

Oxidation of O-Chloro anilineResults :4. R e s u l t s :

The results of the kinetics of oxidation of O-chloro aniline by potassium bromate in sulphuric acid medium is reported here. All reactions are carried out in pseudo first order conditions. Appropriate concentrations of potassium bromate, O-chloro aniline and sulphuric acid were taken to prepare the reaction mixtures. The 5 ml reaction mixtures is aliquoted periodically and titrated by usual iodometric method. Experiment 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 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.

4.1 Determination of order of reaction :

Order of reaction with respect to bromate was determined by isolation method. The concentration of potassium bromate was varied from 2.5×10^{-3} M to 12.5×10^{-3} M at constant concentration of 5×10^{-2} M O-chloro aniline. The reaction was studied at $30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. However, order with respect to O-chloro aniline could not be determined by isolation method, because concentration of O-Chloro aniline is higher than bromate. Hence, comparable concentration of bromate and O-chloro-aniline were selected to determine the overall order of the reaction. For this purpose bromate concentration was kept constant (1×10^{-2} M), while concentration of O-chloro aniline was varied from 4×10^{-2} M to 7×10^{-2} M.

4.2.1 Effect of potassium bromate variation :

The variation of concentration of bromate at constant substrate concentration (5×10^{-2} M) at 30°C , are given in the table No.4.2.1. The plot of $\log_{10}(a-x)$ versus time (t) is straight line, shown in fig. No.4.2.1. It is seen that the values of k are constant. This shows that, there is no effect of variation of bromate concentration on the value of k. Therefore order with respect to bromate is one.

4.2.2 Effect of Variation of O-chloro-aniline Concentration

The concentration of O-chloro aniline was varied from $4 \times 10^{-2} \text{M}$ to $7 \times 10^{-2} \text{M}$ keeping the concentration of bromate constant ($1 \times 10^{-2} \text{M}$). The results are included in the table No.4.2.2. A plot of $\log_{10}(a-x)$ versus time (t) is straight line (Fig.No.4.2.2). The values of k increase with the concentration of O-chloro-aniline. However the ratio $k / [\text{O-chloro Aniline}]$ is fairly constant, which shows that first order with O-chloro aniline. By differential method²² it is also seen for the calculation of order is one (Table No.4.2.3 Graphical value of order is one (Fig.No.4.2.3.)).

It is also confirmed by the graph of $\log_{10} k$ versus $\log_{10} C_0$. Table No.4.2.4. The graph is straight line having slope approximately equal to one. (Fig.No.4.2.4). This clearly indicate that order with respect to O-chloro aniline is one.

4.3 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 values of rate constant increase, while the O-chloro aniline and bromate concentrations was kept constant. The results are given in the table No.4.2.5. and the values of k are given by the graph of $\log_{10}(a-x)$ versus time (t) (Fig. No.4.2.5.). The order with respect to Acid is one plot of $\log_{10} k$ versus $\log_{10} C_0$. Slope equal $^+0$ one Fig. No.4.2.9. . Table No. 4.2.9.

4.4 Effect of temperature on reaction rate and calculation of thermodynamic parameters.

The reaction was studied at four different temperatures (298°K , 303°K , 308°K and 313°K). The results are given in the table No.4.2.6. Graphical representation of $\log_{10}(a-x)$ versus time (t) is shown in Fig.No.4.2.6. From the values of specific reaction rate k_r at different temperatures, it is seen that temperature coefficient of reaction is 2.02.

From the Arrhenius equation ²³ given in Chapter No.3 The energy of activation E_a , and frequency factor A was calculated, for this $\log_{10} k$ versus $\frac{1}{T}$ was plotted. Fig.No.4.2.7. Table No.4.2.7 which is straight line, E_a was obtained from the slope. This value was found to be $13.17 \text{ K cal mole}^{-1}$.

This above value of E_a was used to calculate the frequency factor A .

The graph of $\log_{10} K/T$ versus $\frac{1}{T}$ was plotted which is straight line. Table No.4.2.7. Fig No.4.2.8. Which was used to calculate ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger from the usual relations which are used in Chapter No.3.

The values of energy of activation E_a , frequency factor (A), entropy of activation (ΔS) enthalpy of activation (ΔH) and free energy of activation are given in the table No.4.2.8.

4.5. Free radical detection and end product Analysis :

The absence of free radical was shown by the acrylonitrile³⁰ test, which gives no precipitate to the reaction mixture. In a reaction mixture one ml of acrylonitrile was added, but there is no formation of precipitate takes place, which indicates the absence of free radical.

End product identified was to be chloroderivative of quinone^{40 10}:

4.6 Salt Effect :

It is found that there is no salt effect on the reaction rate. The salts used were sodium sulphate, Potassium sulphate and magnesium sulphate.

4.7 Stoichiometry :

To determine the stoichiometry of bromate and O-chloro aniline, the reaction mixture was of $2.5 \times 10^{-2} \text{M}$ bromate and $1 \times 10^{-2} \text{M}$ O-chloro aniline. The blank and back readings were taken and the difference of these two were used to find out the stoichiometry. It is found to be 1:1 for bromate and O-chloro aniline.

