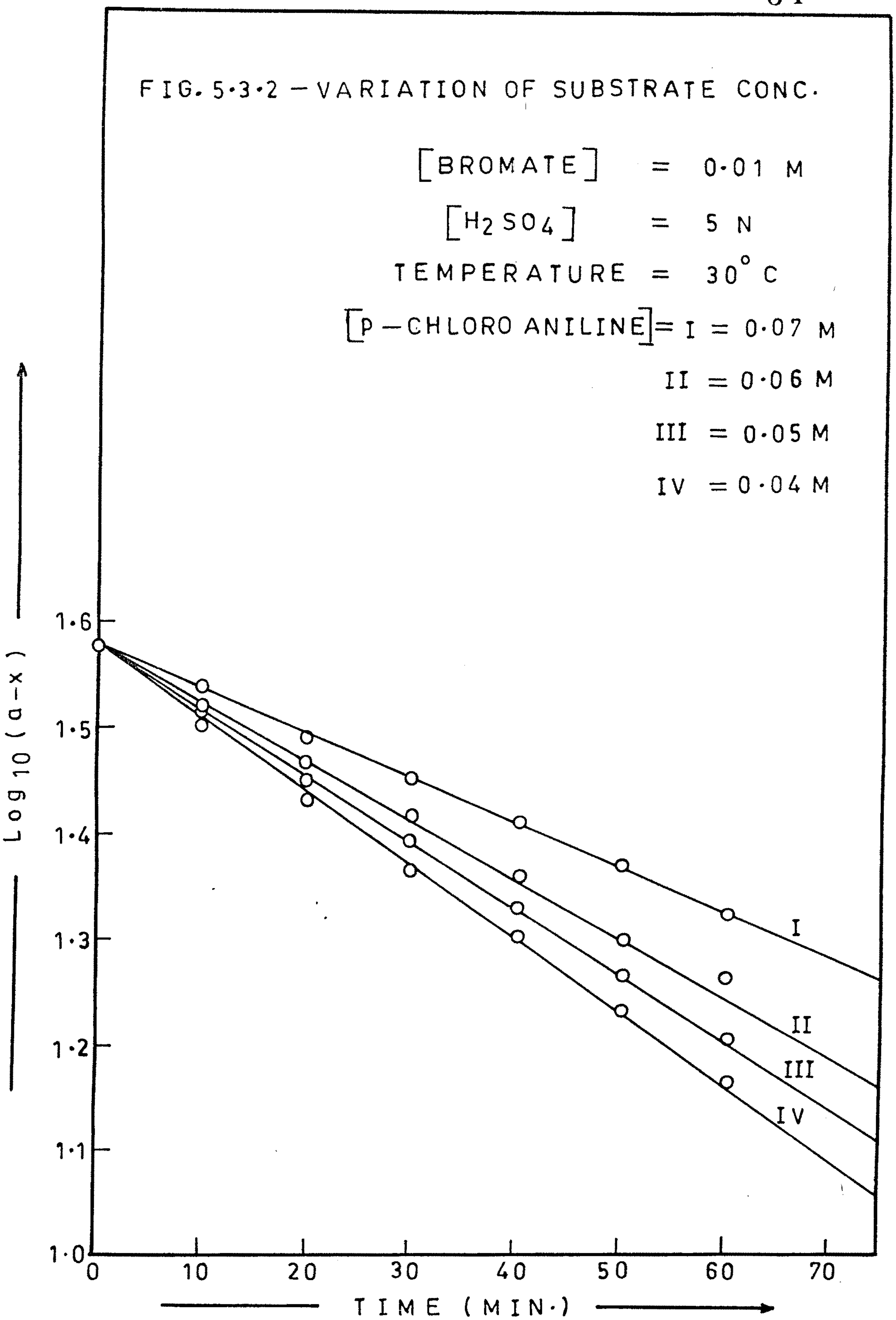


FIG. 5·3·2 — VARIATION OF SUBSTRATE CONC.
[BROMATE] = 0·01 M
[H_2SO_4] = 5 N
TEMPERATURE = 30° C
[P — CHLORO ANILINE] = I = 0·07 M
II = 0·06 M
III = 0·05 M
IV = 0·04 M
Log 10 (a−x)
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0
10
20
30
40
50
60
70
TIME (MIN·)
I
II
III
IV

FIG. 5·3·3 — VARIATION OF SUBSTRATE CONC.

