CHAPTER-III

RESULTS AND DISCUSSION

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TREATMENT OF KINETIC DATA

First, experiments were carried out in order to select suitable temperture and concentration range of the reactants. It was observed that the reaction proceeds with measurable velocity at 30°C at concentration of amine of 2.0 X 10^{-2}M and that of chloramine-B of 2.0 X 10^{-3}M. The concentration of standard sodium thiosulphate was 5.0 X 10^{-4}M. Kinetic studies were carried out under pseudo first order conditions keeping amine concentration excess (i.e.10 times)over the concentration of CAB, at ionic strength of 0.5M ($NaClO_4$) in 50% V/V ethanol.

The rate constants of all the runs were calculated from the plot of log (a-x) versus time in minutes.

The effects of the following parameters on the kinetics of the reaction were studied.

I) Effects of concentration of chloramine-B.

II) Effect of concentration of amine.

III) Effect of temperature.

IV) Effect of concentration of hydrochloric acid medium.

V) Effect of hydrogen ion concentration at constant chloride ion concentration (kept at 0.12M by adding NaCl).

VI) Effect of chloride ion concentration at constant hydrogen ion concentration (0.05M)

VII) Effect of ionic strength.

VIII) Effect of change in solvent composition.

I) EFFECT OF CONCENTRATION OF CHLORAMINE-B :

In order to investigate the effect of concentration of chloramine-B on the reaction, kinetic runs were performed in which concentration of CAB was varied whereas that of amine and hydrochloric acid medium were kept constant.

The rate constant k was found to be increased in case of both amines studied. The plots of log [CAB] versus time are linear, indicating first order dependance on the concentration of chloramine-B (Fig.2.1.1; 2.2.1).

When the concentration of CAB was varied from 1.5 X 10^{-3}M to 3.0 X 10^{-3}M the rate constant values were increased from 3.99 X 10^{4}sec^{-1} to 4.10 X 10^{-4} sec^{-1}(i.e. almost constant) in case of O-toluidine at constant concentration i.e. 2.0 X 10^{-2}M Table 2.1.1).

In case of meta-toluidine the reaction rate constant was almost constant when [CAB] was varied from 2.0 X 10^{-3}M to 3.5 X 10^{-3}M. The rate constant was changed from 3.56 X 10^{4}sec^{-1} to 3.77 X 10^{-4} sec^{-1} (Table 2.1.1). The [m-T] was kept constant at 2.0 X 10^{-2}M.

Thus the first order rate constants are found to be independent of initial concentration of CAB.

II) EFFECT OF CONCENTRATION OF AMINE :

An increase in the concentration of amine increased the rate of reaction when the concentration of CAB was kept constant. The concentrations of amines were varied from 2.0 X 10^{-2} to 4.0 X 10^{-2}M while the concentration of CAB was kept constant at 2.0 X 10^{-3}M; the rate constant values were found to increase as shown below.

Amine studied	Value of 'k' sec^{-1}
o-toluidine	3.44 X 10^{-4} to 5.39 X 10^{-4} (Table 2.1.2)
m-toluidine	3.42 X 10^{-4} to 5.37 X 10^{-4} (Table 2.2.2)

A plot of log k versus log [amine] gave a straight line of slope 0.56 for o-toluidine indicating a fractional order dependance on substrate concentration.(Fig.3.1.1, Table 3.1.1).

In case of o-toluidine the rate constant value was increased by 56.7% for 100% increase in [o-T].

In case of meta-toluidine the rate constant value was inceased by 57.0% for 100% increase in [m-T.].

The plot log k versus log [amine] gave a straight line with slope 0.64 indicating fractional order dependance of rate on [m.T] (Fig. 3.2.1 Table 3.2.1).

TABLE 3.1.1

Chlorination of ortho-toluidine by chloramine-B.
Calculation of order with respect to ortho-toluidine
Temperature = 303^{o}K.

Sr.No.	[amine] (M)	log amine	k (sec^{-1}) X 10^{4}	log k
1.	0.020	- 1.6990	3.60	-3.4437
2.	0.030	- 1.5229	4.38	-3.3579
3.	0.035	- 1.4559	5.05	-3.2972
4.	0.040	- 1.3979	5.39	-3.2684

Order w.r.t. o-T = 0.56

TABLE 3.2.1

Chlorination of meta-toluidine by chloramine-B.
Calculation of order with respect to meta-toluidine.
Temperature = 303^{o}K.

Sr.No.	[amine] M	log amine	k (sec^{-1}) X 10^{4}	log k
1.	0.020	- 1.6990	3.42	- 3.4660
2.	0.025	- 1.6021	3.93	- 3.4056
3.	0.035	- 1.4560	4.80	- 3.3188
4.	0.040	- 1.3979	5.37	- 3.2698

Order w.r.t. m-T = 0.64

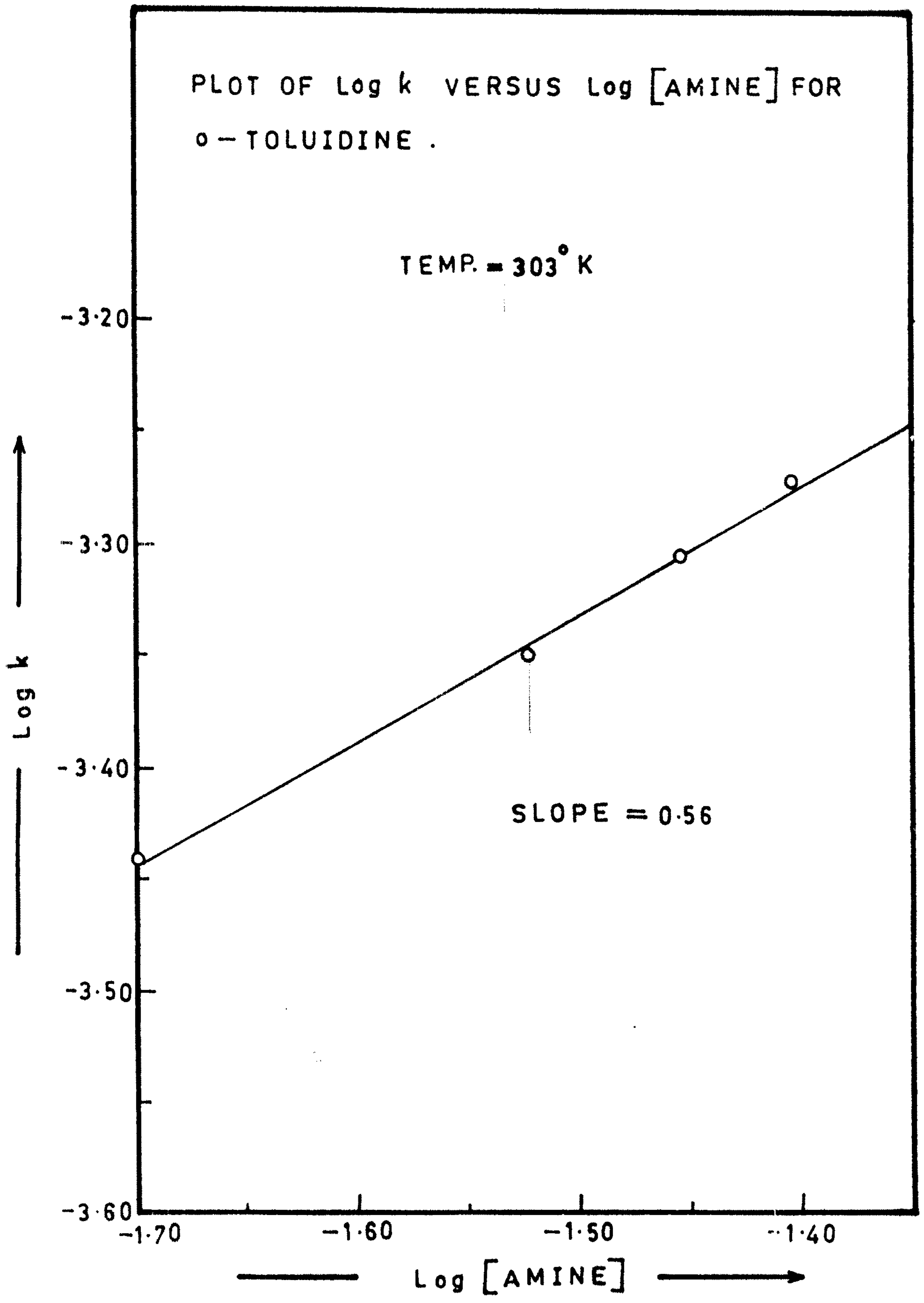

PLOT OF Log k VERSUS Log [AMINE] FOR o – TOLUIDINE .
TEMP. = 303° K
SLOPE = 0·56
-3·20
-3·30
-3·40
-3·50
-3·60
Log k
-1·70
-1·60
-1·50
-1·40
Log [AMINE]

FIG. 3·1·1

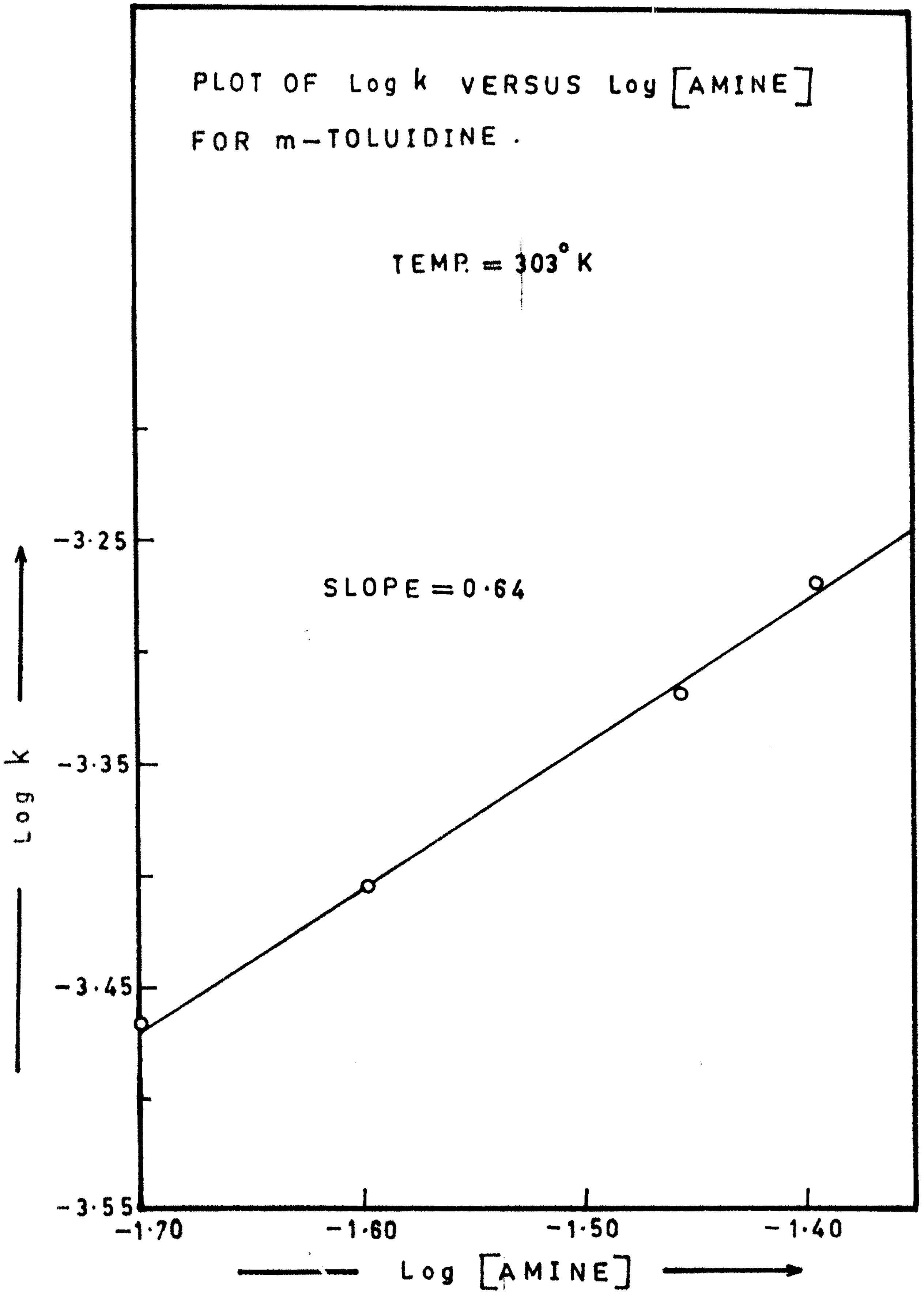

PLOT OF Log k VERSUS Log [AMINE]
FOR m-TOLUIDINE.
TEMP. = 303° K
SLOPE = 0·64
Log k
-3·25
-3·35
-3·45
-3·55
-1·70
-1·60
-1·50
-1·40
Log [AMINE]

FIG. 3·2·1

III) EFFECT OF TEMPERATURE :

In order to determine the frequency factor,(A), energy of activation (Ea), enthalpy of activation ($\Delta H^{\neq}$), free energy of activation ($\Delta G^{\neq}$) and entropy of activation ($\Delta S^{\neq}$), the reaction was studied at different temperatures between 25°C to 40°C. The rate of reaction was found to increase with increase in the temperature in both the amines studied.

