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CHAPTER - III  
SEC - I KINETICS OF OXIDATION OF  
O-TOLUIDINE

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## CHAPTER - III

## SECTION - I

3.1 KINETICS OF OXIDATION OF o-TOLUIDINE :

Preliminary experiments were performed in order to decide the suitable temperature and concentration of the reactants. It was observed that the reaction proceeds with measurable velocity at  $35^{\circ}\text{C}$  and when the concentrations of o-Toluidine was  $2.5 \times 10^{-2}\text{M}$  and that of potassium bromate was  $2.5 \times 10^{-3}\text{M}$  and that of sulphuric acid was  $1.25\text{M}$ . The kinetic data have been recorded in Table 3.1.1

TABLE 3.1.1

[o-Toluidine] =  $2.5 \times 10^{-2}\text{M}$        $[\text{H}_2\text{SO}_4] = 1.25\text{M}$   
 $[\text{KBrO}_3] = 2.5 \times 10^{-3}\text{M}$       Temp =  $35^{\circ}\text{C}$ ,  $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 2 \times 10^{-3}\text{M}$

Time (min)	Vol. of $\text{Na}_2\text{S}_2\text{O}_3$ (ml)	$k \times 10^2 \text{min}^{-1}$
0	38.40	-
5	36.20	1.1799
10	33.20	1.4550
15	30.80	1.4702
20	29.00	1.4038
25	26.50	1.4836
30	25.80	1.3226
35	23.30	1.4274
40	22.30	1.3586
45	20.80	1.3624
50	19.30	1.3759
55	18.20	1.3575
60	16.70	1.3877
Mean $k \times 10^2 \text{min}^{-1}$		1.3825

A perusal of the above data closely shows that pseudo first order specific rate is almost constant. In this experiment the *o*-Toluidine concentration is in excess over the potassium bromate concentration.

### 3.1.1 EFFECT OF VARIATION OF POTASSIUM BROMATE CONCENTRATION :

In order to investigate the effect of potassium bromate concentration, it was also considered necessary to employ the data of the kinetic runs to determine the order of the reaction with respect to potassium bromate, keeping the concentrations of *o*-Toluidine and that of sulphuric acid unchanged. For this purpose the reaction was carried out at five different concentrations of potassium bromate by keeping the concentrations of other reagents constant. Table 3.1.2 embodies the result of these kinetic runs and for the sake of comparison, the data of the Table 3.1.1. has also been incorporated in it. The data has been represented in Fig 3.1.1. The values of first order rate constant (viz.  $k$ ) have been evaluated from the initial slope of the curves, shown in Fig 3.1.1 as well as calculated at different times by integration method, which are in good agreement with each other.

An examination of the data (Table 3.1.2) shows that when the *o*-Toluidine concentration is in excess, the pseudo first order rate constant ( $k$ ) calculated in each

case is almost constant. Hence, the rate of disappearance of potassium bromate obeys the first order kinetics.

In order to confirm the order of reaction w.r.t. potassium bromate, the values of  $[-dc_o/dt]$  were determined by plotting the volume of  $\text{Na}_2\text{S}_2\text{O}_3$  [equivalent to  $\text{KBrO}_3$ ] against time for different initial concentration of potassium bromate and recorded in the Table 3.1.3. The value of the order of reaction with respect to  $\text{KBrO}_3$  has been evaluated from the plot of  $\log [-dc_o/dt]$  Vs  $\log C_o$  [Fig. 3.1.2], where  $C_o$  is the initial concentration of  $\text{KBrO}_3$ , which comes out to be 0.95. The values of  $[-dc_o/dt]$  and conc.  $[\text{KBrO}_3]$  i.e.  $C_o$  are substituted in the Van't Hoff<sup>60</sup> equation i.e.

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

and then the order of reaction was calculated. The values of 'n' calculated, thereby have been recorded in Table 3.1.4. This confirms the first order behaviour of the reaction with respect to potassium bromate.

TABLE 3.1.2

Variation of Potassium Bromate Concentration

[o-Toluidine] =  $2.5 \times 10^{-2}$  M      Temp =  $35^{\circ}$  C[H<sub>2</sub>SO<sub>4</sub>] = 1.25 M      [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O] =  $2 \times 10^{-3}$  M

[KBrO <sub>3</sub> ] x 10 <sup>+3</sup> M	0.625	1.25	1.875	2.5	3.125
Time (min)	Vol. (in ml) of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O				
0	10.30	19.10	29.10	38.40	48.00
5	9.70	17.80	27.00	36.20	44.80
10	8.90	16.80	25.10	33.20	42.20
15	8.40	15.50	23.50	30.80	39.30
20	7.80	14.50	21.80	29.00	36.30
25	7.40	13.50	20.60	26.50	33.40
30	6.90	12.70	19.10	25.80	31.20
35	6.40	11.90	17.90	23.30	28.80
40	6.00	11.20	16.70	22.30	26.50
45	5.60	10.50	15.70	20.80	25.30
50	5.30	9.80	14.80	19.30	24.50
55	4.90	9.40	14.00	18.20	22.30
60	4.60	8.60	12.70	16.70	20.10
Graphically k x 10 <sup>2</sup> min <sup>-1</sup>	1.3723	1.3258	1.3874	1.3617	1.3869
Mean k x 10 <sup>2</sup> min <sup>-1</sup>	1.3465	1.3485	1.3938	1.3825	1.4036

TABLE 3.1.3

$[\text{KBrO}_3]_0 \times 10^3 \text{M}$	$(-\frac{dc_o}{dt}) \times 10^4$	$\log C_o$	$\log (-\frac{dc_o}{dt})$
0.625	0.6060	- 3.2041	- 4.2175
1.250	1.1564	- 2.9030	- 3.9560
1.875	1.6980	- 2.7269	- 3.7700
2.50	2.2528	- 2.6020	- 3.6772
3.125	2.8180	- 2.5051	- 3.5803

TABLE 3.1.4

Order with respect to Potassium Bromate

$[\text{KBrO}_3]_0 \times 10^3 \text{M}$	$(-\frac{dc_o}{dt}) \times 10^4$	Order of reaction 'n'
0.625	0.6060	0.93
1.250	1.1564	
1.250	1.1564	0.95
1.875	1.6980	
1.875	1.6980	0.98
2.50	2.2528	
2.50	2.2528	1.00
3.125	2.8180	

### 3.1.2 EFFECT OF VARIATION OF o-TOLUIDINE CONCENTRATION

In order to investigate the effect of o-Toluidine concentration on the rate of oxidation of o-Toluidine, the Toluidine concentration was varied from  $0.625 \times 10^{-2} \text{M}$  to  $3.125 \times 10^{-2} \text{M}$ , keeping the concentration of potassium bromate and that of sulphuric acid constant. The results of these kinetic runs are recorded in Table 3.1.5 and represented graphically in Fig 3.1.3.

The results contained in Table 3.1.5 show that the first order rate constant increases with increase in the initial concentration of Toluidine. The plots of  $\log C$  against time 't' (Fig 3.1.3) were linear. The second order rate constant

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

where  $k_2$  = second order rate constant

$k_1$  = first order rate constant

was found to be constant. [Table 3.1.6], indicating the first order dependence of the rate on Toluidine concentration.