PLOT OF $Log_{10}(-\frac{dc}{dt})_0$ VERSUS $Log_{10} C_0$.

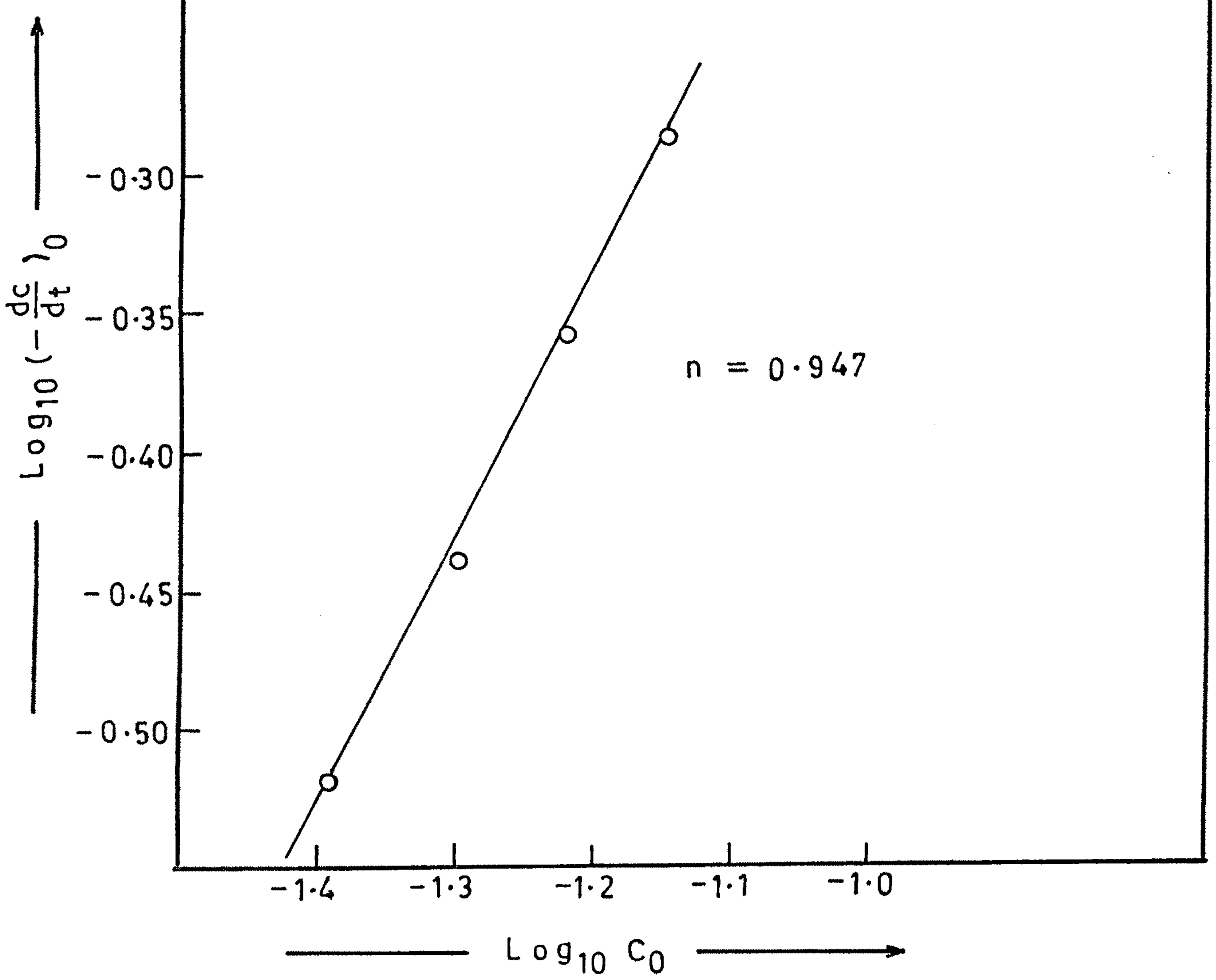