S.Arrhenius[72] was first to account for the effect of temperature on the reaction rate. He developed an equation relating the specific reaction rate and temperature called as Arrhenius equation.

$$k = A.e^{-Ea/RT} \qquad .....(1)$$

where,

k = reaction rate or rate constant

A = pre-exponential term or frequency factor

Ea = Energy of activation

R = Gas constant

Arrhenius equation can also be written as-

$$\log k = \log A - \frac{Ea}{2.303RT} \qquad .....(2)$$

For the reaction obeying Arrhenius equation, the plot of log k versus 1/T is always straight line with negative slope. From the slope and intercept of the plot, the values of energy of activation and frequency factor can be calculated.

Another more sophisticated approach was given by formation of some activated complex at the top of energy barrier.[73] Activated complex behaves like the stable molecule with two exceptions, one of its vibrational degrees of freedom is considered forzen, and no account will be taken of it in formulating statistical mechanical partition functions; the missing vibration is replaced by a fourth translational degree of freedom which the system uses as it approaches the top of the potential barrier along the reaction co-ordinate, crosses over the top, and finally rearranges or dissociates into products by the time it reaches region of relative stability associated with its final state.

The rate of reaction is controlled by the rate at which the activated complex decomposes to product. The reaction sequence given by this theory is as follows.

$$A + B \rightleftharpoons X^{\neq} \longrightarrow \text{Products}$$

The theory is termed as the absolute reaction rate theory or activated complex theory. The rate constant

$$k_r = \frac{kT}{h} \cdot \frac{Q^{\neq}}{Q_A \cdot Q_B} \cdot \frac{e^{-Eo/RT}}{\cancel{RT}} \qquad \ldots..(3)$$

where,

Q = Partition function

k = Boltzmann constant

Eo = Activation energy at absolute zero. i.e. The difference in energy between the lowest energy levels in the initial and transition states.

h = Plank's constant

The equilibrium constant $K^{\neq}$ for the formation of activated complex is given by -

$$K^{\neq} = \frac{Q^{\neq}}{Q_A \cdot Q_B} \cdot e^{-Eo/RT} \qquad .....(4)$$

Equation (3) reduces to

$$k_r = \frac{kT}{h} K^{\neq} \qquad .....(5)$$

So,

$$= \frac{kT}{h} \cdot e^{-\Delta G^{\neq}/RT} \qquad .....(6)$$

where $\Delta G^{\neq}$ is the free energy of activation.

The above equation can also be written as -

$$k_r = \frac{kT}{h} \cdot e^{+\Delta S^{\neq}/R} \cdot e^{-\Delta H^{\neq}/RT} \qquad .....(7)$$

or

$$\log(k_r/T) = \log(k/h) + \frac{\Delta S^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT}$$

$$.....(8)$$

From the plot of log k_r/T versus 1/T the values of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ can be calculated from the intercept and slope of the plot.

In the present work, the energy of activation (Ea) and frequency factor (A) were calculated from the Arrhenius plot of log k versus 1/T. The slope of Arrhenius plot gives the value of $\frac{Ea}{2.303R}$ while the intercept gives the value of log (A) (Fig. 3.1.2; 3.2.2. Table 3.1.2 and 3.2.2) from which the values of Ea and A were calculated.

For o-toludine and m-toluidine the values of 'Ea' are found to be 11.56 and 13.02 K.cal/mole respectively. The corresponding values of frequency factor were 7.82 X 10^4 and 7.48 X 10^5 sec^{-1} respectively.

The values of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ were evaluated from the plot of log k_r/T versus 1/T (Fig.3.1.3, 3.2.3). The values of $\Delta G^{\neq}$ were calculated from the relation

$$\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} \quad .....(9)$$

The $\Delta H^{\neq}$ values were calculated from the slopes of plot of log k_r/T versus 1/T by the relation -

$$\Delta H^{\neq} = 2.303 \ R \ X \ slope.$$

The values of $\Delta S^{\neq}$ were calculated from the intercept by the equation -

$$I = \log k/h + \Delta S^{\neq}/2.303R$$

The values of $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for o-toluidine and m-toluidine are shown in Table 3.1.3 and 3.2.3.

Thus from the above tables it is seen that the values of entropy of activation are negative and frequency factor values are small. Thus the results show that the activated complex must be rigid and solvated. The kinetic and thermodynamic parameters studied suggest that chlorinaation of both amines proceed via similar mechanism.

TABLE 3.1.2

Chlorination of ortho-toluidine by Chloramine-B.
Effect of temperature.
[CAB] = 2.0×10^{-3}M; [o-T] = 2×10^{-2}M.
[HCl] = 0.05M; $[Na_2S_2O_3]$ = 5.0×10^{-4}M.
Ionic Strength = 0.5M.

Temperature (^cK)	$k \times 10^4$ (Sec^{-1})	log k	$\frac{10^3}{T}$	Energy of activation (Ea) (Kcal/mole)	Frequency factor (A) sec^{-1}
298	2.60	-3.5850	3.356	11.56	7.82×10^4
303	3.60	-3.4428	3.301		
308	4.94	-3.3063	3.246		
313	6.14	-3.2118	3.196		

TABLE 3.2.2

Chlorination of meta-toluidine by Chloramine-B

Effect of temperature

[CAB] = 2.0×10^{-3}M; [o-T] = 2.0×10^{-2}M

[HCl] = 0.05M [$Na_2S_2O_3$] = 5.0×10^{-4}M

Ionic Strength = 0.5M

Temperature (°K)	k X 10^4 (sec^{-1})	log k	$\frac{10^3}{T}$	Energy of Activation (Ea) Kcal/mole	Frequency factor (A) sec^{-1}
298	2.02	-3.6939	3.356		
303	3.22	-3.4917	3.301		
308	4.27	-3.3689	3.246	13:02	7.48×10^5
313	5.65	-3.2480	3.196		

TABLE 3.1.3

Chlorination of ortho-toluidine by Chloramine-B

Effect of temperature

[CAB] = 2.0×10^{-3}M [o.T] = 2.0×10^{-2}M

[HCl] = 0.05M [$Na_2S_2O_3$] = 5.0×10^{-4}M

$\frac{10^3}{T}$	k/T x 10^6	log k/T	Free energy of activation ($\Delta G^{\neq}$) Kcal/mole	Enthalpy of activation ($\Delta H^{\neq}$) Kcal/mole	Entropy of activation ($\Delta S^{\neq}$) e.u
3.356	0.8723	-6.0592			
3.309	1.1881	-5.9212	+38.36	10.91	-22.54
3.246	1.6039	-5.8049			
3.196	1.9616	-5.7073			

TABLE 3.2.3

Chlorination of meta-toluidine by Chloramine-B
Effect of temperature
[CAB] = 2.0 X 10^{-3}M; [m.T] = 2.0 X 10^{-2}M
[HCl] = 0.05M [$Na_2S_2O_3$] = 5.0 X 10^{-4}M.
Ionic Strength = 0.5M

$\frac{10^3}{T}$	k/T 10^3	log k/T	Free energy of activation ($\Delta G^{\neq}$) K.Cal/mole	Enthalpy of activation ($\Delta H^{\neq}$) K.cal/mole	Entropy of activation ($\Delta S^{\neq}$) e.u.
3.356	0.0678	-6.1681			
3.301	1.0627	-5.9731	+14.09	18.30	-22.68
3.246	1.3863	-5.8575			
3.196	1.8051	-5.5407			

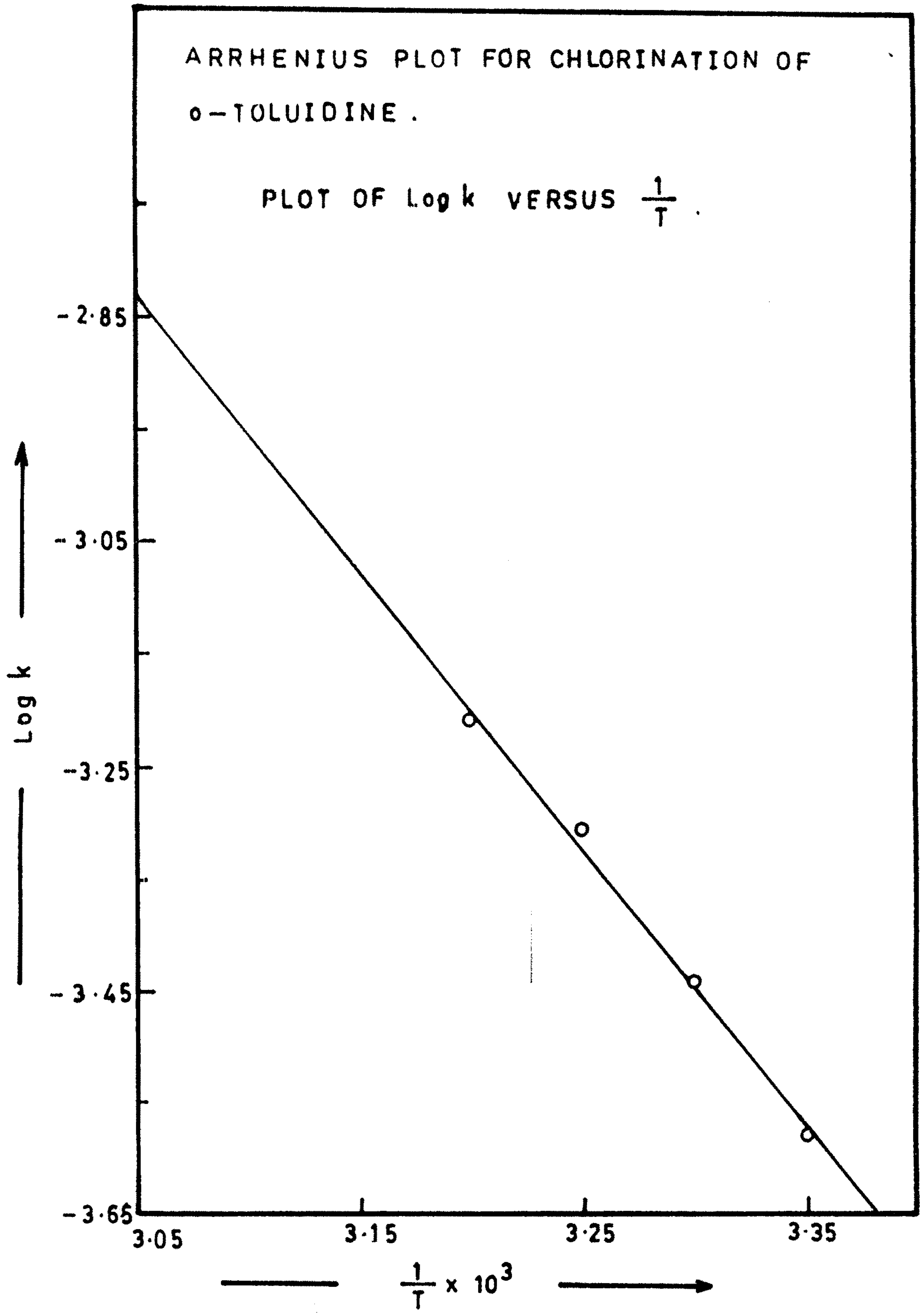

ARRHENIUS PLOT FOR CHLORINATION OF
o-TOLUIDINE.
PLOT OF Log k VERSUS $\frac{1}{T}$.
-2·85
-3·05
-3·25
-3·45
-3·65
Log k
3·05
3·15
3·25
3·35
$\frac{1}{T} \times 10^3$