TABLE 3.1.5

Variation of *o*-Toluidine Concentration

$[\text{KBrO}_3] = 2.5 \times 10^{-3} \text{ M}$       Temp =  $35^\circ\text{C}$   
 $[\text{H}_2\text{SO}_4] = 1.25 \text{ M}$        $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}] = 2 \times 10^{-3} \text{ M}$

$[\text{o-Toluidine}] \times 10^2 \text{ M}$	0.625	1.250	1.875	2.5	3.125
Time (min)	Vol. (in ml) of $\text{Na}_2\text{S}_2\text{O}_3$				
0	38.90	38.80	38.30	38.40	38.50
5	38.10	37.50	36.50	36.20	35.10
10	37.60	36.10	34.30	33.20	31.90
15	36.90	34.90	32.70	30.80	29.20
20	36.20	33.80	30.90	29.00	26.50
25	35.70	32.20	29.30	26.50	24.50
30	34.20	31.10	27.50	25.80	22.00
35	34.00	29.90	25.80	23.30	20.10
40	33.70	29.00	24.40	22.30	18.80
45	32.70	27.60	23.10	20.80	17.00
50	32.30	26.70	21.20	19.30	16.00
55	32.00	25.40	20.80	18.20	14.80
60	31.60	24.70	20.10	16.70	13.80
Graphically $k \times 10^2 \text{ min}^{-1}$	0.3571	0.7563	1.1118	1.3785	1.8217
Mean $k_1 \times 10^2 \text{ min}^{-1}$	0.3702	0.7319	1.0931	1.3825	1.8155

TABLE 3.1.6

[o-Toluidine] x 10 <sup>2</sup> M	k <sub>1</sub> x 10 <sup>2</sup> min <sup>-1</sup>	k <sub>2</sub> mole <sup>-1</sup> min <sup>-1</sup>
0.625	0.3702	0.5923
1.250	0.7319	0.5855
1.875	1.0931	0.5829
2.50	1.3825	0.5530
3.125	1.8155	0.5809

The order with respect to Toluidine was determined by Van't Hoff differential method.<sup>60</sup> The volume of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> [equivalent to KBrO<sub>3</sub>] was plotted against time for different initial concentration of Toluidine. From these curves, the value of (-dc<sub>o</sub>/dt) in each case was determined from the initial slope which indicates value of initial rate, have been given in the Table 3.1.7. The values of (-dc<sub>o</sub>/dt) and conc. (Toluidine) i.e. C<sub>o</sub> are substituted in the Van't Hoff<sup>60</sup> equation i.e.

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

and then the order of reaction was calculated. The values of (-dc<sub>o</sub>/dt) for different initial concentration of Toluidine and the values of 'n' calculated, thereby have been recorded in Tables 3.1.7 and 3.1.8, respectively.

In order to confirm the order of reaction w.r.t. o-Toluidine, from the plot of  $\log(-dc_o/dt)$  Vs  $\log C_o$  where  $C_o$  is the initial concentration of o-Toluidine [represented in Fig 3.1.4], the value of the order w.r.t. o-Toluidine has been evaluated which comes out to be 0.95. This confirms the first order behaviour of the reaction w.r.t. o-Toluidine.

TABLE 3.1.7

$[o\text{-Toluidine}]_o \times 10^2 \text{M}$	$-(dc_o/dt) \times 10^4$	$\log C_o$	$\log(-dc_o/dt)$
0.625	0.600	- 2.2040	- 4.2218
1.250	1.1520	- 1.9030	- 3.9385
1.875	1.730	- 1.7269	- 3.7619
2.50	2.280	- 1.6020	- 3.6420
3.125	2.890	- 1.5051	- 3.5391

TABLE 3.1.8

Order with respect to o-Toluidine

$[o\text{-Toluidine}]_o \times 10^2 \text{M}$	$-(dc_o/dt) \times 10^4$	Order of reaction 'n'
0.625	0.600	0.94
1.250	1.152	
1.250	1.152	1.00
1.875	1.730	
1.875	1.730	0.96
2.50	2.280	
2.50	2.280	1.06
3.125	2.890	

### 3.1.3 : EFFECT OF VARIATION OF SULPHURIC ACID CONCENTRATION :

The reaction was studied in strong acidic medium. In order to study the effect of acid concentration on the rate of oxidation of *o*-Toluidine, the concentration of sulphuric acid was varied from 1.0 to 2.0 M, keeping the concentrations of other reagents constant. The results of these kinetic runs are recorded in Table 3.1.9. A plot of  $\log C$  Vs time was a straight line (Fig. 3.1.5). First order rate constant obtained by calculation and graphically are included in Table 3.1.9. It is seen that these values of  $k$  are not constant, but increase with concentration of  $H_2SO_4$ .

The order with respect to  $H_2SO_4$  was determined by Van't Hoff<sup>60</sup> differential method. The volume of  $Na_2S_2O_3$  [equivalent to bromate] was plotted against time for different initial concentrations of acid. From these curves, the values of  $(-dc_0/dt)$  in each case was determined from the initial slope, which indicates value of initial rate, have been in the Table 3.1.10. The values of  $(-dc_0/dt)$  and concentration i.e.  $C_0$  are substituted in the Van't Hoff equation and then the order of reaction was calculated. The values of 'n' calculated thereby have been recorded in Table 3.1.11.

In order to confirm the order of reaction with respect to acid, from the plot of  $\log (-dc_0/dt)$  Vs  $\log C_0$ , where  $C_0$  is the initial concentration of acid (represented in Fig 3.1.6), the value of the order has been evaluated which comes out to be 1.12. This confirms the first order behaviour of the reaction with respect to sulphuric acid.

TABLE 3.1.9

Effect of Variation of Sulphuric Acid Concentration

 $[\text{KBrO}_3] = 2.5 \times 10^{-3} \text{ M}$       Temp =  $35^\circ\text{C}$ 
 $[\text{o-Toluidine}] = 2.5 \times 10^{-2} \text{ M}$        $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 2 \times 10^{-3} \text{ M}$ 

$[\text{H}_2\text{SO}_4] \text{ M}$	1.0	1.25	1.50	1.75	2.00
Time(min)	Vol (in ml) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$				
0	38.30	38.40	38.60	38.50	38.60
5	36.60	36.20	36.10	34.50	34.30
10	34.60	33.20	33.00	31.10	30.00
15	32.20	30.80	30.00	27.70	26.30
20	30.60	29.00	27.40	24.40	23.40
25	29.40	26.50	25.50	22.00	20.50
30	27.00	25.80	23.00	19.60	18.60
35	25.70	23.30	21.50	18.60	16.40
40	24.20	22.30	20.00	16.40	14.80
45	22.60	20.80	18.50	15.20	13.20
50	21.60	19.30	17.70	13.50	11.50
55	21.00	18.20	15.70	12.80	10.70
60	19.80	16.70	14.60	11.30	10.20
Graphically $k \times 10^2 \text{ min}^{-1}$	1.1151	1.3568	1.6298	2.0549	2.4058
Mean <sub>2</sub> $k \times 10^2 \text{ min}^{-1}$	1.0950	1.3825	1.6001	2.1429	2.4203

TABLE 3.1.10

$[H_2SO_4]_0^M$	$(-dc_o/dt) \times 10^4$	$\log C_o$	$\log (-dc_o/dt)$
1.0	1.610	0.000	- 3.7931
1.25	2.06	0.0969	- 3.6861
1.50	2.56	0.1761	- 3.5917
1.75	3.05	0.2430	- 3.5157
2.00	3.56	0.3010	- 3.4485

TABLE 3.1.11

Order with respect to Sulphuric Acid

$[H_2SO_4]_0^M$	$(-dc_o/dt) \times 10^4$	Order of reaction 'n'
1.00	1.61	_____ 1.10
1.25	2.06	
1.25	2.06	_____ 1.19
1.50	2.56	
1.50	2.56	_____ 1.13
1.75	3.05	
1.75	3.05	_____ 1.15
2.00	3.56	

3.1.4 EFFECT OF ADDED SALTS ON REACTION RATE :

In order to study the effect of added salts on the rate of oxidation of *o*-Toluidine, the concentration of salts was varied from  $2.5 \times 10^{-3} \text{ M}$  to  $12.50 \times 10^{-3} \text{ M}$  by keeping the concentration of other reactants constant. The results of these kinetic runs are recorded in Table 3.1.12. It is observed from this table that the effect of salts is negligible. The salts used were potassium sulphate, zinc sulphate and cadmium sulphate.