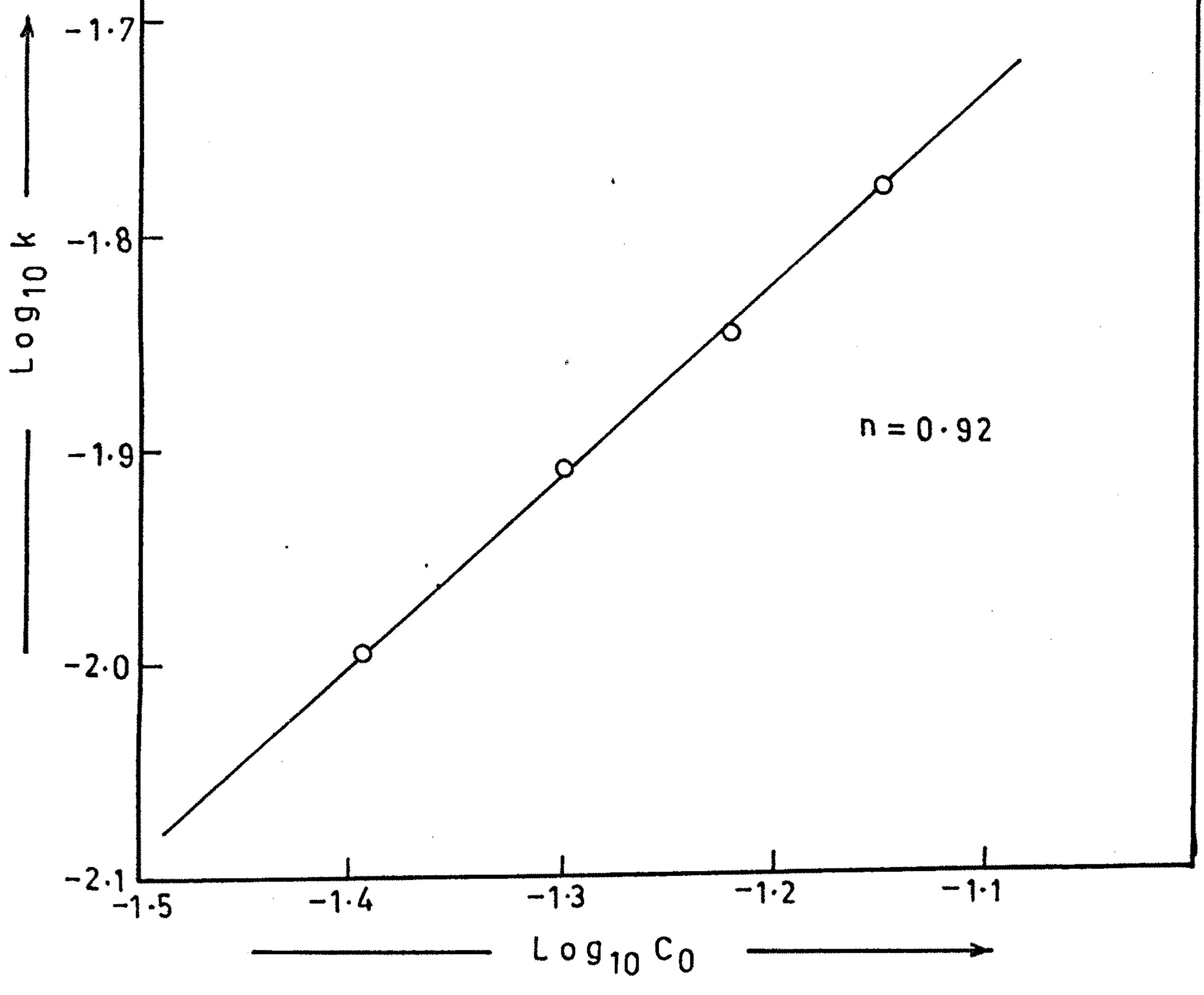


FIG.5·3·4 — VARIATION OF SUBSTRATE CONC.

PLOT OF $Log_{10} k$ VERSUS $Log_{10} C_0$.