FIG. 3·1·2

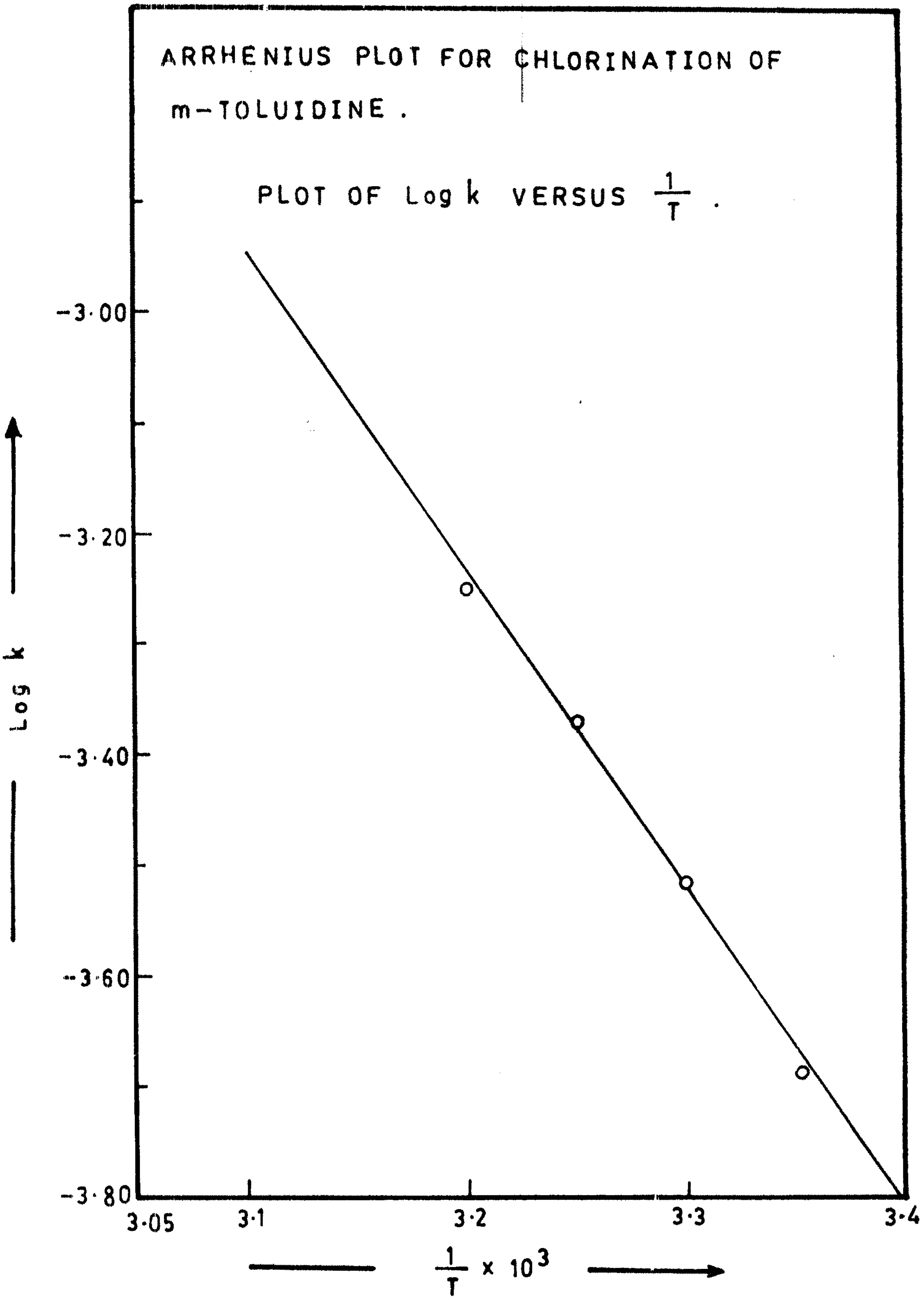
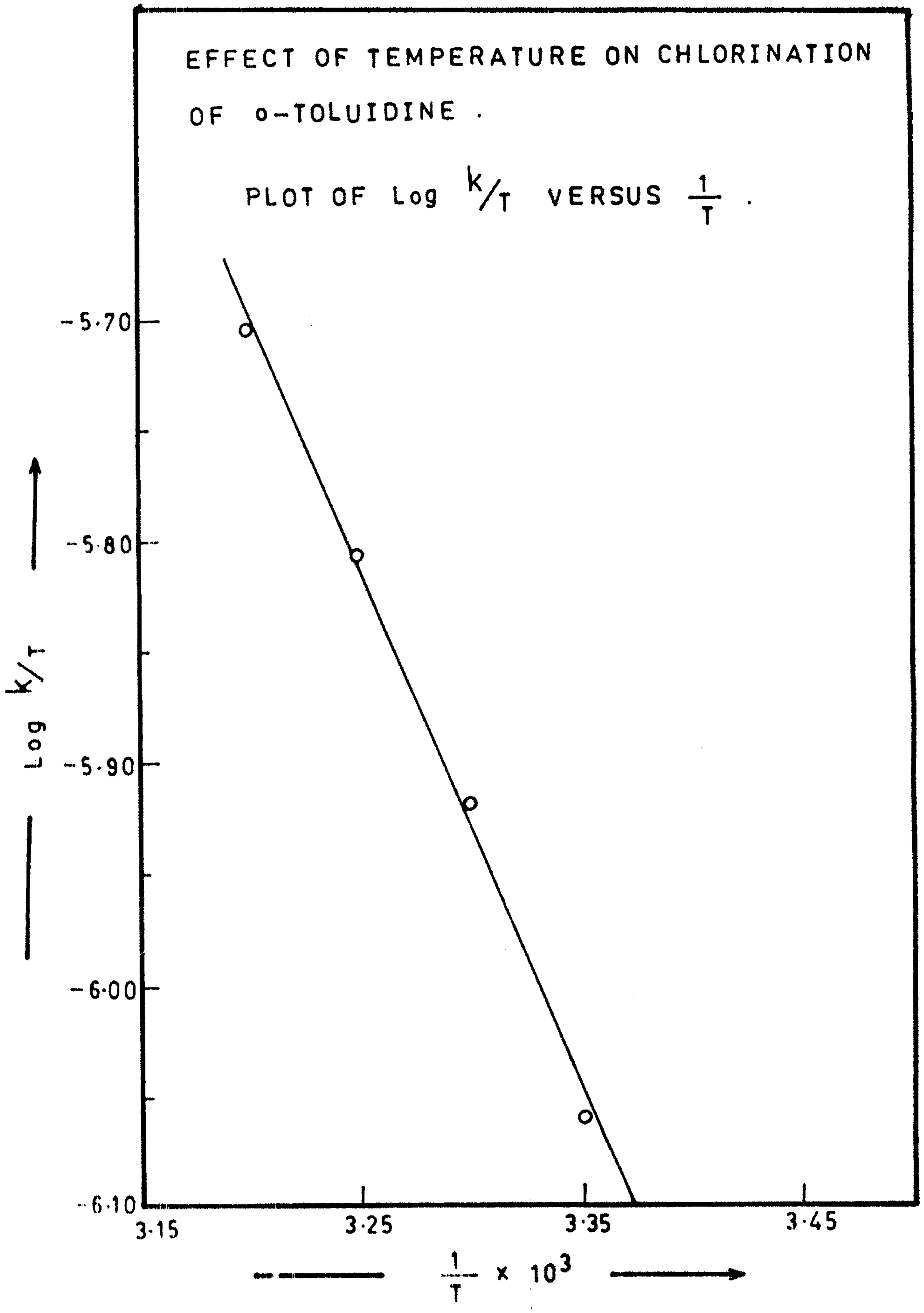

ARRHENIUS PLOT FOR CHLORINATION OF m-TOLUIDINE.
PLOT OF Log k VERSUS 1/T.
-3·00
-3·20
-3·40
-3·60
-3·80
Log k
3·05
3·1
3·2
3·3
3·4
1/T × 10^3

FIG. 3·2·2



EFFECT OF TEMPERATURE ON CHLORINATION OF o-TOLUIDINE.

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

FIG. 3-1-3

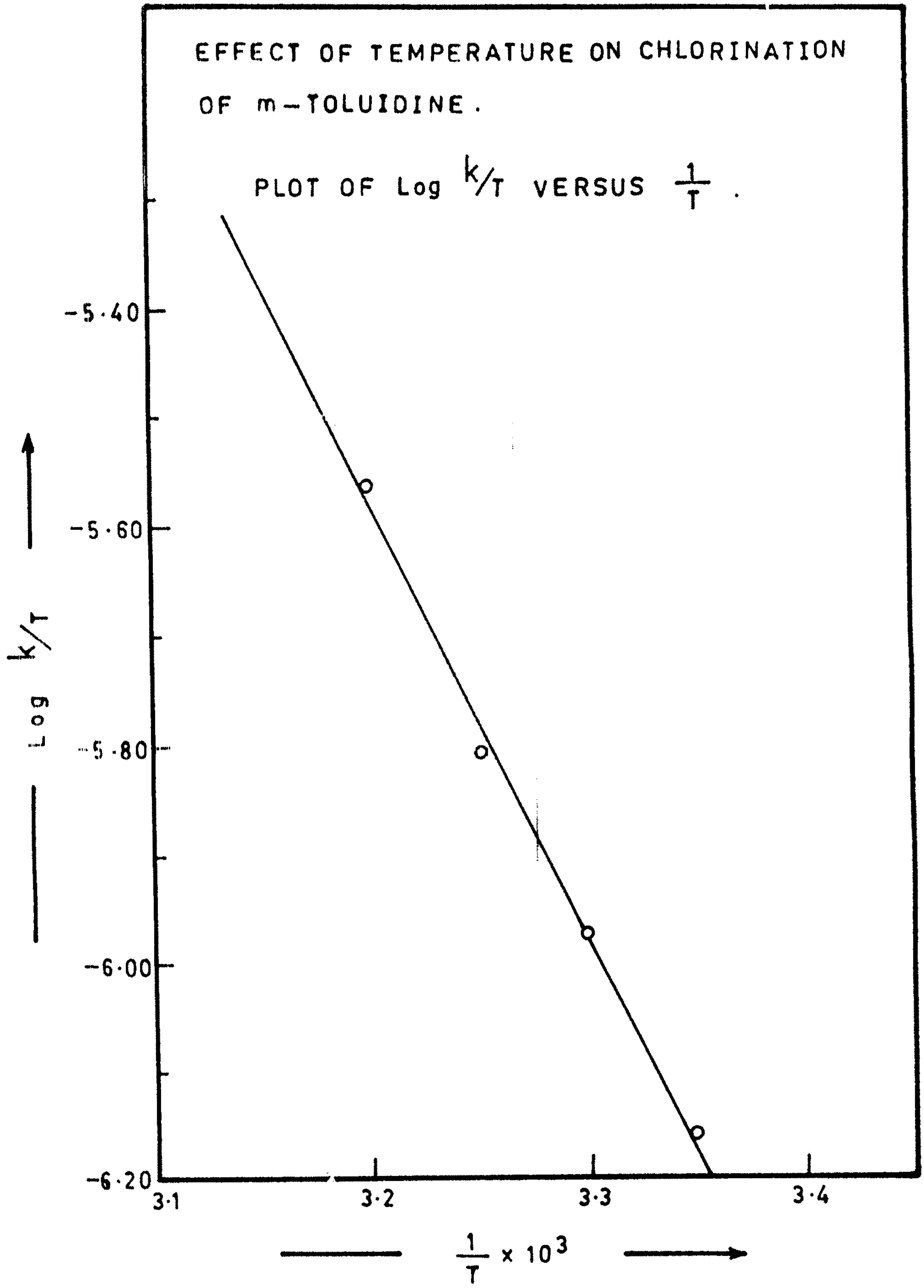

EFFECT OF TEMPERATURE ON CHLORINATION OF m-TOLUIDINE.
PLOT OF Log k/T VERSUS 1/T.
-5·40
-5·60
-5·80
-6·00
-6·20
Log k/T
3·1
3·2
3·3
3·4
1/T x 10³

FIG. 3·2·3

IV) EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID MEDIUM

To investigate the effect of change of concentration of hydrocoloric acid medium, on the rate of chlorination of amines, the concentration of HCl medium was varied from 0.03M to 0.07M, keeping all other-concentrations constant. It is found that the rate of reaction increases with the increase in [HCl], in both the amines studied (Fig. 3.1.4; 3.2.4 Table 3.1.4, 3.2.4).