Variation of Concentration of Oxidant (KBrO_3)[O-Chloro Aniline] = $5 \times 10^{-2} \text{M}$

[Sulphuric Acid] = 5N

[Sodium Thiosulphate] = $2 \times 10^{-3} \text{M}$ Temperature = 30°C

[Potassium Bromate] 10^{-3}M	2.5	5	7.5	10.0	12.5
time (min)	(a-x)	(a-x)	(a-x)	(a-x)	(a-x)
0	9.6	18.5	27.8	36.7	45.3
5	8.4	16.5	24.4	32.8	40.2
10	7.3	14.5	21.4	28.3	35.1
15	6.5	12.7	18.8	24.9	30.3
20	6.8	11.3	16.7	22.0	27.6
25	5.2	10.1	14.8	19.7	24.9
30	4.7	9.1	13.3	17.5	22.5
35	4.2	8.2	12.2	16.0	20.2
40	3.8	7.4	11.2	14.5	18.0
45	-	6.8	10.2	13.4	16.5
50	3.2	6.4	9.4	12.5	15.5
60	2.9	5.8	8.2	11.0	14.0
55	-	6.1	8.8	11.7	14.8
K graphically Permin)	2.303×10^{-2}	2.30×10^{-2}	2.303×10^{-2}	2.30×10^{-2}	2.303×10^{-2}
K Sec^{-1}	3.838×10^{-4}	3.838×10^{-4}	3.838×10^{-4}	3.838×10^{-4}	3.838×10^{-4}



Table No. 4.2.2

Variation of Concentration of substrate

[O-Chloro Aniline]

[Potassium Bromate] = $1 \times 10^{-2} \text{ M}$

[Sulphuric Acid] = 5 N

[Sodium Thiosulphate] = $2 \times 10^{-3} \text{ M}$ (Temperature) = 30°C

[O-Chloro Aniline] 10^{-2} M	4	5	6	7
Time (min)	(a-x)	(a-x)	(a-x)	(a-x)
0	36.1	36.1	36.0	36.0
5	32.8	32.0	31.3	30.6
10	29.4	28.3	26.8	25.6
15	26.4	24.5	23.0	21.5
20	24.0	21.9	20.2	18.0
25	21.7	19.5	18.0	16.0
30	20.0	17.5	15.8	14.3
35	18.3	16.0	14.0	12.8
40	17.0	14.6	13.0	11.5
45	15.6	13.4	12.0	10.6
50	14.5	12.4	11.0	9.8
55	13.6	11.7	10.2	9.2
60	12.7	11.0	9.5	8.6
K graphically (Permin)	1.772×10^{-2}	2.303×10^{-2}	2.590×10^{-2}	3.243×10^{-2}
K Sec^{-1}	2.953×10^{-4}	3.838×10^{-4}	4.316×10^{-4}	5.405×10^{-4}

Table No.4.2.3

Order with respect to O-Chloro Aniline

[O-Chloro Aniline] $10^{-2}M$	$-\frac{(dc)}{(dt)}$	$\log_{10}C_0$	$\log_{10}\left(\frac{-dc}{dt}\right)$
4.0	0.7857	-1.3979	-0.1047
5.0	0.9166	-1.3010	-0.03778
6.0	1.1	-1.2219	+0.04139
7.0	1.222	-1.1549	+0.08715

Table No.4.2.4

[O-Chloro Aniline] $10^{-2}M$	K	$\log_{10}K$	$\log_{10}C_0$
4.0	1.772×10^{-2}	-1.7515	-1.3979
5.0	2.303×10^{-2}	-1.6377	-1.3010
6.0	2.590×10^{-2}	-1.5867	-1.2219
7.0	3.243×10^{-2}	-1.4890	-1.1549

Effect of Sulphuric Acid Concentration

[Potassium Bromate] = $1 \times 10^{-2} \text{M}$ [O-Chloro Aniline] = $5 \times 10^{-2} \text{M}$ [Sodium Thiosulphate] = $2 \times 10^{-3} \text{M}$ Temperature = 30°C

[Sulphuric Acid] (N)	4	5	6	7	8
Time (Min)	(a-x)	(a-x)	(a-x)	(a-x)	(a-x)
0	36.8	36.8	36.8	36.5	36.4
5	34.0	32.5	31.9	29.7	29.0
10	30.8	28.5	27.2	24.5	22.4
15	28.0	24.8	23.2	20.2	18.4
20	25.4	22.0	20.2	17.5	15.5
25	23.0	19.5	17.9	15.0	13.6
30	21.0	17.5	16.0	13.4	12.2
35	19.4	16.0	14.5	12.0	11.3
40	17.8	14.8	13.3	11.0	10.5
45	16.6	13.6	12.3	10.5	10.0
50	15.5	12.7	11.6	10.0	9.5
55	14.5	11.8	11.0	9.5	9.0
60	13.6	11.0	10.4	-	-
k graphically (Permin)	1.772×10^{-2}	2.215×10^{-2}	2.878×10^{-2}	3.57×10^{-2}	4.064×10^{-2}
K Sec ⁻¹	2.953×10^{-4}	3.691×10^{-4}	4.796×10^{-4}	5.95×10^{-4}	6.775×10^{-4}

Table No.4.2.6

Effect of Temperature

[Potassium Bromate]	=	1×10^{-2} M
[O.Chloro Aniline]	=	5×10^{-2} M
[Sodium Thiosulphate]	=	2×10^{-3} M
[Sulphuric Acid]	=	5N

Temperature	25	30	35	40
OC				
Time	(a-x)	(a-x)	(a-x)	(a-x)
0	38.4	37.9	37.9	37.9
5	35.2	33.2	31.3	29.4
10	31.8	29.0	26.0	22.6
15	28.9	25.6	21.6	17.4
20	26.1	22.2	18.5	13.6
25	24.0	19.9	16.3	11.2
30	21.9	17.8	14.1	9.5
35	20.0	16.1	12.5	8.3
40	18.5	14.6	11.4	7.4
45	17.0	13.5	10.6	6.7
50	15.9	12.5	9.8	6.4
55	15.0	11.7	9.2	6.1
60	14.2	11.0	8.8	-
K graphically (permin)	1.783×10^{-2}	2.407×10^{-2}	3.476×10^{-2}	5.076×10^{-2}
K Sec ⁻¹	2.971×10^{04}	4.011×10^{-4}	$4.011 \times 10^{0-4}$	8.46×10^{-4}