TABLE 3.1.12

$[\text{KBrO}_3] = 2.5 \times 10^{-3} \text{ M}$        $[\text{H}_2\text{SO}_4] = 1.25 \text{ M}$   
 $[\text{o-Toluidine}] = 2.5 \times 10^{-2} \text{ M}$     Temp =  $35^\circ \text{C}$      $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}] = 2 \times 10^{-3} \text{ M}$

$[\text{K}_2\text{SO}_4] \times 10^3 \text{ M}$	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 \text{ min}^{-1}$	1.4255	1.3675	1.3296	1.3947	1.3564
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$[\text{ZnSO}_4] \times 10^3 \text{ M}$	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 \text{ min}^{-1}$	1.4300	1.3825	1.4137	1.3351	1.3762
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$[\text{CdSO}_4] \times 10^3 \text{ M}$	2.50	5.00	7.50	10.00	12.50
$k \times 10^2 \times \text{min}^{-1}$	1.3782	1.3616	1.3765	1.3505	1.3006

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A

### 3.1.5 EFFECT OF TEMPERATURE ON REACTION RATE AND CALCULATION OF THERMODYNAMIC PARAMETERS :

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 25°C to 45°C. The result of these kinetic runs have been tabulated in Table 3.1.13 and shown graphically in Fig 3.1.7. It is seen from the Table 3.1.13, that the specific rate has approximately doubled for 10°C rise in temperature. A plot of  $\log k$  Vs  $1/T$  as shown in Fig. 3.1.8 (Table 3.1.14) is found to be linear indicating that the reaction obeys Arrhenius relationship. The value of energy of activation ( $E_a$ ) evaluated from slope of this curve comes out to be 13.384 K. cal mole<sup>-1</sup>. The Arrhenius equation has been used directly to calculate energy of activation, which comes out to be 13.083 K. cal mole<sup>-1</sup>. On the basis of this graphical value, the frequency factor ( $A$ ), free energy of activation ( $\Delta G^\ddagger$ ) and entropy of activation ( $\Delta S^\ddagger$ ) have been calculated by using the following equation :

$$\text{Arrhenius}^{61} \text{ equation,}$$

$$k_r = A \cdot e^{-E_a/RT} \quad \dots(i)$$

$$\text{or } \log k_r = \log A - \frac{E_a}{2.303RT} \quad \dots(ii)$$

$$\log k_1 - \log k_2 = \frac{-E_a}{2.303 R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad \dots(iii)$$

91 The values of  $\log kr/T$  have been plotted against  $1/T$  which is shown in Fig 3.1.9. The plot was 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  $\Delta H^\ddagger = 12.698 \text{ K cal mole}^{-1}$  was obtained. The following equations were used to calculate  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$ .

$$\log \frac{kr}{kT/h} = \frac{-\Delta H^\ddagger}{2.303 RT} + \frac{\Delta S^\ddagger}{2.303 R} \quad \dots(iv)$$

$$\Delta S^\ddagger = 2.303 R \log \frac{A \cdot h}{kT} \quad \dots(v)$$

$$\text{and } \Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad \dots(vi)$$

In above equations 'kr' is the specific rate, 'k' is the Boltzmann constant and h - is the plank's constant. Other symbols carry their usual meanings.

The various energy parameters, obtained have been recorded in Table 3.1.15.

From these values of  $E_a$  and A the rate constant kr is related to temperature T by the relation

$$kr = 7.649 \times 10^5 e^{-13384/RT}$$

TABLE 3.1.13

## Effect of Temperature

[o-Toluidine] =  $2.5 \times 10^{-2}$  M       $[H_2SO_4] = 1.25$  M  
 $[KBrO_3] = 2.5 \times 10^{-3}$  M,       $[Na_2S_2O_3] = 2 \times 10^{-3}$  M

Temp (T)	25°C	30°C	35°C	40°C	45°C
Time(min)	Vol. (in ml) of $Na_2S_2O_3 \cdot 5H_2O$				
0	38.60	38.80	38.40	38.50	38.60
5	37.30	36.60	36.20	34.60	33.50
10	36.40	34.90	33.20	30.90	28.65
15	35.30	33.00	30.80	27.90	24.45
20	33.80	31.00	29.00	24.80	20.80
25	32.60	29.90	26.50	22.30	18.55
30	31.60	28.10	25.80	20.10	16.05
35	30.40	26.80	23.30	18.70	14.00
40	29.30	25.50	22.30	17.30	12.40
45	28.30	24.70	20.80	15.40	10.35
50	27.00	22.40	19.30	14.00	8.90
55	26.40	22.00	18.20	12.60	7.80
60	25.50	20.90	16.70	11.50	7.05
Graphically $k \times 10^2 \text{ min}^{-1}$	00.7161	1.0476	1.4049	2.0552	2.9321
Mean $k \times 10^2 \text{ min}^{-1}$	0.6697	1.0682	1.3825	2.1002	2.9286

TABLE 3.1.14

$T^{\circ}\text{k}$	$1/T \times 10^3$	$k_r \times 10^2 \text{min}^{-1}$	$\log k_r$	$\log k_r/T$
298	3.3557	0.7161	- 2.1450	- 4.6192
303	3.3003	1.0476	- 1.9798	- 4.4612
308	3.2467	1.4049	- 1.8523	- 4.3409
313	3.1948	2.0552	- 1.6871	- 4.1826
318	3.1446	2.9321	- 1.5328	- 4.0352