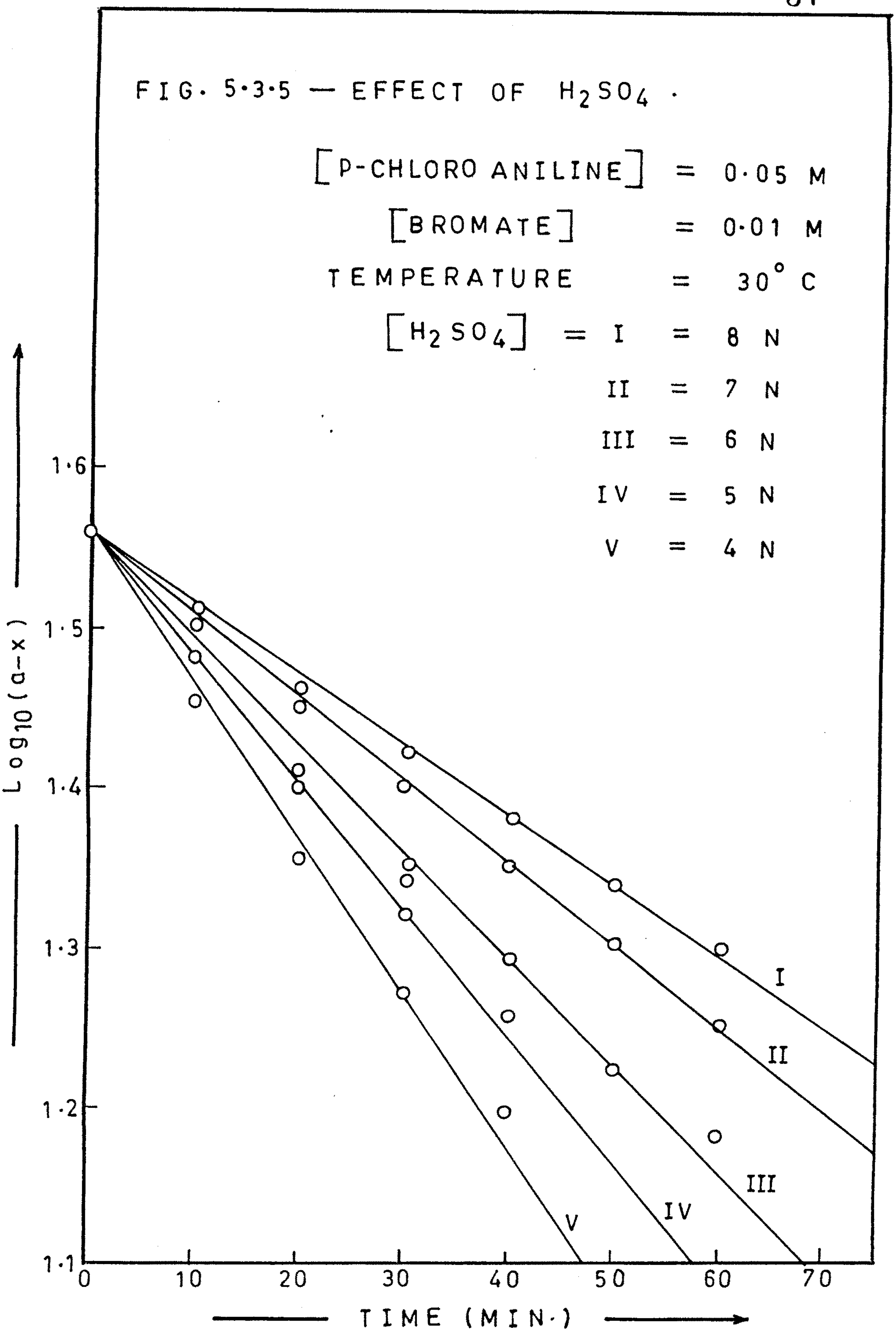


FIG. 5·3·5 — EFFECT OF H_2SO_4.
[P-CHLORO ANILINE] = 0·05 M
[BROMATE] = 0·01 M
TEMPERATURE = 30° C
[H_2SO_4] = I = 8 N
II = 7 N
III = 6 N
IV = 5 N
V = 4 N
$Log_{10}(a-x)$
1·6
1·5
1·4
1·3
1·2
1·1
0
10
20
30
40
50
60
70
TIME (MIN.)
I
II
III
IV
V

FIG.5·3·6 — EFFECT OF TEMPERATURE.