Table No.4.2.7

Temp O_K	$\frac{1}{T} \times 10^3$	K	$\log_{10} K$	$\log_{10} K/T$
298	3.355	1.783×10^{-2}	-1.7488	-4.2230
303	3.301	2.407×10^{-2}	-1.6188	-4.0999
308	3.246	3.476×10^{-2}	-1.4589	-3.9474
313	3.195	5.046×10^{-2}	-1.2970-	-3.7925

Table No. 4.2.8

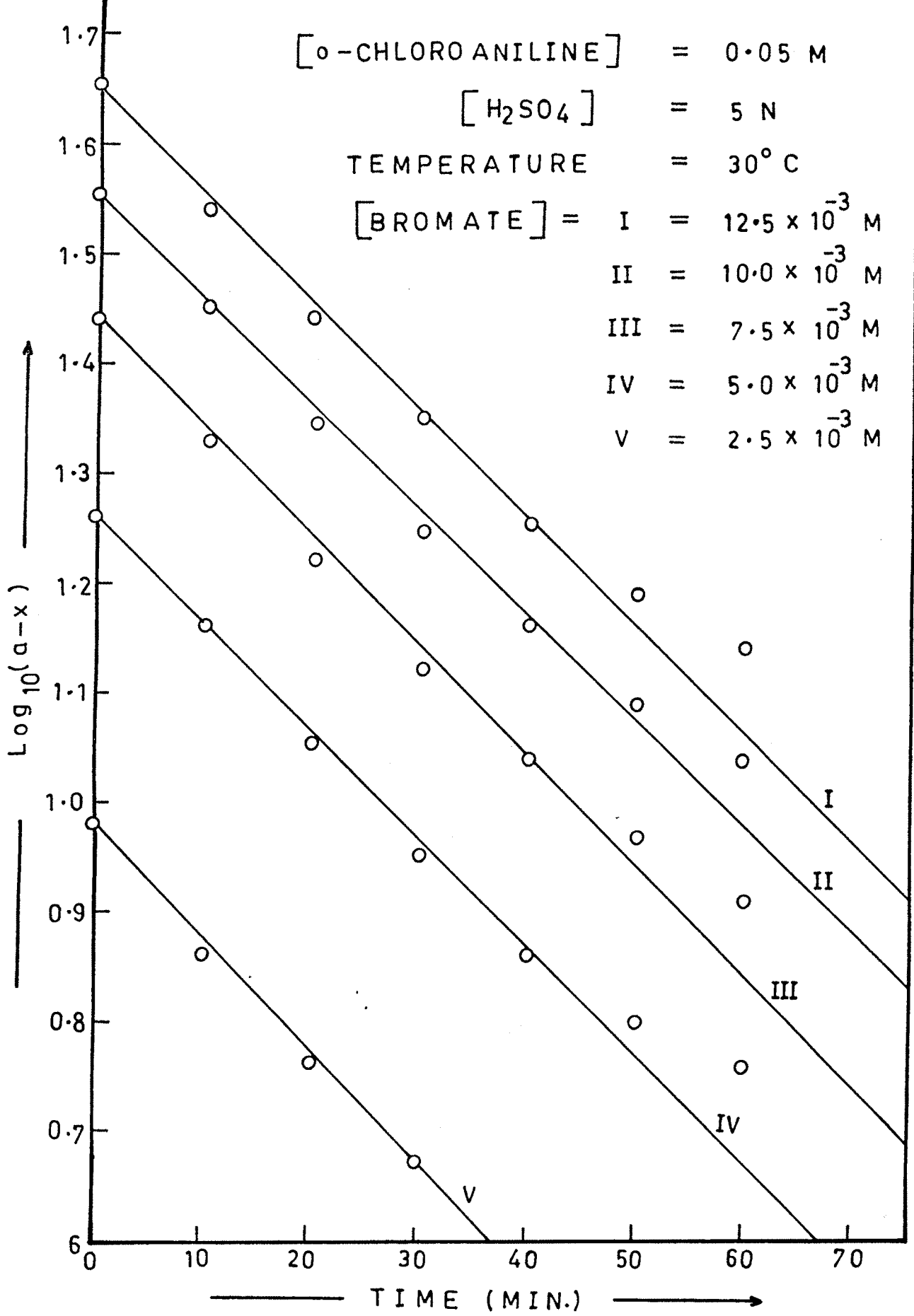
Temperature T (°K)	per min. K	Temperature coefficient	Energy of Activation Ea, K.Cal mol ⁻¹	Enthapy of Activation ΔH #	Frequency Factor (A) Sec ⁻¹	Entropy of Activation ΔS # e.u.	Free energy of Activation ΔG # K cal mol ⁻¹
298	1.783×10^{-2}						
303	2.407×10^{-2}	1.9495	13.71	12.1562	5.445×10^7	-27.1653	20.450
308	3.476×10^{-2}	2.0963					
313	5.046×10^{-2}						

Table No.4.2.9

Order with respect to Acid.

[Sulphuric Acid] N	K	Log ₁₀ K	Log ₁₀ Co
4	1.772 x 10 ⁻²	-1.7515	0.6020
5	2.215 x 10 ⁻²	-1.6546	0.6990
6	2.878 x 10 ⁻²	-1.5409	0.7782
7	3.570 x 10 ⁻²	-1.4473	0.8450
8	4.064 x 10 ⁻²	-1.3911	0.9030

FIG.4.2.1 - VARIATION OF CONC. OF OXIDANT (KBrO₃).