FIG:3-1-1 — EFFECT OF  $\text{KBrO}_3$  CONCENTRATION

$$[\text{O-T}]_0 = 2.5 \times 10^{-2} \text{ M}$$

$$[\text{H}_2\text{SO}_4]_0 = 125 \text{ M}$$

$$\text{TEMP} = 35^\circ \text{C}$$

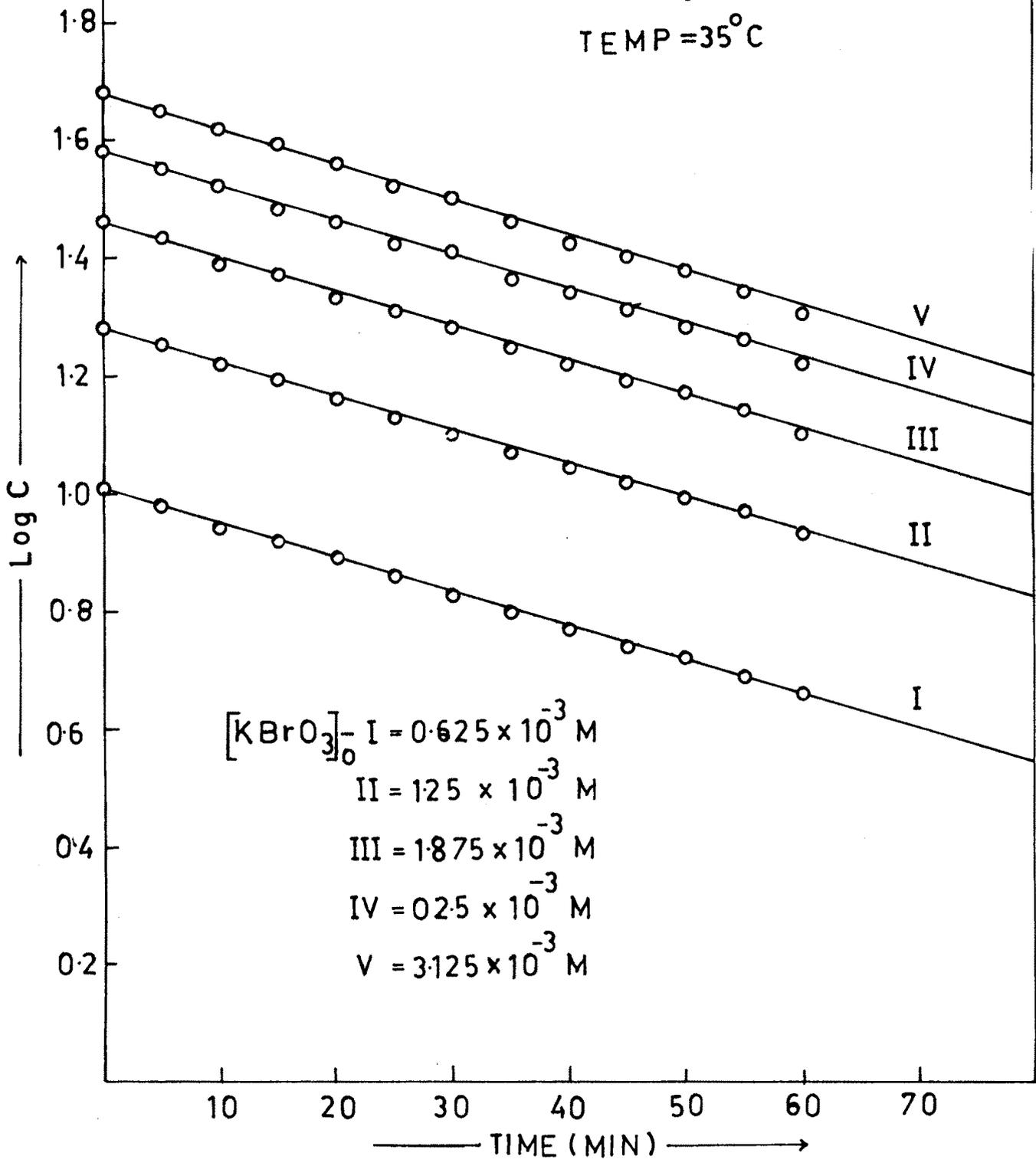


FIG: 3-12 ———  $\text{Log} \left[ \frac{dc}{dt} \right]_0$  Vs  $\text{Log } C_0$