The plot of log k versus log [HCl] is found to be linear. The order dependance on the gross concentration of hydrochloric acid medium Fig. 3.1.5; 3.2.5 Table 3.1.5; 3.2.5) was calculated from the slope of the plot.

In case of ortho-toluidine the order dependance on the [HCl] is observed to be 1.36 while in case of meta-toluidine it it is 1.06.

The rate of the reaction was strongly dependent on the concentration of hydrogen ions. When the concentration of HCl is increased above 0.07M then the rate of reaction becomes fast. It is not possible to control the reaction.

TABLE 3.1.4

Chlorination of ortho-toluidine by chloramine-B
Effect of concentration of hydrochloric acid medium
[CAB] = 2.0 X 10^{-3}M; [o-T] = 2.0 X 10^{-2}M
[$Na_2S_2O_3$] = 5.0 X 10^{-4}M; Ionic strength = 0.5M
Temperature = 303^oK.

[HCl]	=	0.04M	0.05M	0.06M	0.07M
Sr.No.	Time (min)	(a-x)	(a-x)	(a-x)	(a- x)
1.	o	15.5	15.5	15.5	15.5
2.	5	14.5	14.1	13.7	12.6
3.	10	13.4	12.5	11.6	10.3
4.	15	12.2	10.6	9.6	8.2
5.	20	11.3	9.7	8.3	6.5
6.	25	10.2	8.5	6.9	5.2
7.	30	9.5	7.8	5.8	4.3
8.	35	9.3	6.6	5.0	3.6
9.	40	8.0	5.9	4.2	2.8
10.	45	7.6	4.2	3.5	-
11.	50	6.7	4.7	2.9	-
k (min^{-1}) X 10^2		1.89	2.46	3.30	4.08
k (sec^{-1}) X 10^4		3.15	4.11	5.51	6.81

TABLE 3.2.4

Chlorination of meta-toluidine by chloramine-B
Effect of concentration of hydrochloric acid medium

$[CAB] = 2.0 \times 10^{-3}$M; $[m\text{-}T] = 2.0 \times 10^{-2}$M
$[Na_2S_2O_3] = 5.0 \times 10^{-4}$M; Ionic strength = 0.5M
Temperature = 303°K.

[HCl]	=	0.03M	0.04M	0.05M	0.06M
Sr.No.	Time (min)	(a-x)	(a-x)	(a-x)	(a-x)
1.	0	15.5	15.5	15.5	15.5
2.	5	13.8	13.7	13.6	13.5
3.	10	13.4	13.0	12.3	11.9
4.	15	11.8	11.9	11.0	10.6
5.	20	11.4	10.8	9.8	9.2
6.	25	10.7	10.0	8.7	8.0
7.	30	9.8	9.1	7.7	7.0
8.	35	9.0	8.1	6.9	6.0
9	40	8.7	8.0	6.0	5.3
10	45	8.0	7.2	5.4	4.6
11.	50	7.5	6.5	4.9	4.0
k $(min^{-1}) \times 10^{2}$		1.35	1.86	2.30	2.88
k$(sec^{-1}) \times 10^{4}$		2.26	3.10	3.83	4.72

TABLE 3.1.5

Chlorination of ortho-toluidine by chloramine-B.
Calculation of order with respect to total HCl
Temperature = $303^{o}K$.

Sr.No.	[HCl] M	Log [HCl]	k (sec^{-1}) X 10^{4}	log k
1.	0.04	- 1.3979	3.15	- 3.5017
2.	0.05	- 1.3010	4.11	- 3.3866
3.	0.06	- 1.2216	5.51	- 3.2588
4.	0.07	- 1.1549	6.81	- 2.1667

Order w.r.t hydrochloric acid medium = 1.36

TABLE 3.2.5

Chlorination of meta-toluidine by chloramine-B.
Calculation of order with respect to total HCl.
Temperature = 303^{o}K

Sr.No.	[HCl] M	log [HCl]	k (sec^{-1}) X 10^{4}	log k
1.	0.03	- 1.5229	2.26	- 3.6449
2.	0.04	- 1.3979	3.10	- 3.5090
3.	0.05	- 1.3010	3.84	- 3.4168
4.	0.06	- 1.2216	4.72	- 3.3270

Order w.r.t. hydrochloric acid medium = 1.06

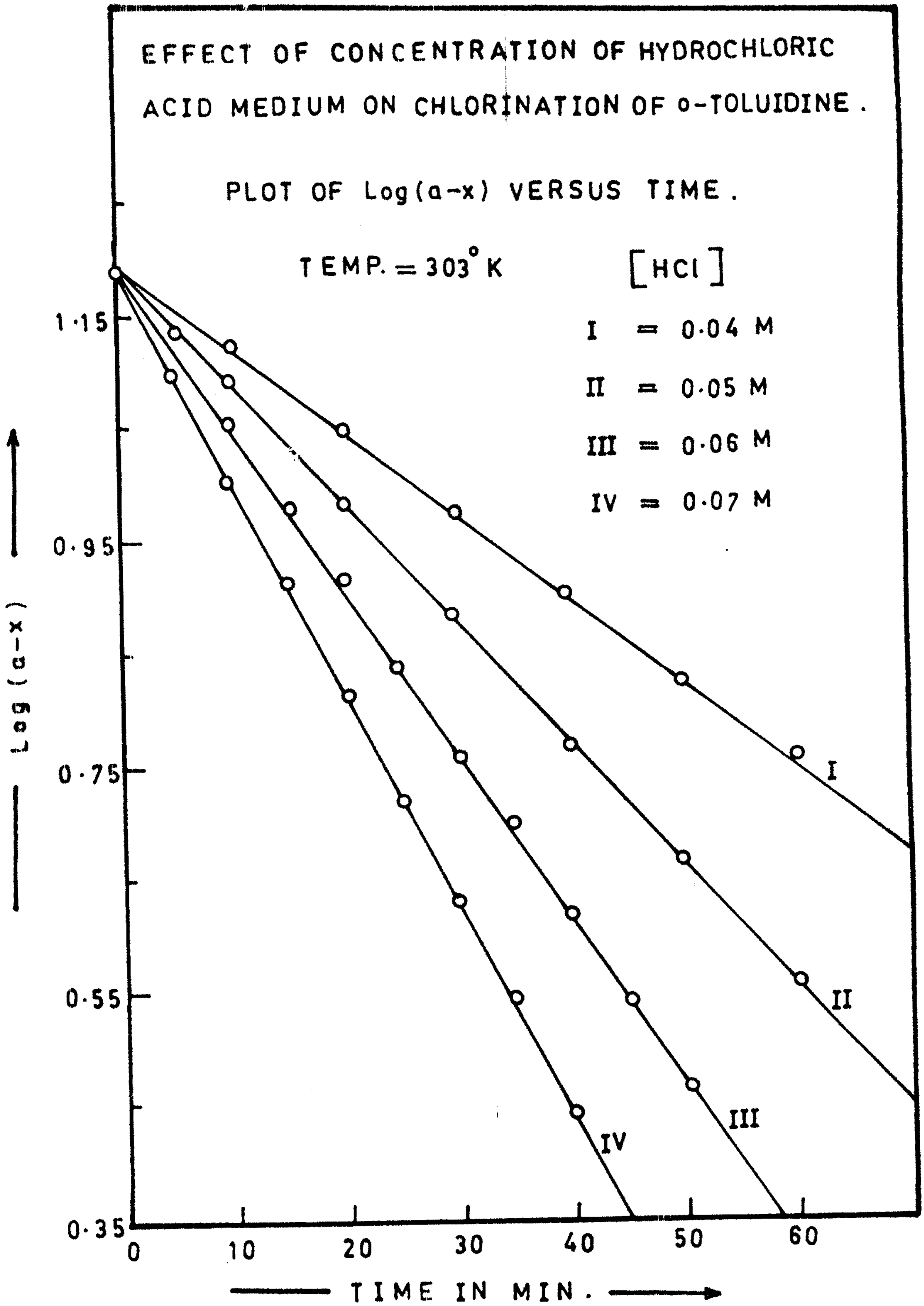

EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID MEDIUM ON CHLORINATION OF o-TOLUIDINE.
PLOT OF Log(a-x) VERSUS TIME.
TEMP. = 303° K
[HCl]
I = 0·04 M
II = 0·05 M
III = 0·06 M
IV = 0·07 M
Log (a-x)
1·15
0·95
0·75
0·55
0·35
0
10
20
30
40
50
60
TIME IN MIN.
I
II
III
IV

FIG. 3·1·4

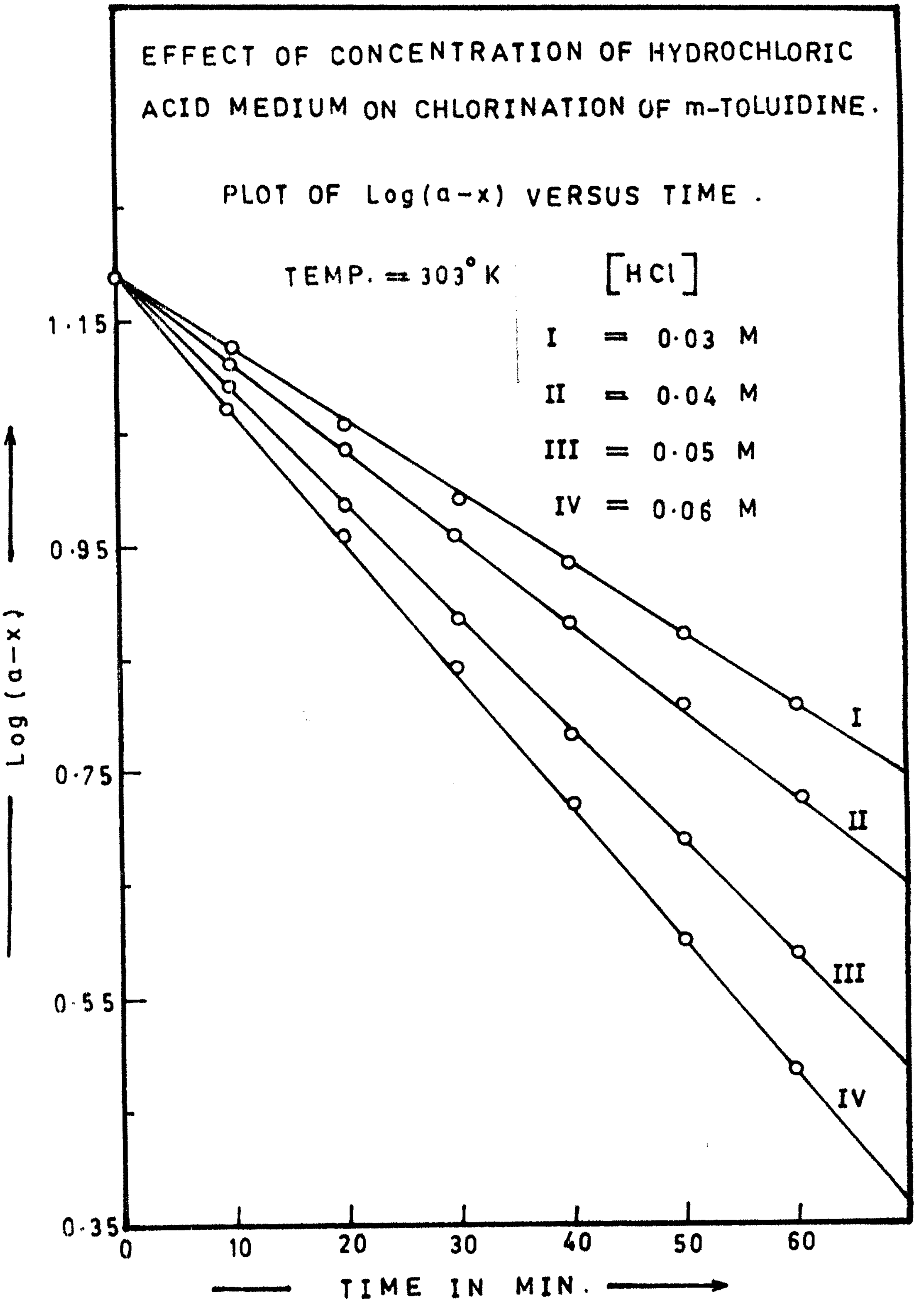

EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID MEDIUM ON CHLORINATION OF m-TOLUIDINE.
PLOT OF Log(a-x) VERSUS TIME.
TEMP. = 303° K
[HCl]
I = 0·03 M
II = 0·04 M
III = 0·05 M
IV = 0·06 M
1·15
0·95
0·75
0·55
0·35
Log (a-x)
0
10
20
30
40
50
60
TIME IN MIN.
I
II
III
IV