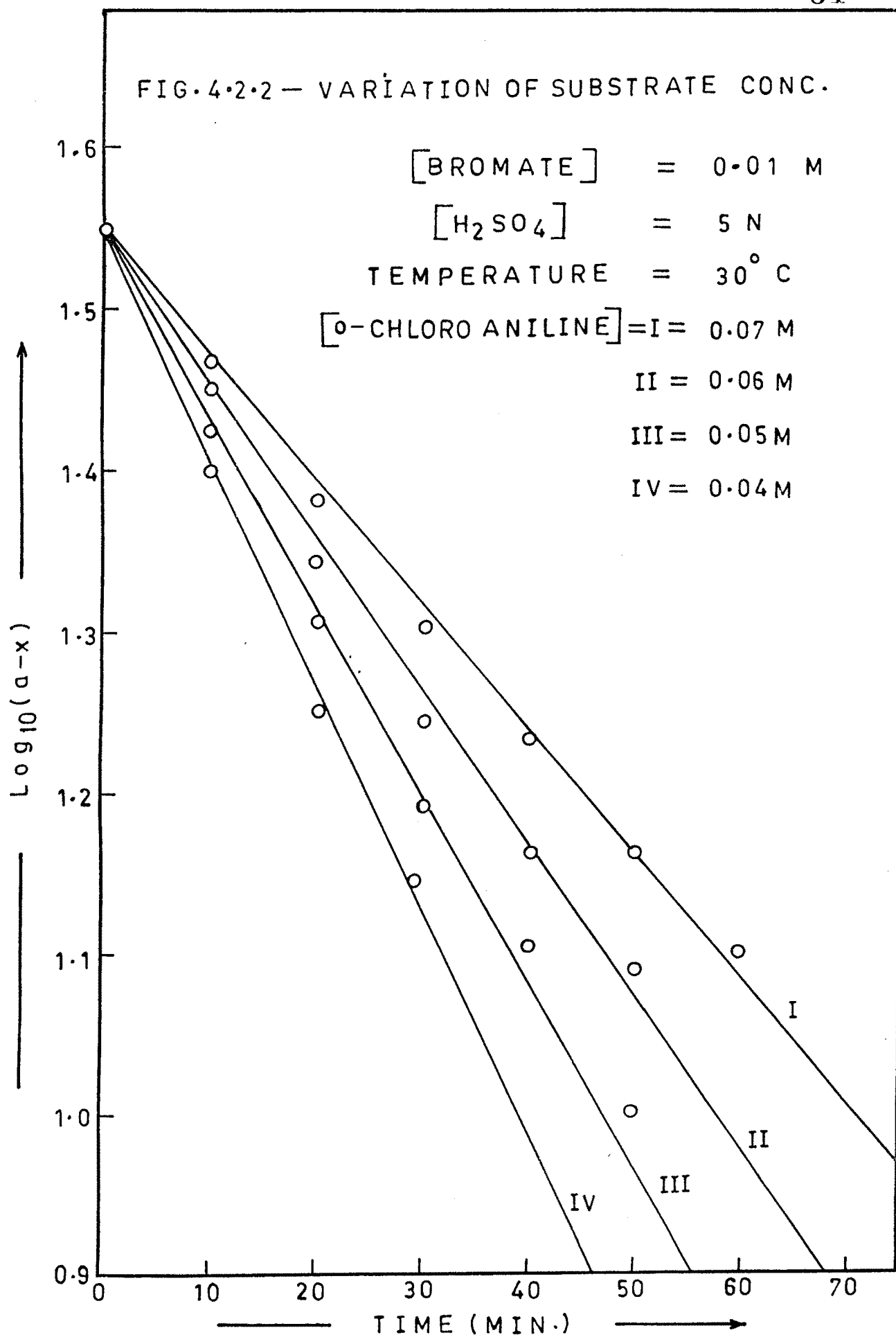


FIG.4.2.3 - VARIATION OF SUBSTRATE CONC.