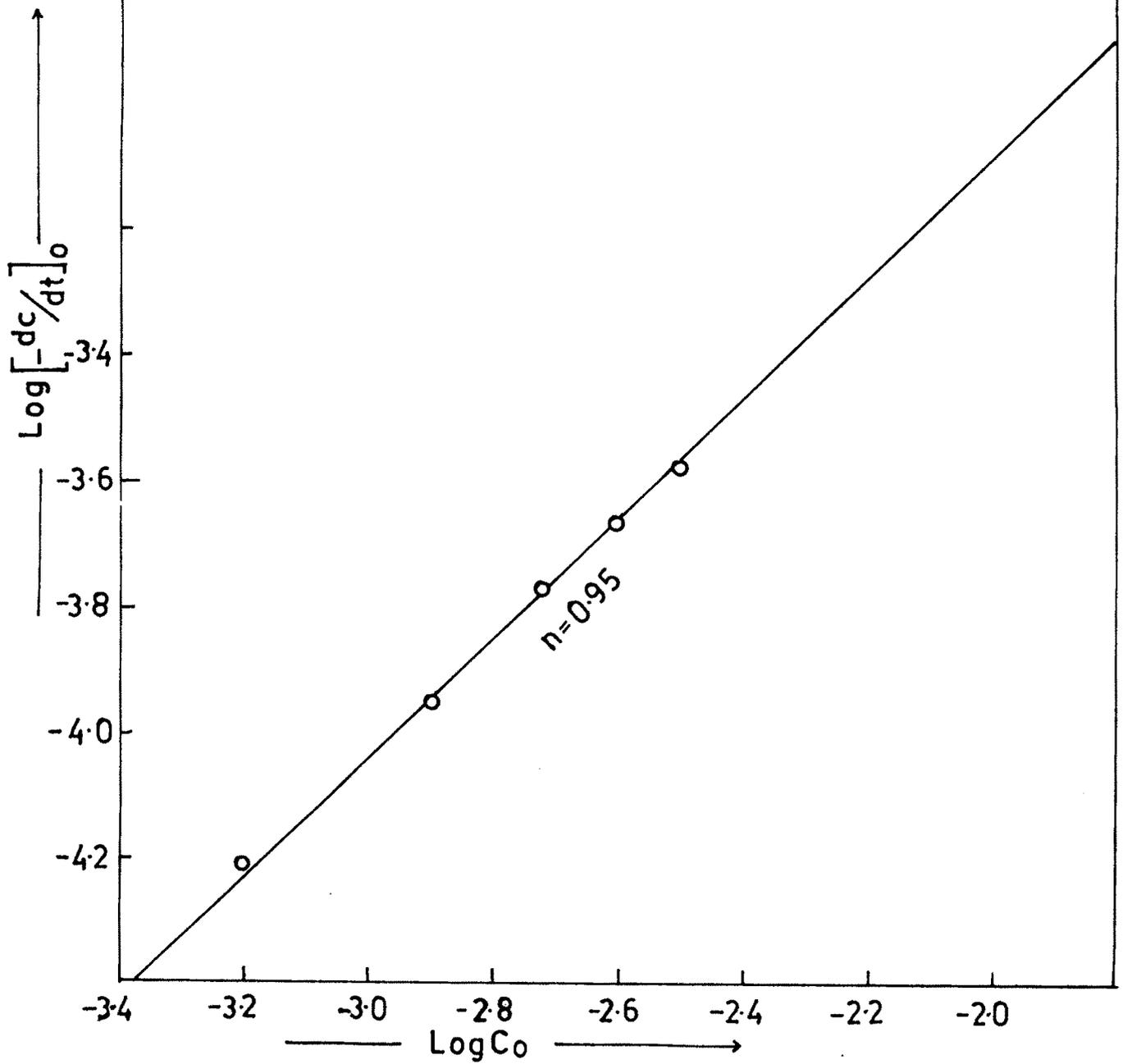


FIG: 3.13 — EFFECT OF  $\phi$ -T CONCENTRATION

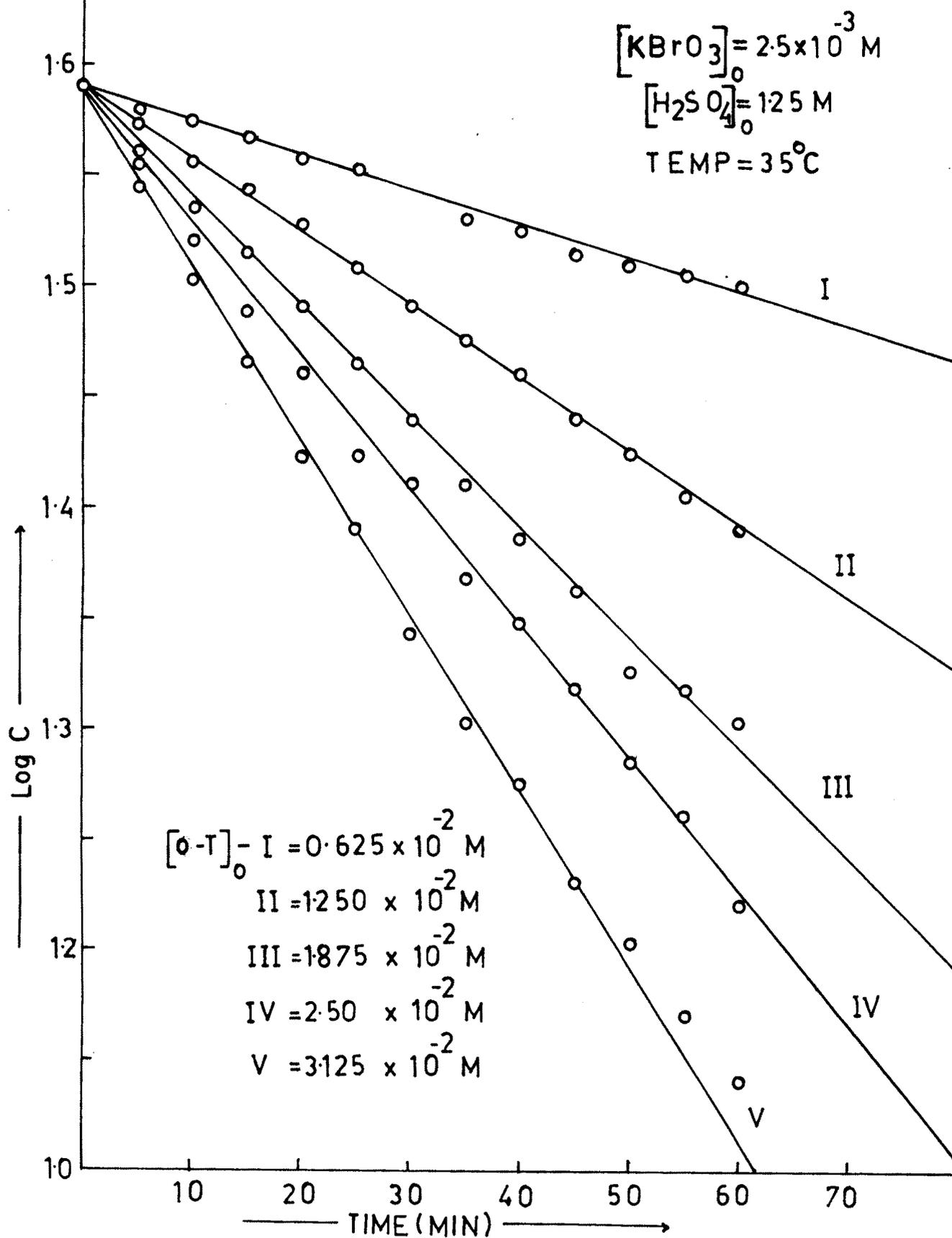


FIG: 3.1.4 ———  $\text{Log}\left[-\frac{dc}{dt}\right]_0$  Vs  $\text{Log } C_0$

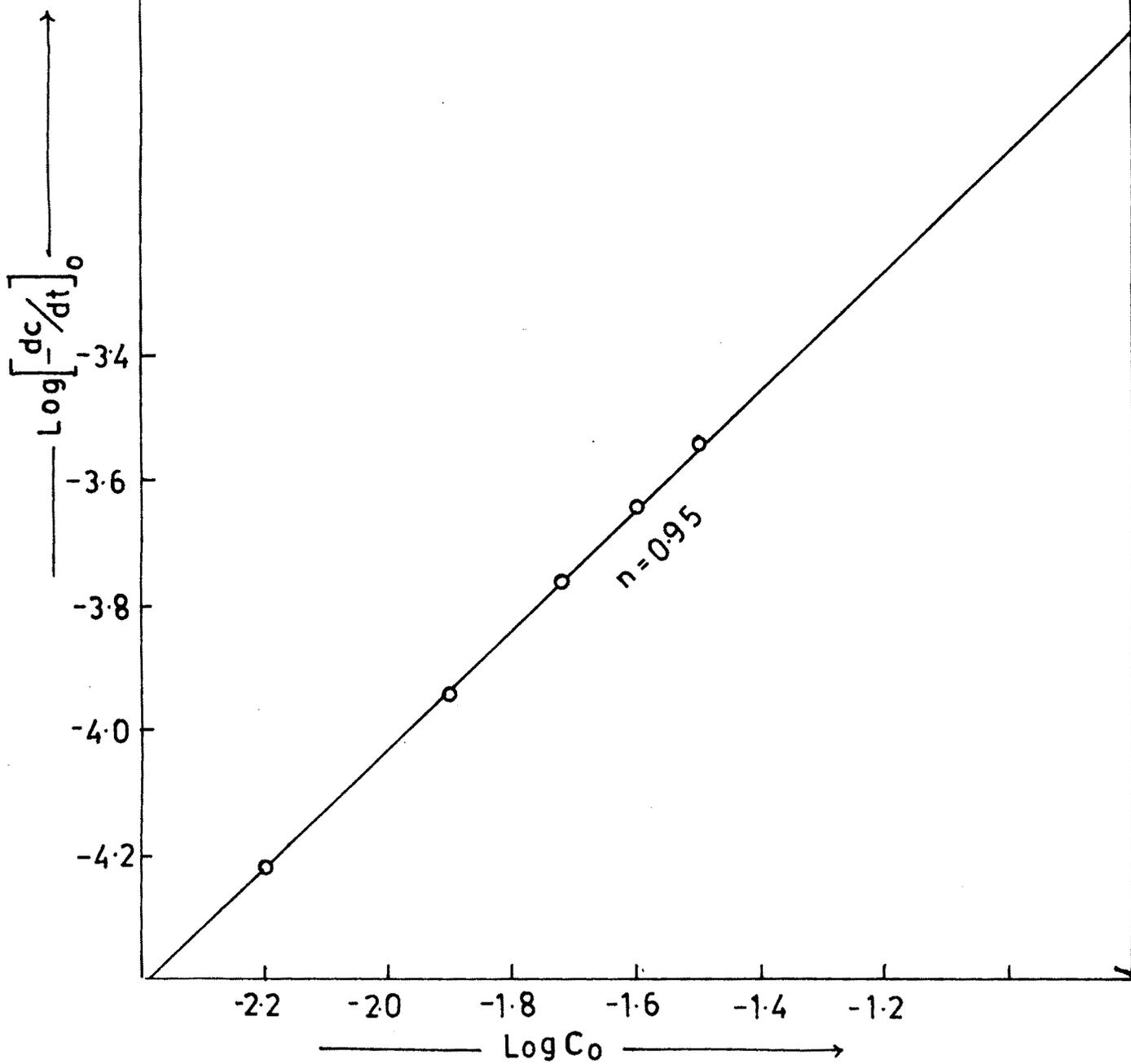


FIG. 3:1:5— EFFECT OF H<sub>2</sub>SO<sub>4</sub> CONCENTRATION

$$[\text{H}_2\text{SO}_4]_0 = \text{I} = 1.00 \text{ M}$$

$$\text{II} = 1.25 \text{ M}$$

$$\text{III} = 1.50 \text{ M}$$

$$\text{IV} = 1.75 \text{ M}$$

$$\text{V} = 2.00 \text{ M}$$

$$[\text{KBrO}_3]_0 = 2.5 \times 10^{-3} \text{ M}$$

$$[\text{o-T}]_0 = 25 \times 10^{-2} \text{ M}$$

$$\text{TEMP} = 35^\circ\text{C}$$

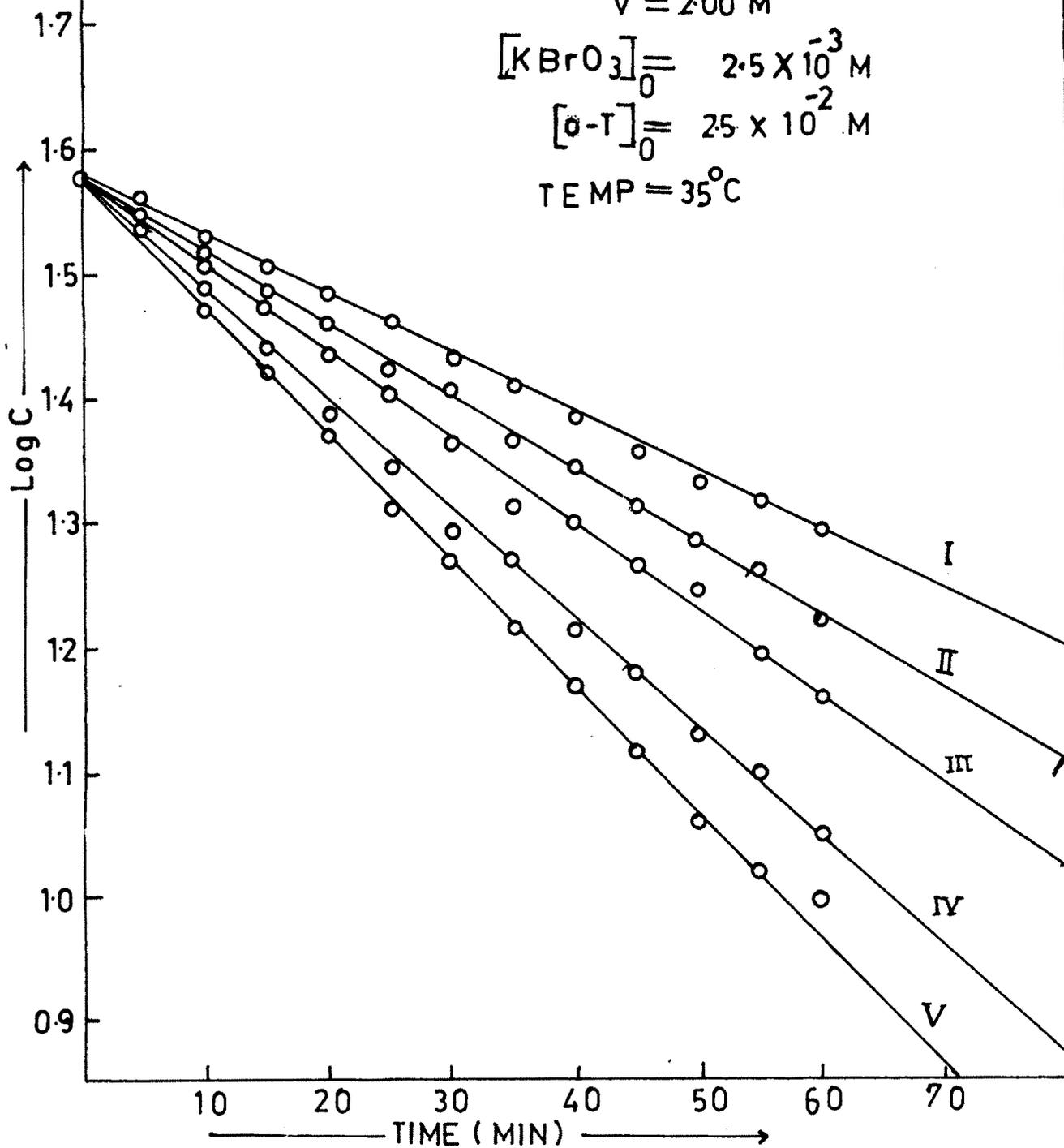


FIG: 31:6 —  $\text{Log}\left[\frac{dc}{dt}\right]_0$  Vs  $\text{Log } C_0$