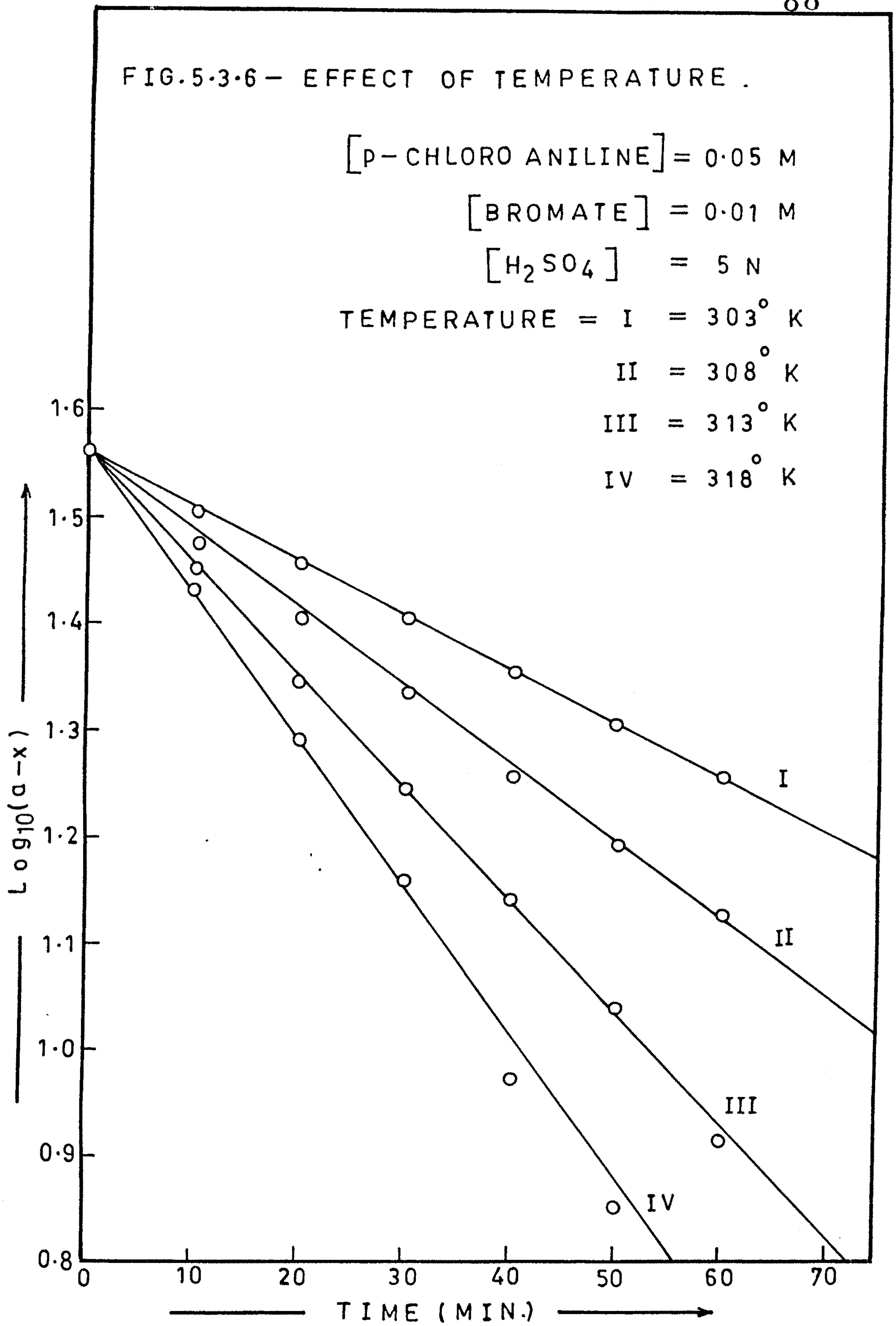