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

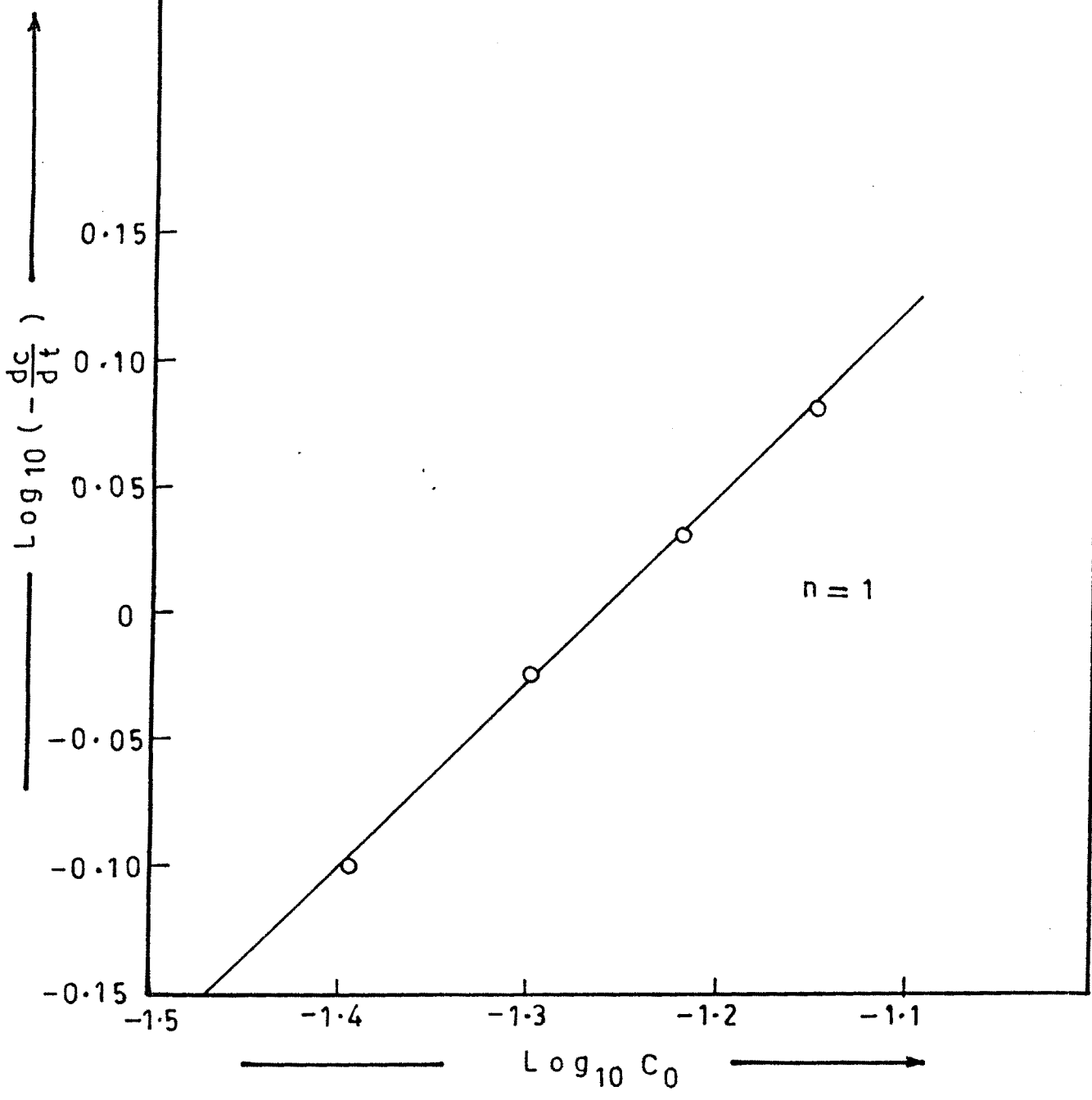


FIG. 4.2.4 — VARIATION OF SUBSTRATE CONC.

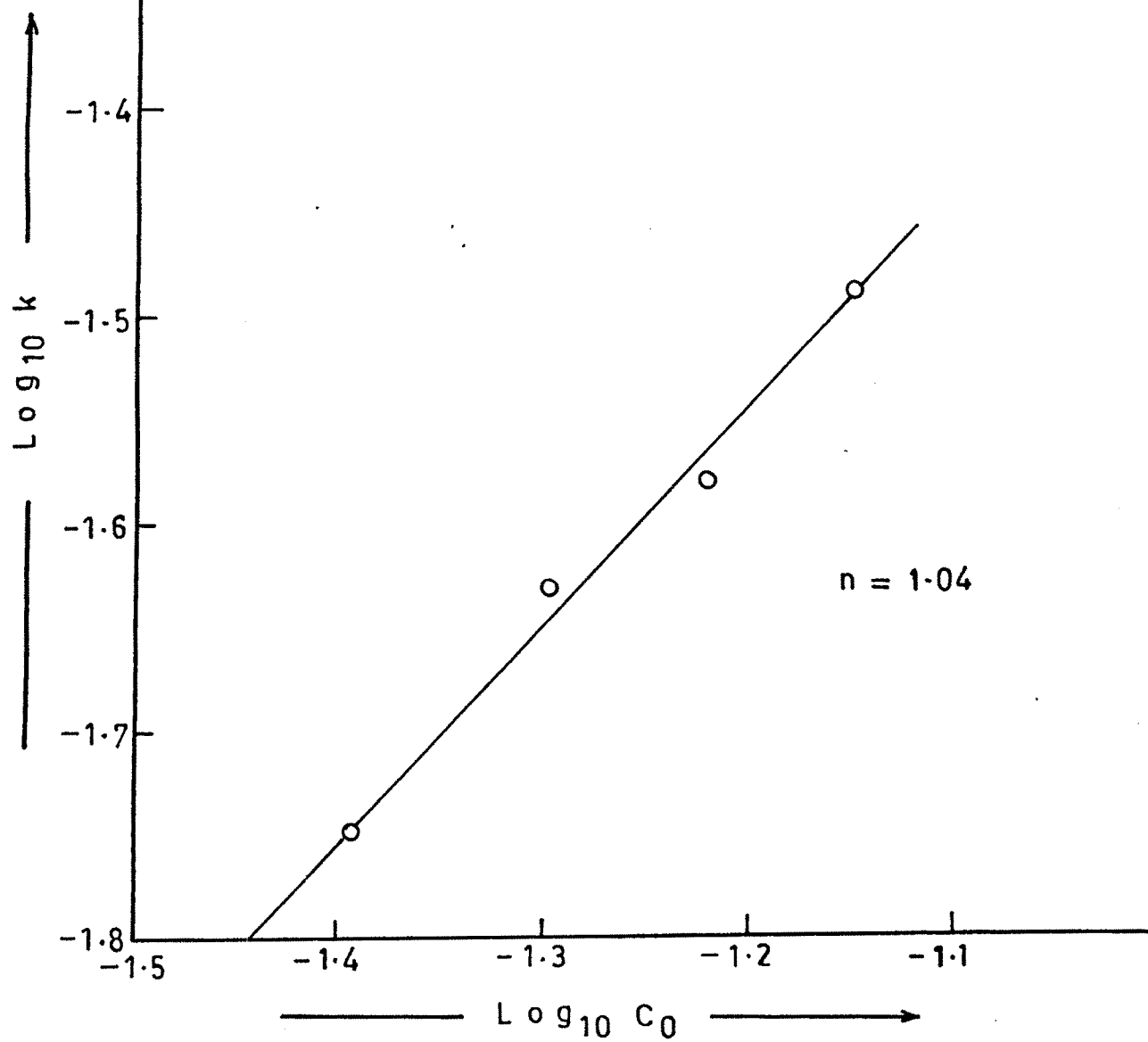
PLOT OF $\text{Log}_{10} k$ VERSUS $\text{Log}_{10} C_0$.