FIG. 3·2·4

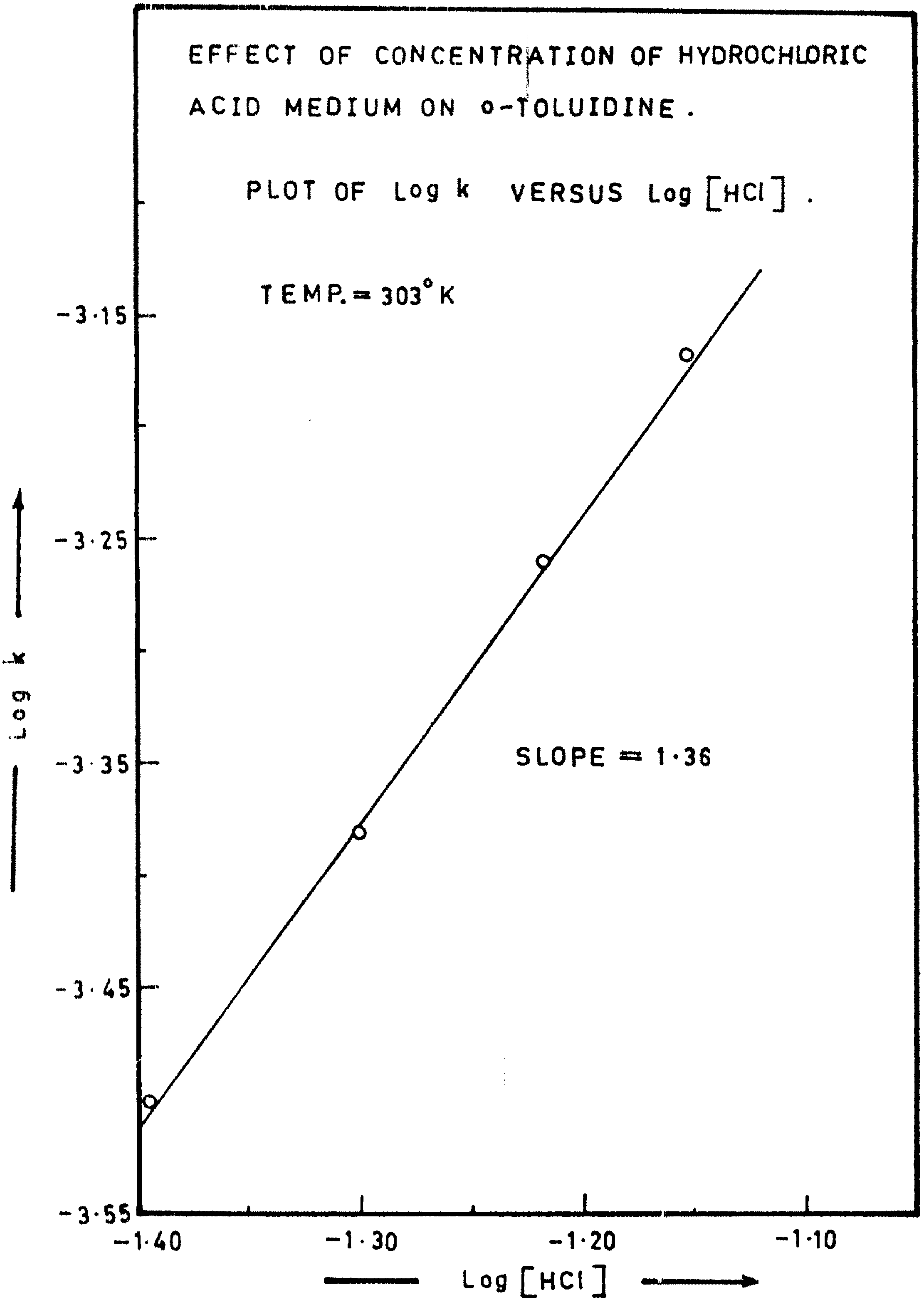
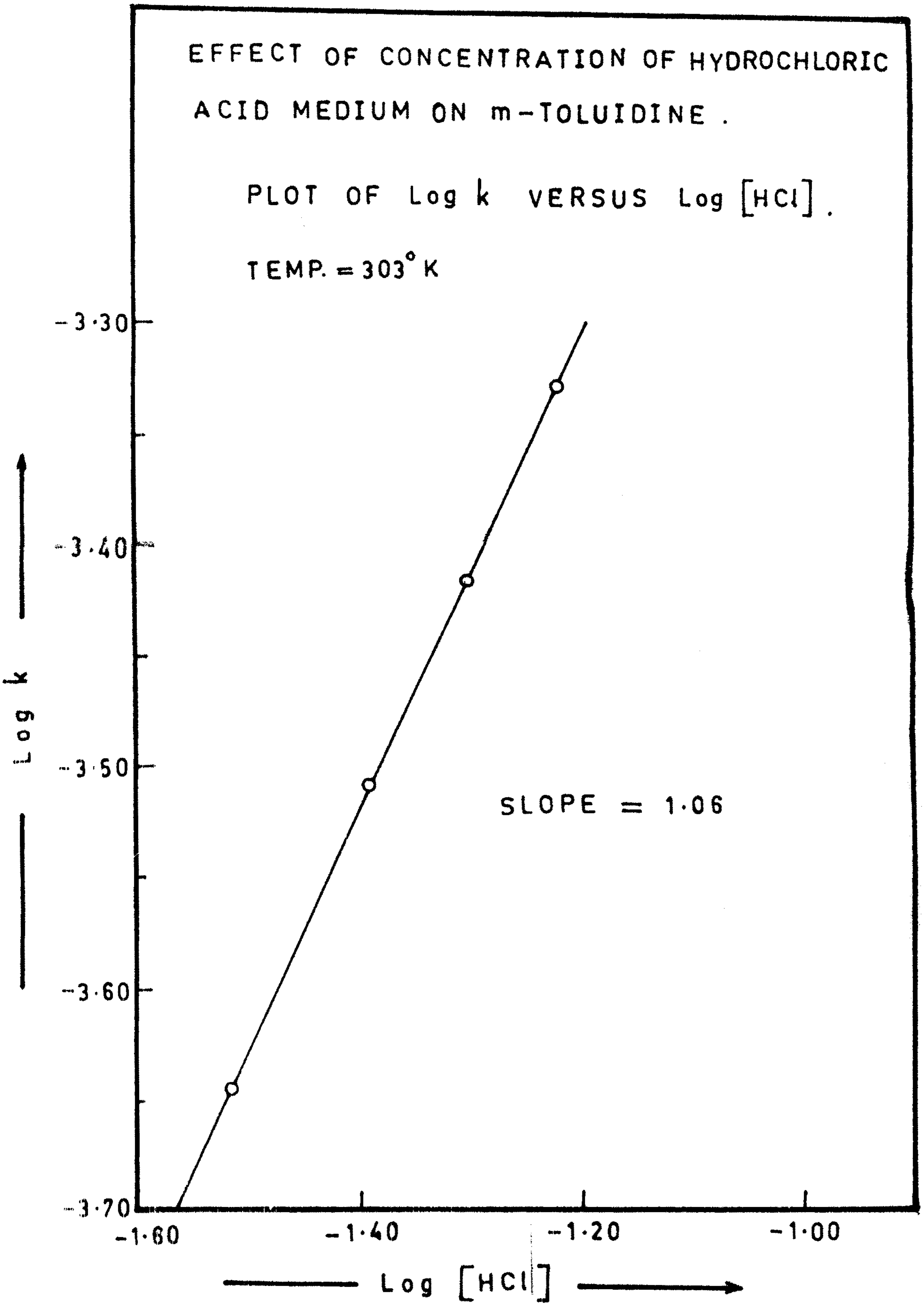

EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID MEDIUM ON o-TOLUIDINE.
PLOT OF Log k VERSUS Log [HCl].
TEMP. = 303° K
SLOPE = 1·36
−3·15
−3·25
−3·35
−3·45
−3·55
−1·40
−1·30
−1·20
−1·10
Log k
Log [HCl]

FIG. 3·1·5



EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID MEDIUM ON m-TOLUIDINE.

PLOT OF Log k VERSUS Log [HCl].

TEMP. = 303° K

FIG. 3·2·5

V) EFFECT OF HYDROGEN ION CONCENTRATION AT CONSTANT CHLORIDE ION CONCENTRATION :

The effect of hydrogen ion concentration on the rate of reaction is studied at constant chloride ion concentration (0.12M) by adding NaCl . The concentration of acid is varied in the range of 0.03M to 0.06M. keeping all other concentrations constant. An examination of the results contained in the Talble 3.1.6 and 3.2.6, it is found that the rate of reaction increases with increase in $[H^+]$(Fig. 3.1.6 and 3.2.6).

The order dependance on the hydrogen ion concentration was calculated from the slope of the plot of log k versus log $[H^+]$ (Fig. 3.1.7 and 3.2.7 Table 3.1.7 and 3.2.7).

Variation of $[H^+]$ indicated an order of 0.97 in case of ortho-toluidine and 0.66 in case of metatoluidine.

From the result it is found that the rate increases with increase in $[H^+]$.

TABLE 3.1.6

Chlorination of ortho-toluidine by chloramine-B
Effect of hydrogen ion concentration at constant

Chloride ion concentration (kept at 0.12M by adding NaCl)
[CAB] = 2.0×10^{-3}M;   [o-T] = 2.0×10^{-2}M
Temperature = 303^{o}K.

[HCl]	=	0.03M	0.04M	0.05M	0.06M
Sr.No.	Time (min)	(a-x)	(a-x)	(a-x)	(a- x)
1.	0	14.7	14.7	14.7	14.7
2.	5	13.1	12.4	11.3	10.2
3	10	11.5	10.2	9.0	7.6
4.	15	10.0	8.7	7.0	5.9
5.	20	8.6	7.1	5.6	4.5
6.	25	7.5	5.9	4.5	3.5
7.	30	6.7	4.9	3.5	2.6
8.	35	5.8	4.2	2.8	2.4
9.	40	5.1	3.4	2.3	-
10.	45	4.6	2.9	-	-
11.	50	3.9	2.4	-	-
k (min^{-1}) X 10^2		2.70	3.63	4.45	5.50
k (sec^{-1}) X 10^4		4.50	6.05	7.42	9.08

TABLE 3.2.6

Chlorination of meta-toluidine by chloramine-B
Effect of hydrogen ion concentration at constant
chloride ion concentration (kept at 0.12M by adding NaCl)
$[CAB] = 2.0 \times 10^{-3}M$; $[m\text{-}T] = 2.0 \times 10^{-2}M$
$[Na_2S_2O_3] = 5.0 \times 10^{-4}M$; Ionic strength = 0.5M
Temperature = $303^{o}K$.