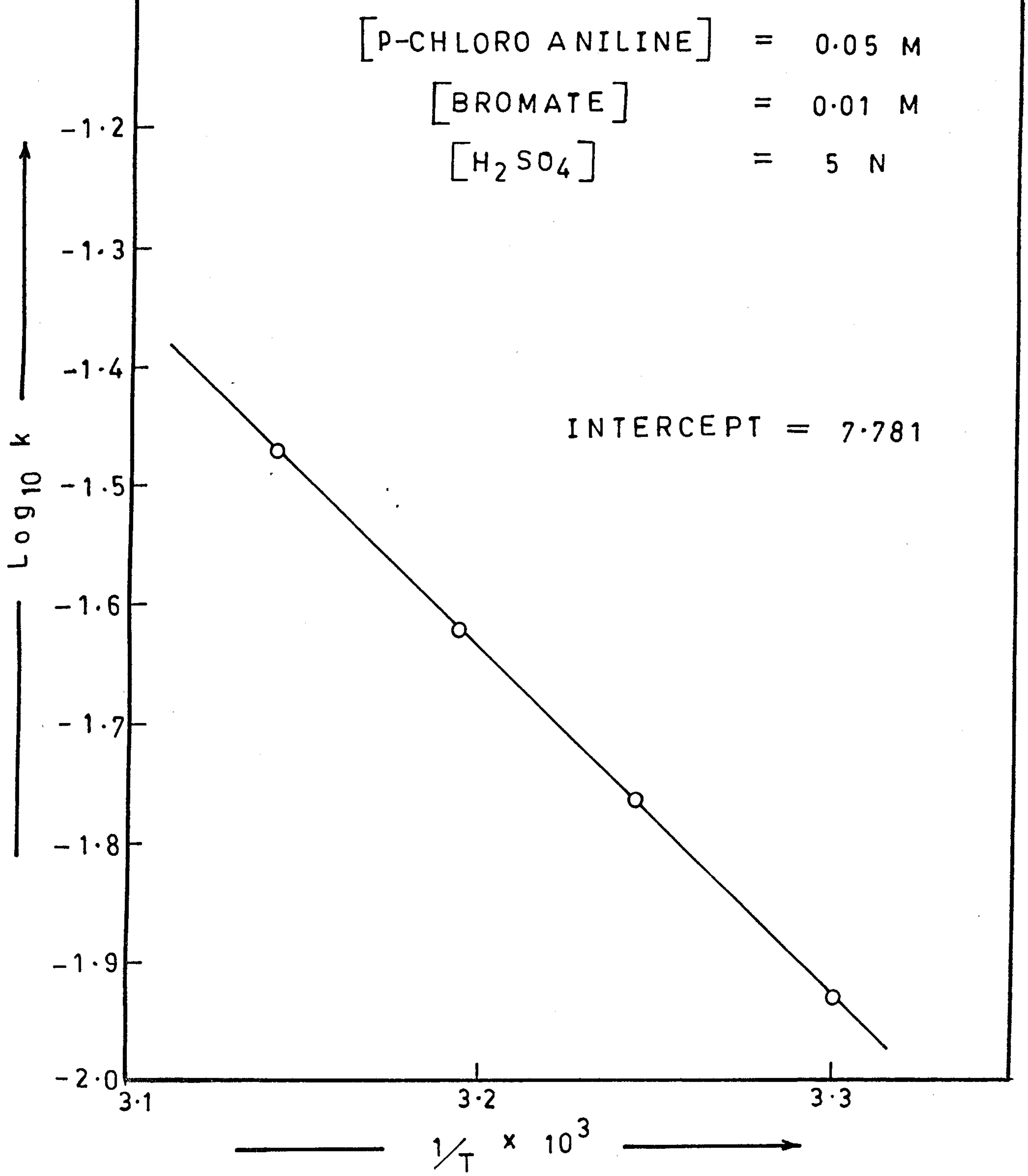