FIG. 4-2-5 — EFFECT OF H_2SO_4 . $[o\text{-CHLORO ANILINE}] = 0.05 \text{ M}$ $[\text{BROMATE}] = 0.01 \text{ M}$ TEMPERATURE = 30° C $[H_2SO_4] = \text{I} = 8 \text{ N}$

II = 7 N

III = 6 N

IV = 5 N

V = 4 N

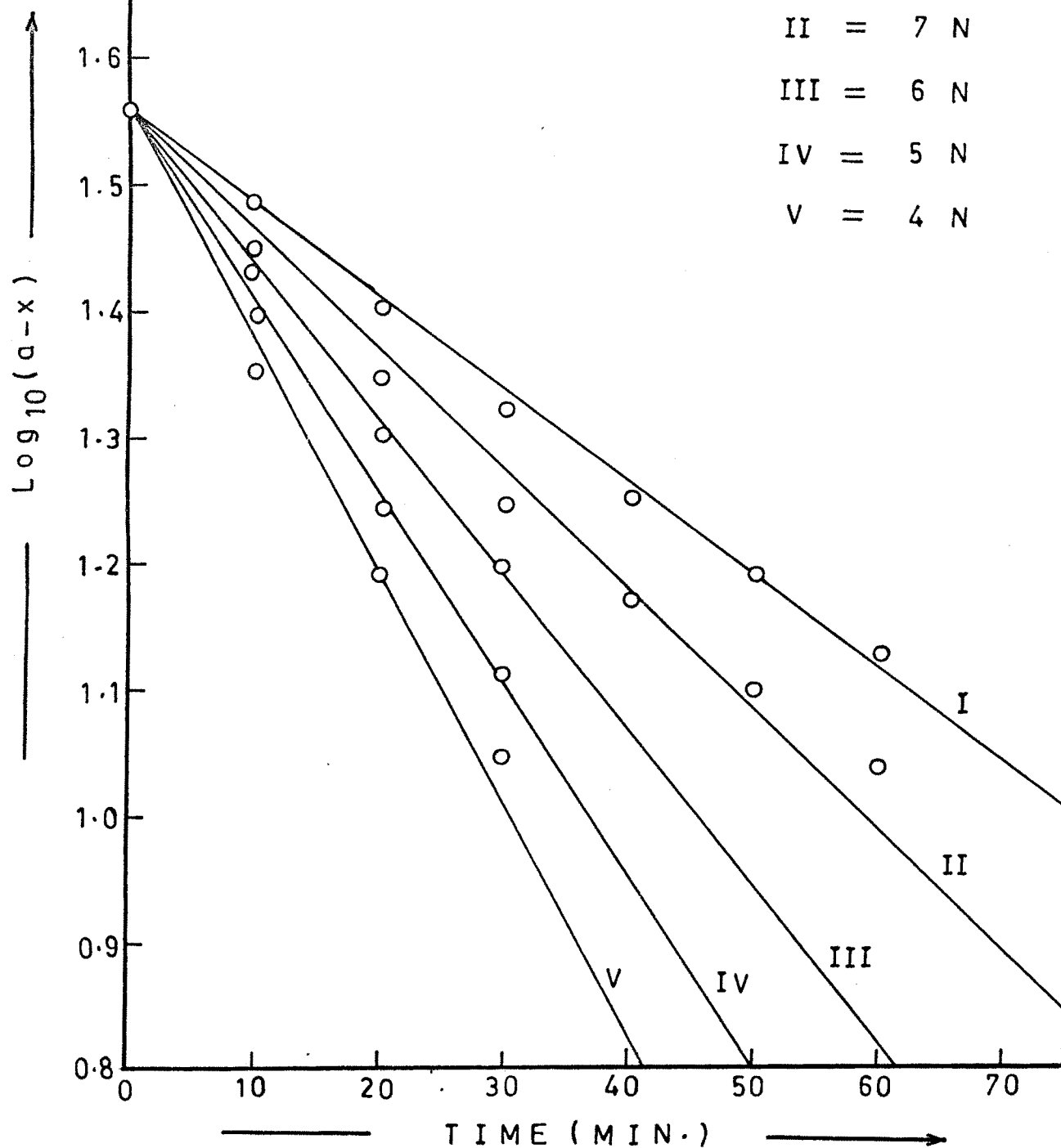


FIG. 4.2.6 — EFFECT OF TEMPERATURE.