$[HCl]$		0.03M	0.04M	0.05M	0.06M
Sr.No.	Time (min)	(a-x)	(a-x)	(a-x)	(a- x)
1.	0	15.4	15.4	15.4	15.4
2.	5	13.3	13.2	13.1	12.6
3.	10	11.3	10.9	10.6	11.3
4.	15	10.1	10.1	9.0	8.0
5.	20	8.7	8.5	7.6	6.4
6.	25	7.5	7.0	6.0	5.2
7.	30	6.5	5.9	5.3	4.0
8.	35	5.5	5.0	4.4	3.2
9.	40	5.0	4.2	3.6	2.5
10.	45	4.3	3.4	3.0	-
11.	50	3.7	3.0	2.5	-
$k\ (min^{-1}) \times 10^{2}$		2.78	3.42	3.93	4.45
$k\ (sec^{-1}) \times 10^{4}$		4.64	5.70	6.55	7.42

TABLE 3.1.7

Chlorination of ortho-toluidine by chloramine-B.
Calculation of order with respect to hydrogen ion concentration.
Temperature = $303^{0}K$.

Sr.No.	$[H^+]$ M	log $[H^+]$	$k(sec^{-1}) \times 10^4$	log k
1.	0.03	- 1.5229	4.50	- 3.3472
2.	0.04	- 1.3979	6.05	- 3.2184
3.	0.05	- 1.3010	7.42	- 3.1296
4.	0.06	- 1.2216	9.08	- 3.0419

Order w.r.t $[H^+]$ = 0.97

TABLE 3.2.7

Chlorination of meta-toludine by chloramine-B.
Calculation of order with respect to hydrogen ion concentration.
Temperature = 303^{o}K.

Sr.No.	$[H^+]$ M	log $[H^+]$	k (sec^{-1}) X 10^4	log k
1.	0.03	- 1.5229	4.64	- 3.3335
2.	0.04	- 1.3979	5.70	- 3.2469
3.	0.05	- 1.3010	6.58	- 3.1813
4.	0.06	- 1.2216	7.43	- 3.1290

Order w.r.t $[H^+]$ = 0.66

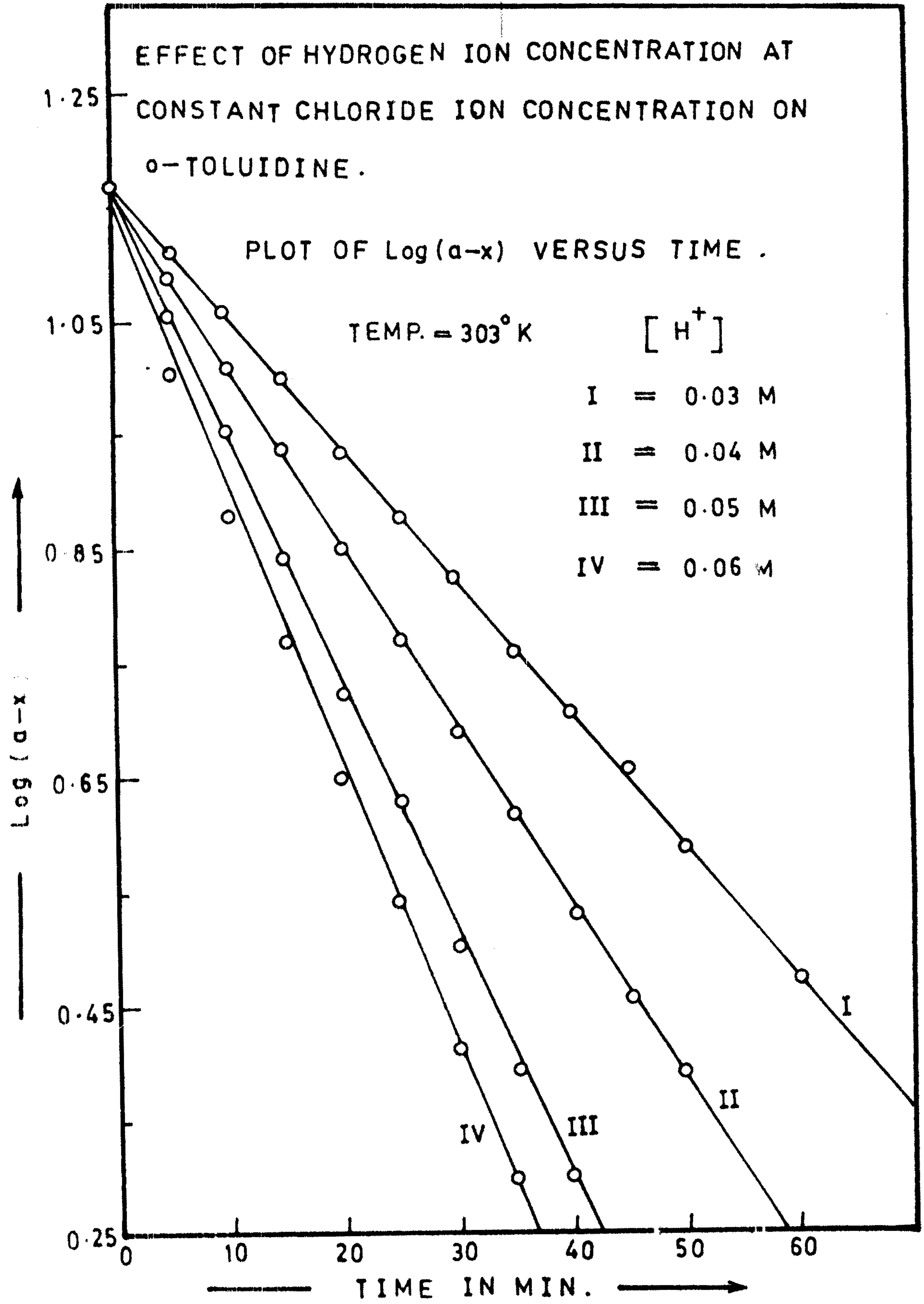

EFFECT OF HYDROGEN ION CONCENTRATION AT CONSTANT CHLORIDE ION CONCENTRATION ON o-TOLUIDINE.
PLOT OF Log(a-x) VERSUS TIME.
TEMP. = 303° K
[H+]
I = 0.03 M
II = 0.04 M
III = 0.05 M
IV = 0.06 M
1.25
1.05
0.85
0.65
0.45
0.25
Log (a-x)
0
10
20
30
40
50
60
TIME IN MIN.
I
II
III
IV

FIG. 3.1.6

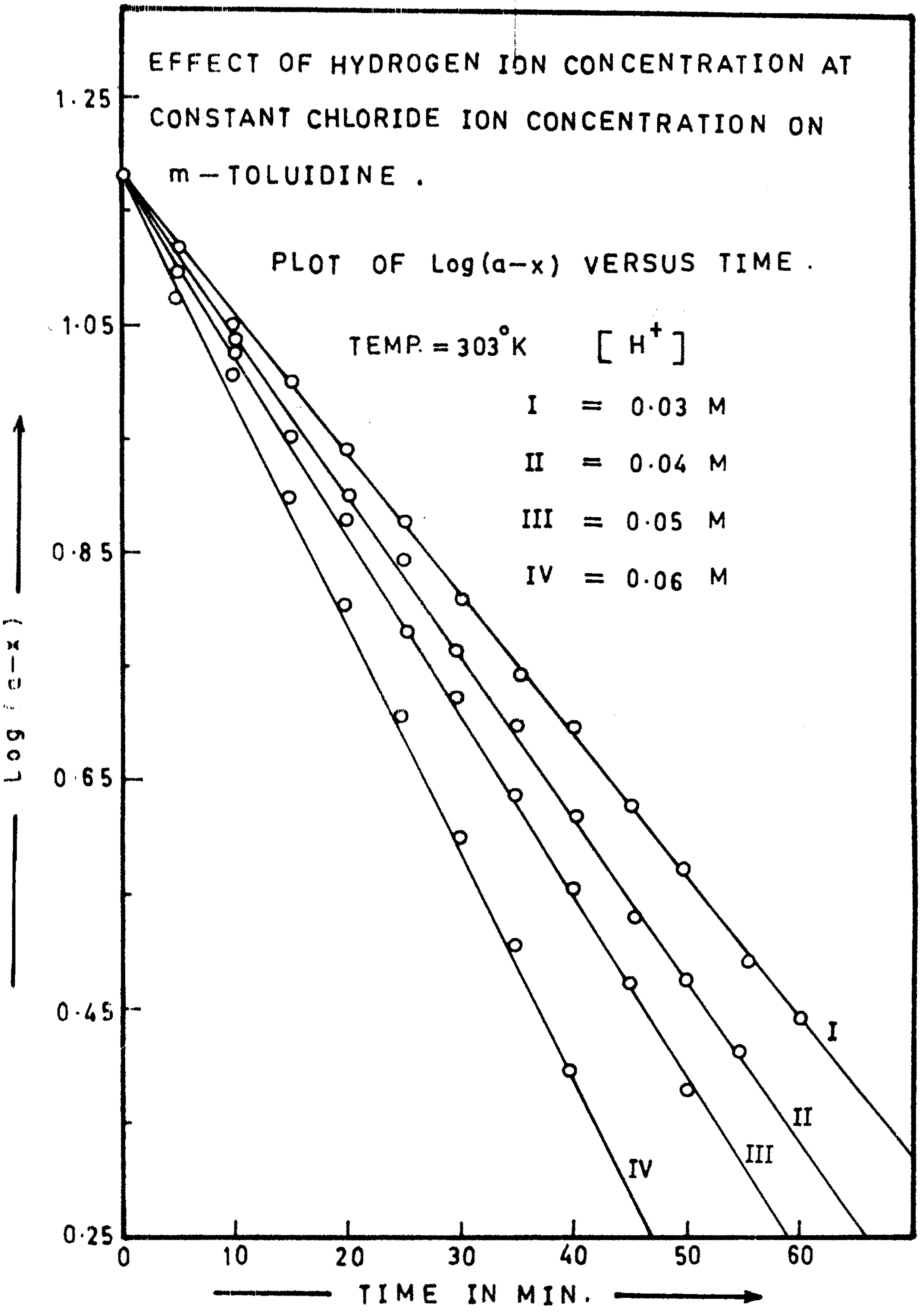

EFFECT OF HYDROGEN ION CONCENTRATION AT CONSTANT CHLORIDE ION CONCENTRATION ON m-TOLUIDINE.
PLOT OF Log(a-x) VERSUS TIME.
TEMP. = 303°K
[H+]
I = 0.03 M
II = 0.04 M
III = 0.05 M
IV = 0.06 M
1.25
1.05
0.85
0.65
0.45
0.25
Log (a-x)
0
10
20
30
40
50
60
TIME IN MIN.
I
II
III
IV