FIG. 5.3.7 — EFFECT OF TEMPERATURE.

PLOT OF $Log_{10} k$ VERSUS $1/T$.



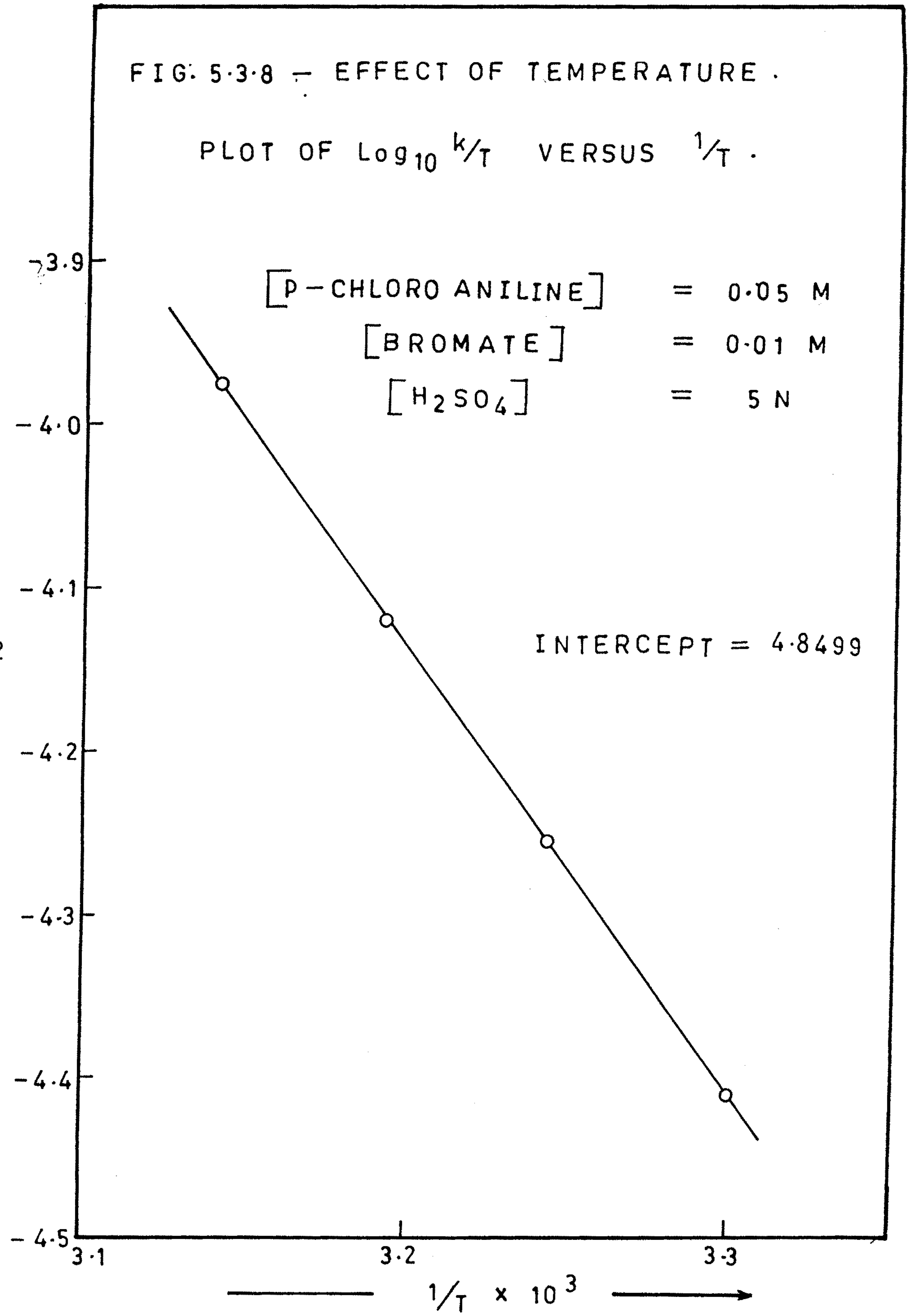


FIG. 5·3·8 — EFFECT OF TEMPERATURE.
PLOT OF Log10 k/T VERSUS 1/T.
[P-CHLORO ANILINE] = 0·05 M
[BROMATE] = 0·01 M
[H2SO4] = 5 N
INTERCEPT = 4·8499
-3·9
-4·0
-4·1
-4·2
-4·3
-4·4
-4·5
3·1
3·2
3·3
Log10 k/T
1/T x 10^3

FIG. 5·3·9 — EFFECT OF H_2SO_4 CONCENTRATION.

PLOT OF $Log_{10} k$ VERSUS $Log_{10} C_0$.