[o-CHLORO ANILINE] = 0.05 M

[BROMATE] = 0.01 M

[H₂SO₄] = 5 N

TEMPERATURE = I = 298° K

II = 303° K

III = 308° K

IV = 313° K

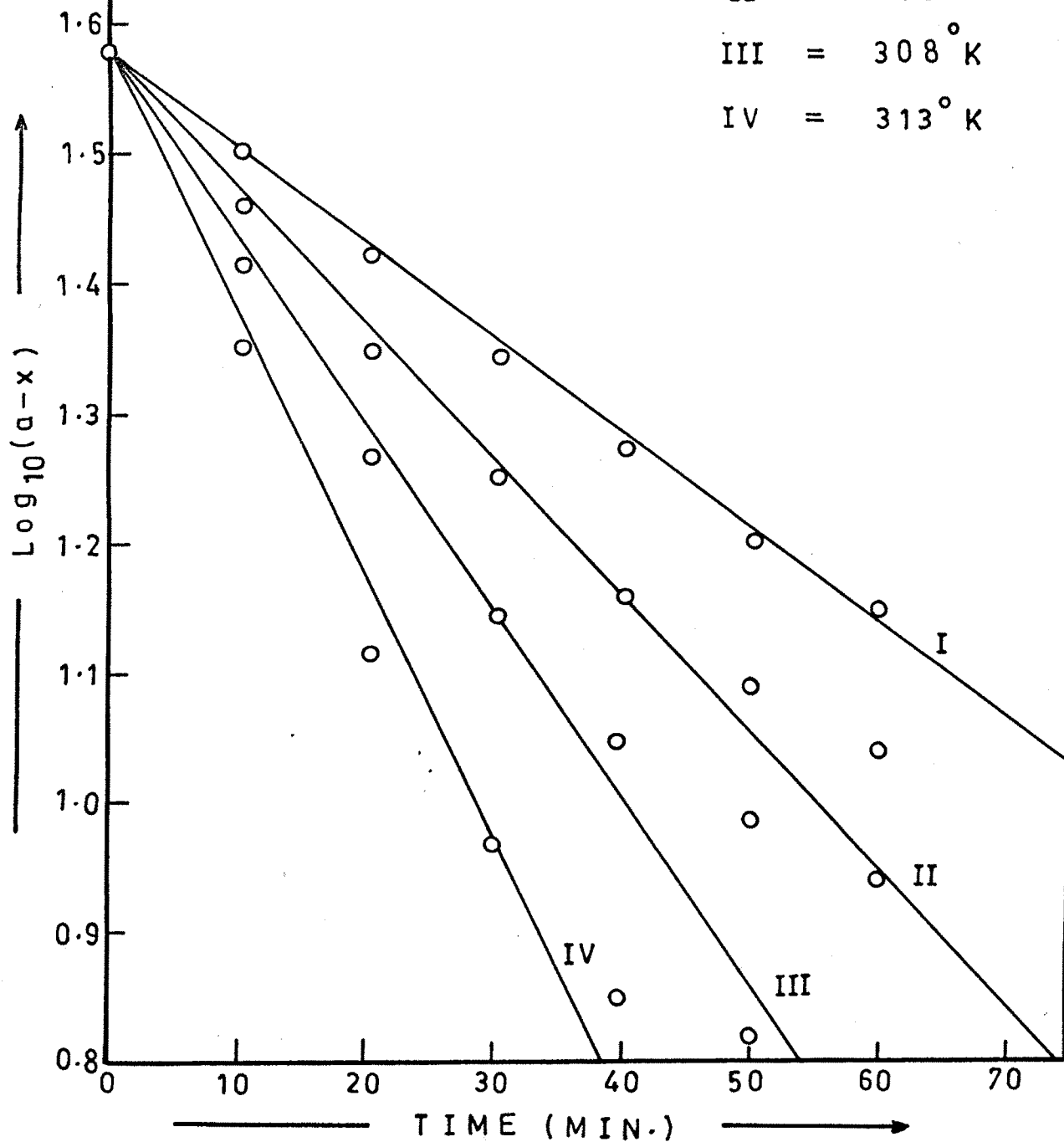


FIG. 4.2.7 - EFFECT OF TEMPERATURE .

PLOT OF $\text{Log}_{10} k$ VERSUS $1/T$.