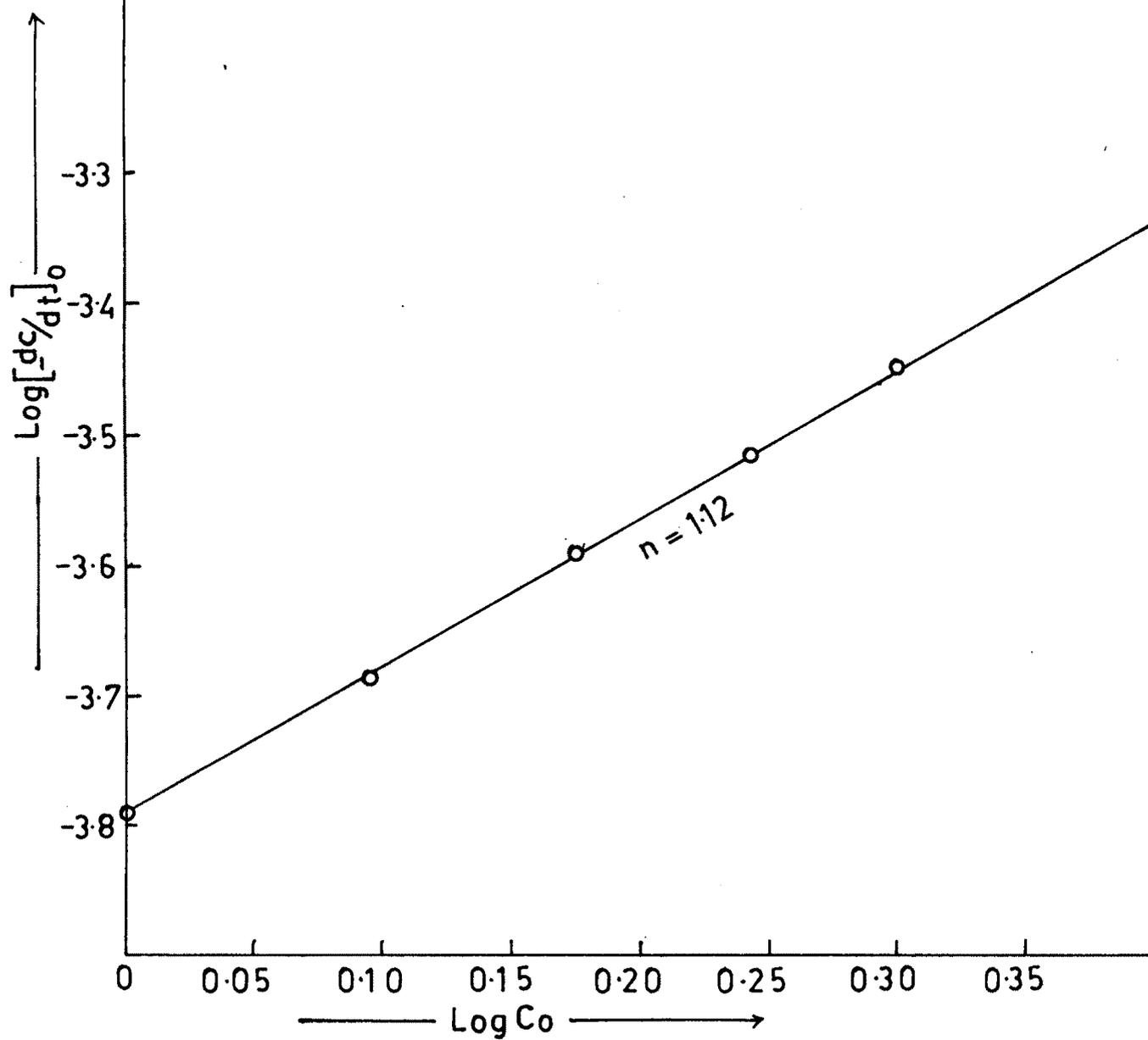


FIG: 3-17 — EFFECT OF TEMPERATURE

$$[\text{KBrO}_3]_0 = 2.5 \times 10^{-3} \text{ M}$$

$$[\text{o-T}]_0 = 2.5 \times 10^{-2} \text{ M}$$

$$[\text{H}_2\text{SO}_4]_0 = 1.25 \text{ M}$$

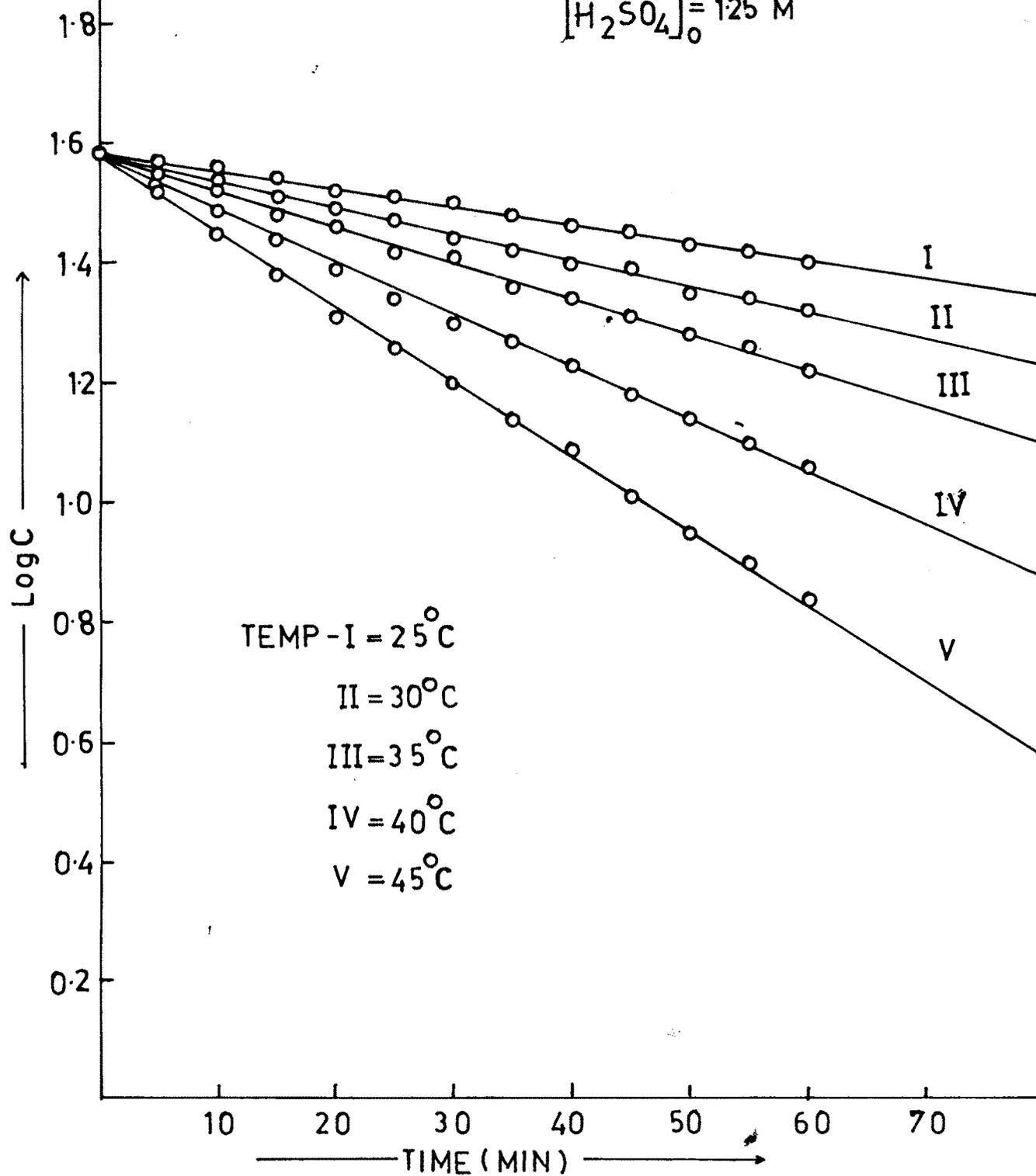


FIG: 3.1.8 ——— Log kr Vs  $\frac{1}{T}$

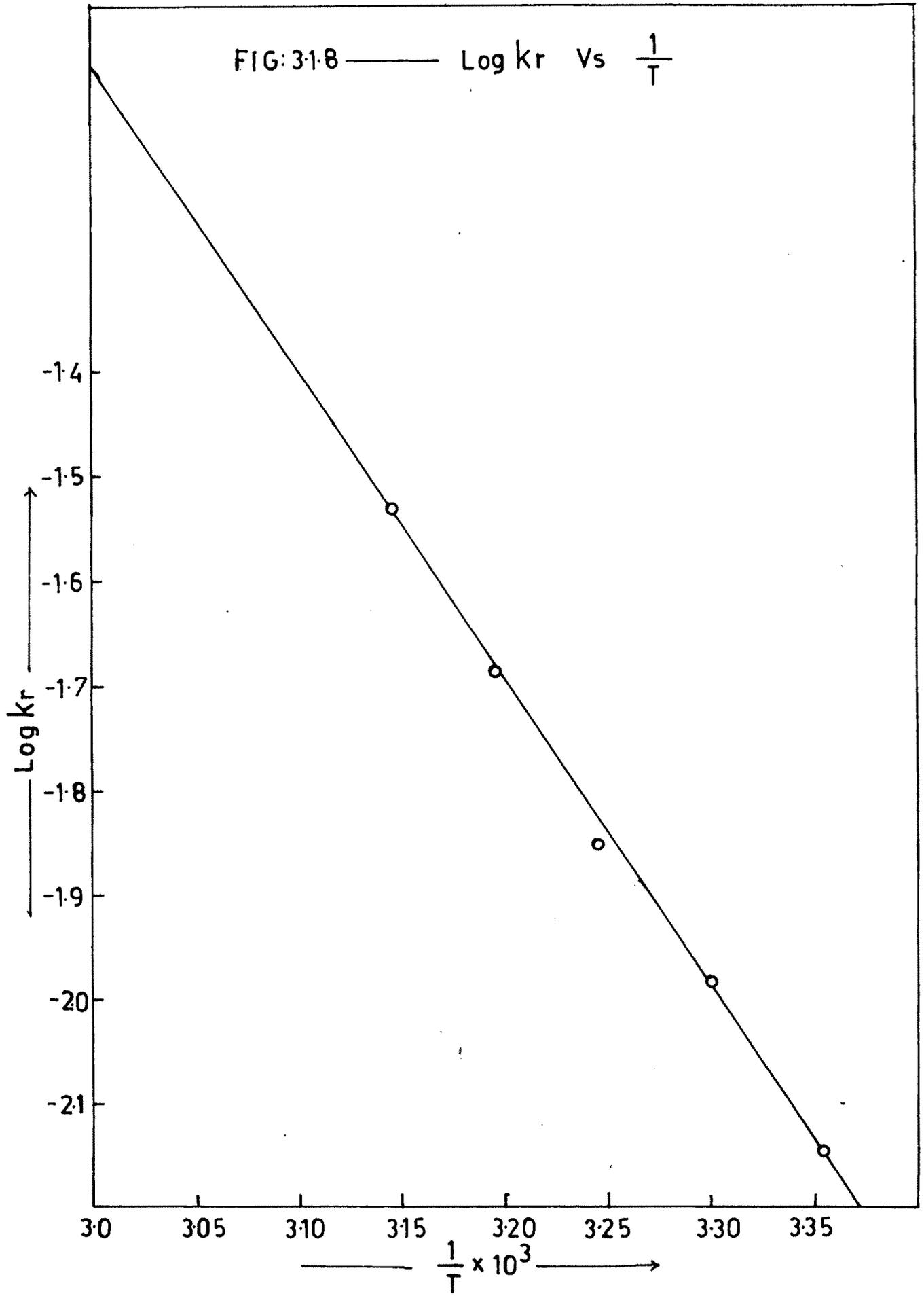


FIG: 3-19 ———  $\text{Log } \frac{k_r}{T}$  Vs  $\frac{1}{T}$

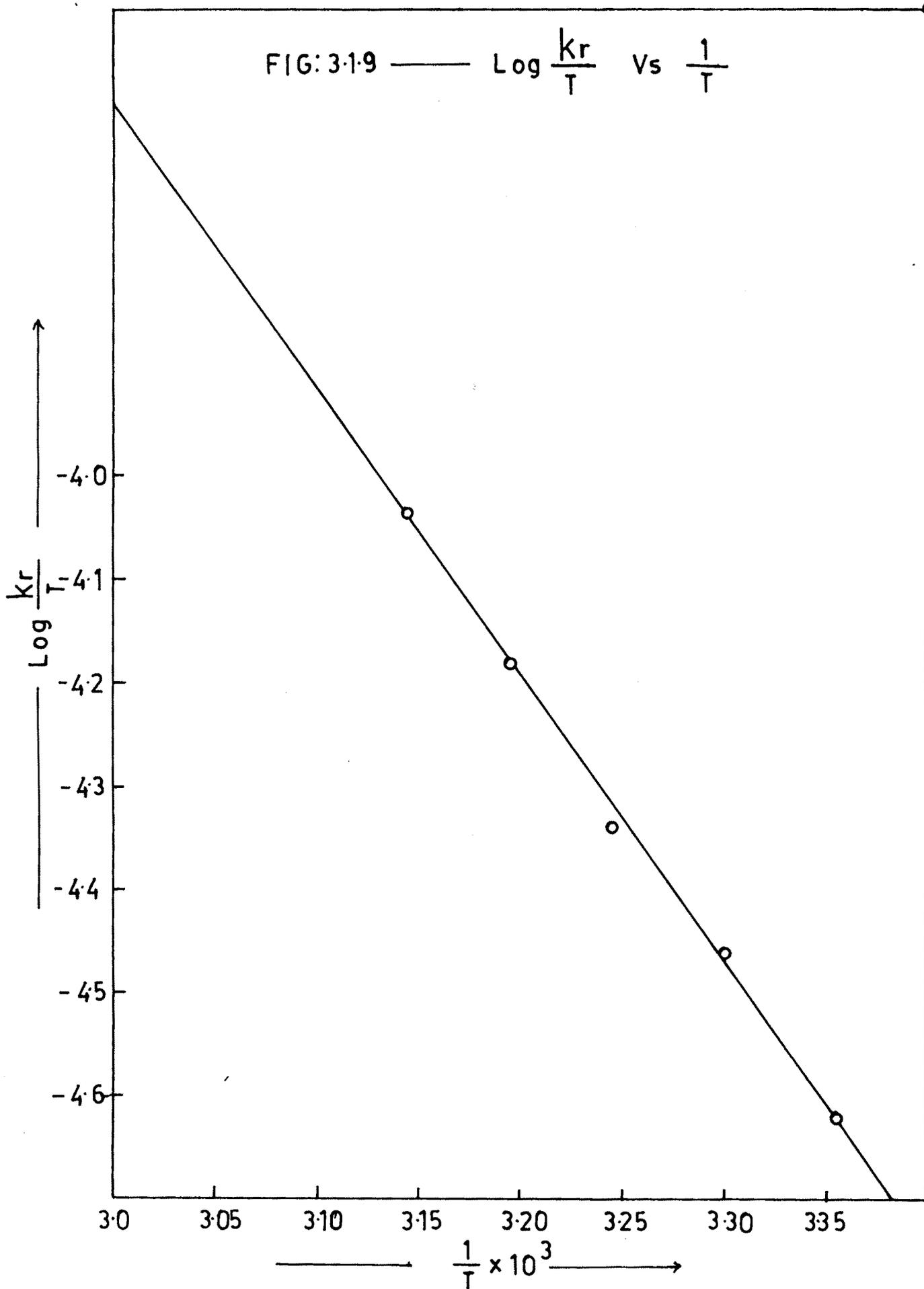


TABLE 3.1.15

## Thermodynamic Parameters

Temp $T^{\circ}\text{K}$	$k_r \times 10^2$ $\text{min}^{-1}$	Temp coefficient	$E_a$ K. cal. $\text{mole}^{-1}$ graph	$E_a$ K. cal. $\text{mole}^{-1}$ Calculation	$\Delta H^{\ddagger}$ K. cal. $\text{mole}^{-1}$	$\text{Sec}^{-1}$ A $\times 10^{-5}$	$\Delta S^{\ddagger}$ e. u.	$\Delta G^{\ddagger}$ K. cal. $\text{mole}^{-1}$