FIG. 3.2.6

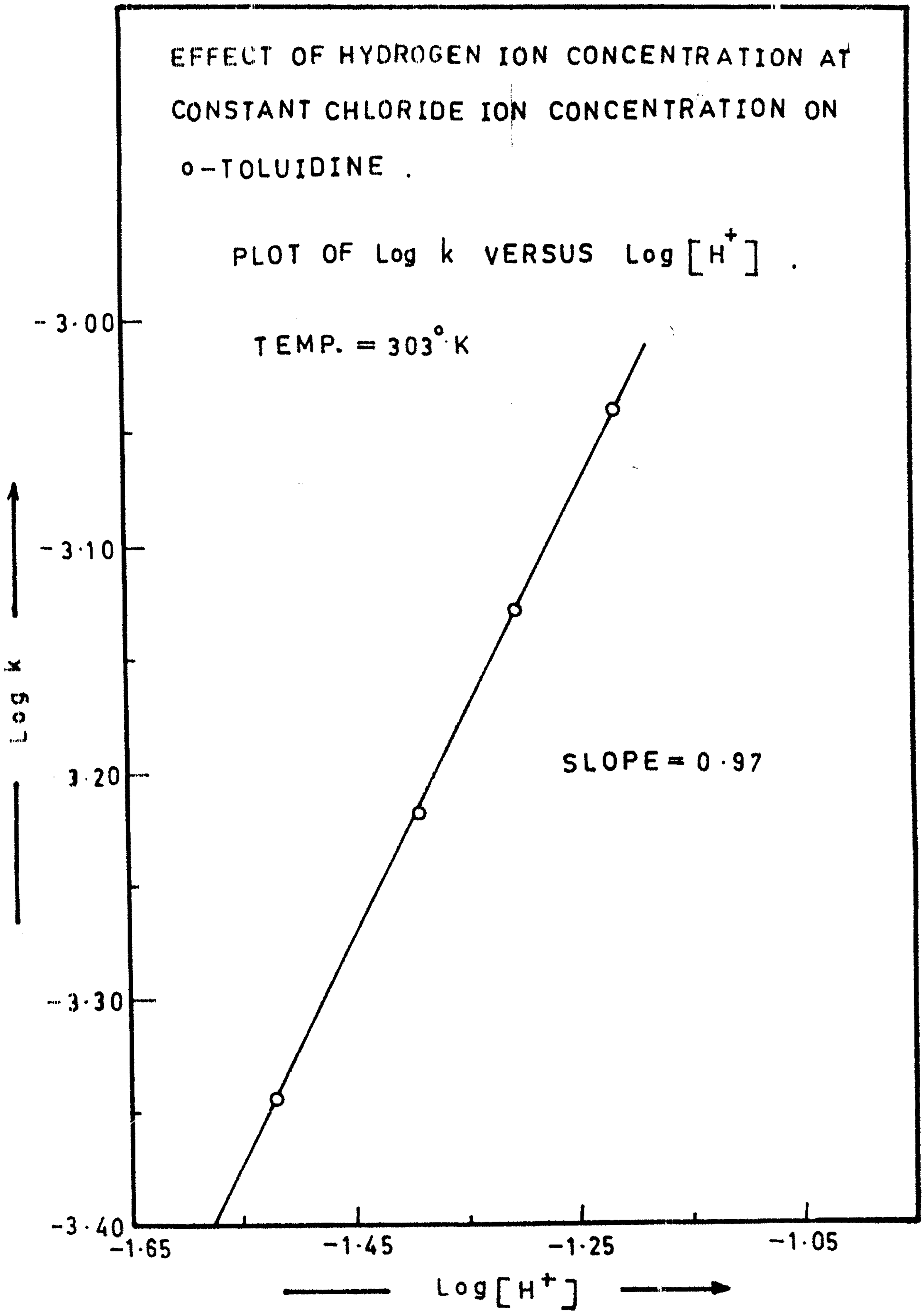
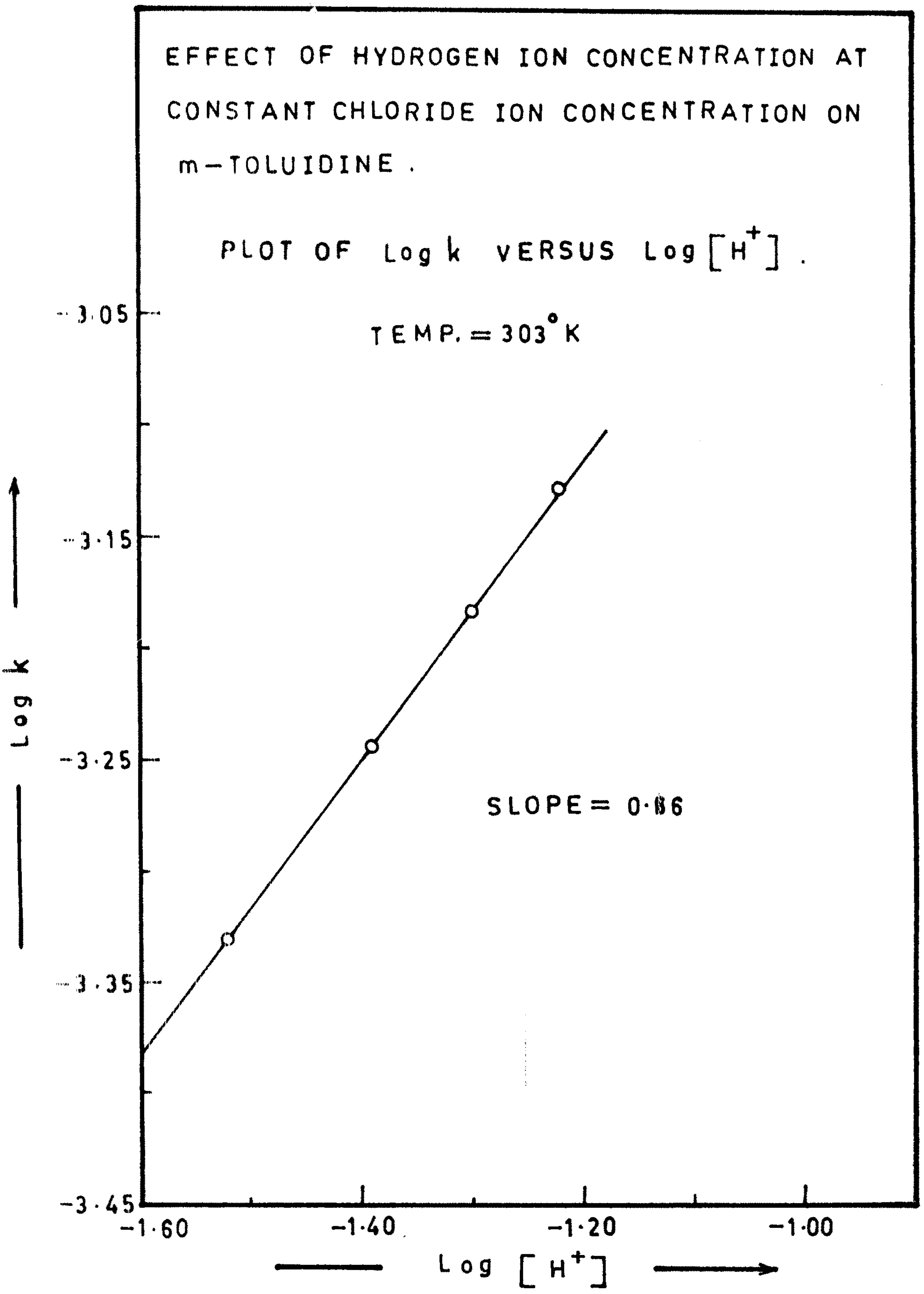

EFFECT OF HYDROGEN ION CONCENTRATION AT CONSTANT CHLORIDE ION CONCENTRATION ON o-TOLUIDINE .
PLOT OF Log k VERSUS Log [H⁺] .
TEMP. = 303° K
SLOPE = 0·97
-3·00
-3·10
3·20
-3·30
-3·40
Log k
-1·65
-1·45
-1·25
-1·05
Log [H⁺]

FIG. 3·1·7



EFFECT OF HYDROGEN ION CONCENTRATION AT CONSTANT CHLORIDE ION CONCENTRATION ON m-TOLUIDINE.

PLOT OF Log k VERSUS Log $[H^+]$.

TEMP. = 303° K

SLOPE = 0·86

FIG. 3·2·7

VI) EFFECT OF CHLORIDE ION CONCENTRATION AT CONSTANT $[H^+]$:

To investigate the effect of addition of chloride ion on the rate of chlorination of amine, the concentration of sodium chloride was varied from 0.06M to 0.1M, keeping all the concentrations constant.

$$[H^+] = 0.05M$$

It is found that the rate of reaction is increased with increase in concentration of chloride ion. (Fig. 3.1.8 and 3.2.8 Table 3.1.8 and 3.2.8).

A plot of log k versus log $[Cl^-]$ gave a straight line of slope 0.39 and 0.40 for ortho-toluidine and meta-toluidine respectively. (Fig. 3.1.9 and 3.2.9 Table 3.1.9 and 3.2.9). From the slope, the order dependance on $[Cl^-]$ is calculated.

TABLE 3.1.8

Chlorination of ortho-toluidine by chloramine-B

Effect of chloride ion concentration by adding NaCl at constant

$[H^+] = 0.05M$

$[CAB] = 2.0 \times 10^{-3}M$; $[o.T] = 2.0 \times 10^{-2}M$

$[Na_2S_2O_3] = 5.0 \times 10^{-4}M$; Ionic strength = 0.5M

Temperature = 303^oK.

[NaCl]	=	0.07M	0.08M	0.09M	1.0M
Sr.No.	Time (min)	(a-x)	(a-x)	(a-x)	(a- x)
1.	0	15.0	15.0	15.0	15.0
2.	5	13.4	13.0	12.8	10.8
3.	10	11.5	10.9	10.7	8.6
4.	15	10.0	9.3	9.9	6.7
5.	20	8.2	7.8	7.6	5.3
6.	25	7.1	6.2	6.1	4.2
7.	30	6.0	5.5	5.1	3.3
8.	35	4.9	4.6	4.3	2.7
9.	40	3.7	3.8	3.4	2.2
10.	45	3.0	3.3	3.0	-
11.	50	2.8	2.7	2.4	-
$k\ (min^{-1}) \times 10^2$		3.42	3.60	3.78	3.90
$k\ (sec^{-1}) \times 10^4$		5.71	6.01	6.30	6.50

TABLE 3.2.8

Chlorination of mata-toluidine by chloramine-B

Effect of chloride ion concentration by adding NaCl at constant

$[H^+] = 0.05M$

$[CAB] = 2.0 \times 10^{-3}M$; $[m.T] = 2.0 \times 10^{-2}M$

$[Na_2S_2O_3] = 5.0 \times 10^{-4}M$ Ionic strength = 0.5M

Temperature = 303^0K.

[NaCl]	=	0.06M	0.07M	0.08M	0.09M
Sr.No.	Time (min)	(a-x)	(a-x)	(a-x)	(a-x)
1.	o	16.6	16.6	16.6	16.6
2.	5	13.9	12.0	11.9	11.2
3.	10	11.7	10.7	10.4	9.0
4.	15	9.8	8.6	8.2	8.0
5.	20	8.2	7.2	6.8	6.0
6.	25	7.0	6.0	5.5	5.2
7.	30	5.9	5.1	4.9	4.1
8.	35	5.0	4.3	3.8	3.4
9.	40	4.2	3.5	3.3	2.6
10.	45	3.5	2.9	2.7	2.2
11.	50	3.1	2.4	2.2	2.1
$k\ (min^{-1}) \times 10^2$		3.32	3.60	3.78	3.96
$k\ (sec^{-1}) \times 10^4$		5.54	6.00	6.30	6.60

TABLE 3.1.9

Chlorination of ortho-toluidine by chloramine-B.
Calculation of order with respect to chloride ion concentration.
Temperature = 303°K.

Sr. No.	$[\bar{Cl}]$ M	log $[\bar{Cl}]$	k (sec^{-1}) X 10^4	log k
1.	0.07	- 1.1549	5.71	- 3.2432
2.	0.08	- 1.0969	6.01	- 3.2209
3.	0.09	- 1.0458	6.30	- 3.2003
4.	0.10	- 1.0000	6.50	- 3.1798

Order w.r.t. $[\bar{Cl}]$ = 0.39

TABLE 3.2.9

Chlorinatioon of meta-toluidine by chloramine-B.
Calculation of order with respect to chloride ion concentration.
Temperature = 303^{0}K.