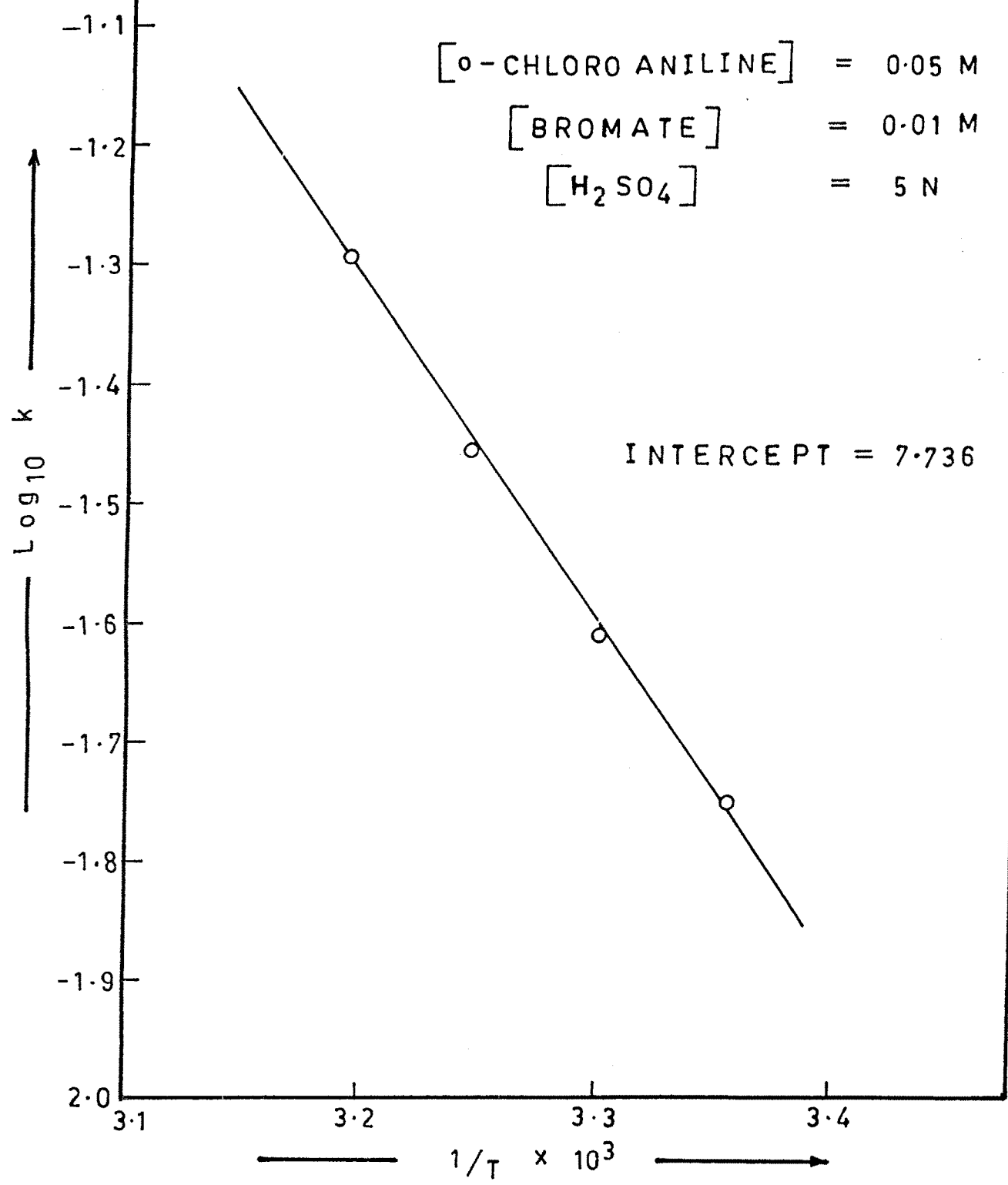


FIG. 4.2.8 - EFFECT OF TEMPERATURE .

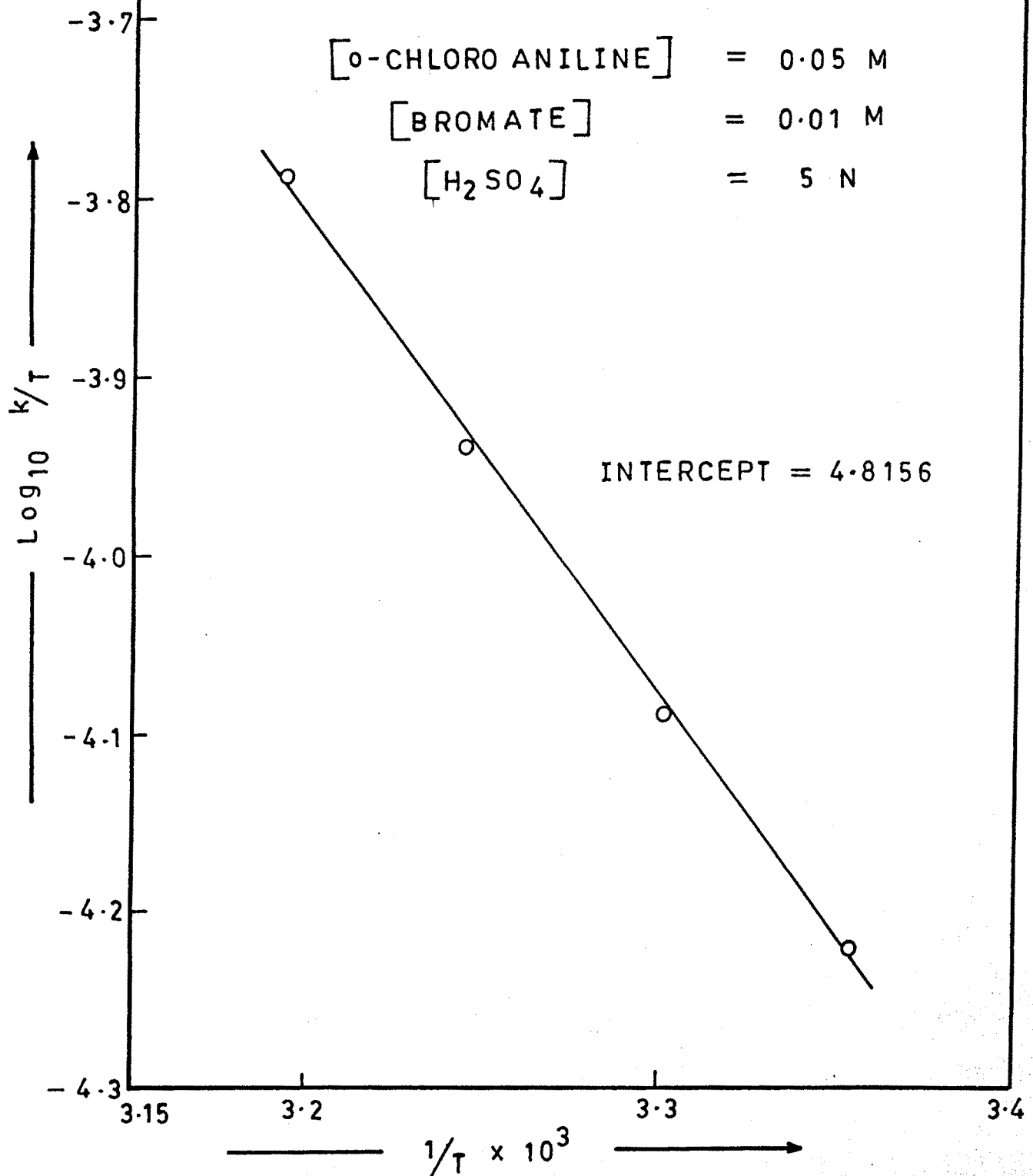
PLOT OF $\text{Log } k/T$ VERSUS $1/T$.

FIG. 4.2.9 - EFFECT OF H_2SO_4 CONCENTRATION.PLOT OF $\text{Log}_{10} k$ VERSUS $\text{Log}_{10} C_0$.