298	0.7161					7.7900	-31.58	22.108
303	1.0476	1.96	13.384	13.029	12.698	7.8488	-31.60	22.272
308	1.4049	1.96		13.138	Graph	7.3335	-31.76	22.480
313	2.0552	2.08				7.5695	-31.73	22.629
318	2.9321					7.6996	-31.73	22.788
Mean		2.00	13.384	13.083	12.698	7.6490	-31.68	22.455

### 3.1. 6 STOICHIOMETRY

To determine the mole ratio of *o*-Toluidine to bromate, the reaction mixture was taken to be  $2.5 \times 10^{-2} M$  *o*-Toluidine and and  $5.0 \times 10^{-2} M$  potassium bromate. The reaction was followed at  $35^{\circ}C$  and sharp break in vol. of  $Na_2S_2O_3$  Vs time plot was taken for calculation of mole ratio. The mole ratio was found to be 1:1 for *o*-Toluidine to potassium bromate.

### 3.1.7 FREE RADICAL DETECTION AND END PRODUCT ANALYSIS :

The reaction did not promote polymerization of acrylonitrile<sup>62</sup> indicating absence of free radical when acrylonitrile (1 ml) was added to the reaction mixture (5 ml) containing both  $KBrO_3$  and *o*-Toluidine, a precipitate was not formed. This clearly indicates that reaction proceeds in absence of free radical formation.

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

The oxidation product *o*-Benzoquinone<sup>31,12</sup> was identified by TLC with the authentic samples prepared by the literature method. Evolution of ammonia<sup>19</sup> during the course of the reaction was also detected.

Ammonia was detected by adding Nessler's reagent in alkaline solution of reaction mixture which has given buff coloured precipitate.