Sr.No.	$[Cl^-]$ M	log $[Cl^-]$	k $(sec^{-1}) \times 10^4$	log k
1.	0.06	- 1.2216	5.54	- 3.2565
2.	0.07	- 1.1549	6.04	- 3.2218
3.	0.08	- 1.0969	6.30	- 3.2007
4.	0.09	- 1.0458	6.60	- 3.1806

Order w.r.t $[Cl^-]$ = 0.40

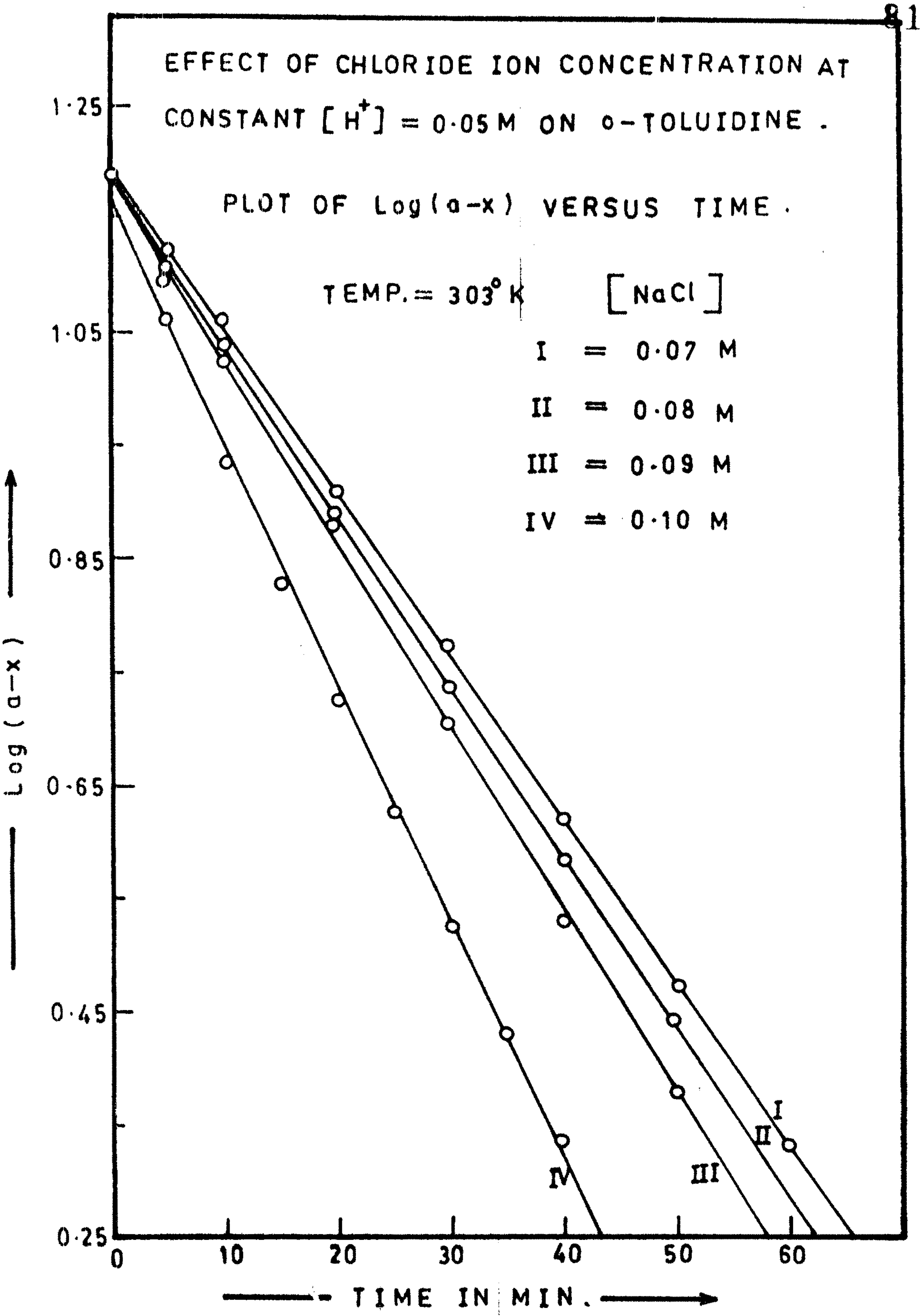

EFFECT OF CHLORIDE ION CONCENTRATION AT
CONSTANT [H$^+$] = 0·05 M ON o-TOLUIDINE.
PLOT OF Log(a-x) VERSUS TIME.
TEMP. = 303° K
[NaCl]
I = 0·07 M
II = 0·08 M
III = 0·09 M
IV = 0·10 M
1·25
1·05
0·85
0·65
0·45
0·25
Log (a-x)
0
10
20
30
40
50
60
TIME IN MIN.
I
II
III
IV

FIG. 3·1·8

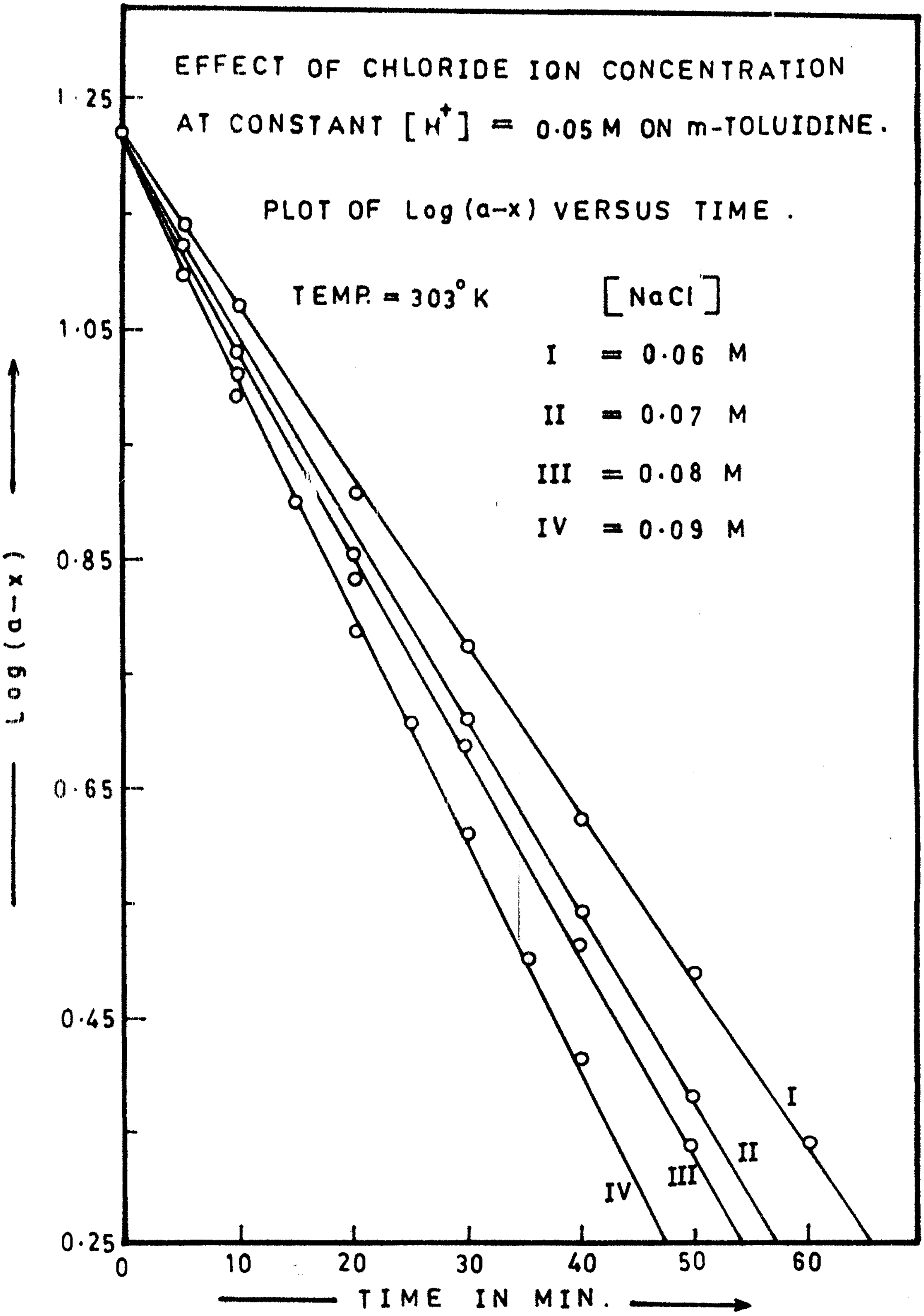

EFFECT OF CHLORIDE ION CONCENTRATION
AT CONSTANT $[H^+]$ = 0·05 M ON m-TOLUIDINE.
PLOT OF Log (a–x) VERSUS TIME.
TEMP. = 303° K
[NaCl]
I = 0·06 M
II = 0·07 M
III = 0·08 M
IV = 0·09 M
1·25
1·05
0·85
0·65
0·45
0·25
Log (a–x)
0
10
20
30
40
50
60
TIME IN MIN.
I
II
III
IV

FIG. 3·2·8

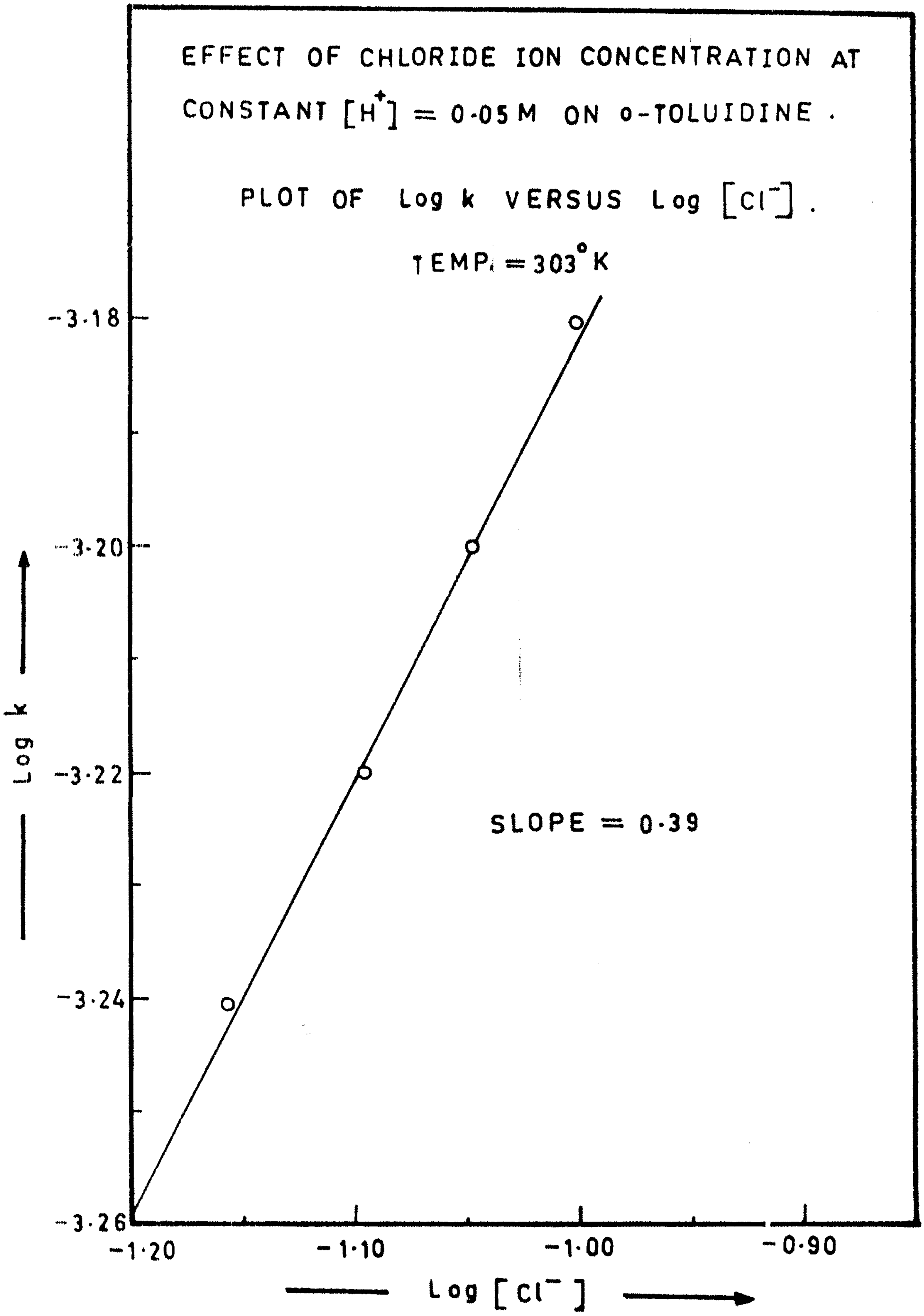

EFFECT OF CHLORIDE ION CONCENTRATION AT
CONSTANT [H$^+$] = 0·05 M ON o-TOLUIDINE.
PLOT OF Log k VERSUS Log [Cl$^-$].
TEMP. = 303° K
SLOPE = 0·39
-3·18
-3·20
-3·22
-3·24
-3·26
Log k
-1·20
-1·10
-1·00
-0·90
Log [Cl$^-$]

FIG. 3·1·9

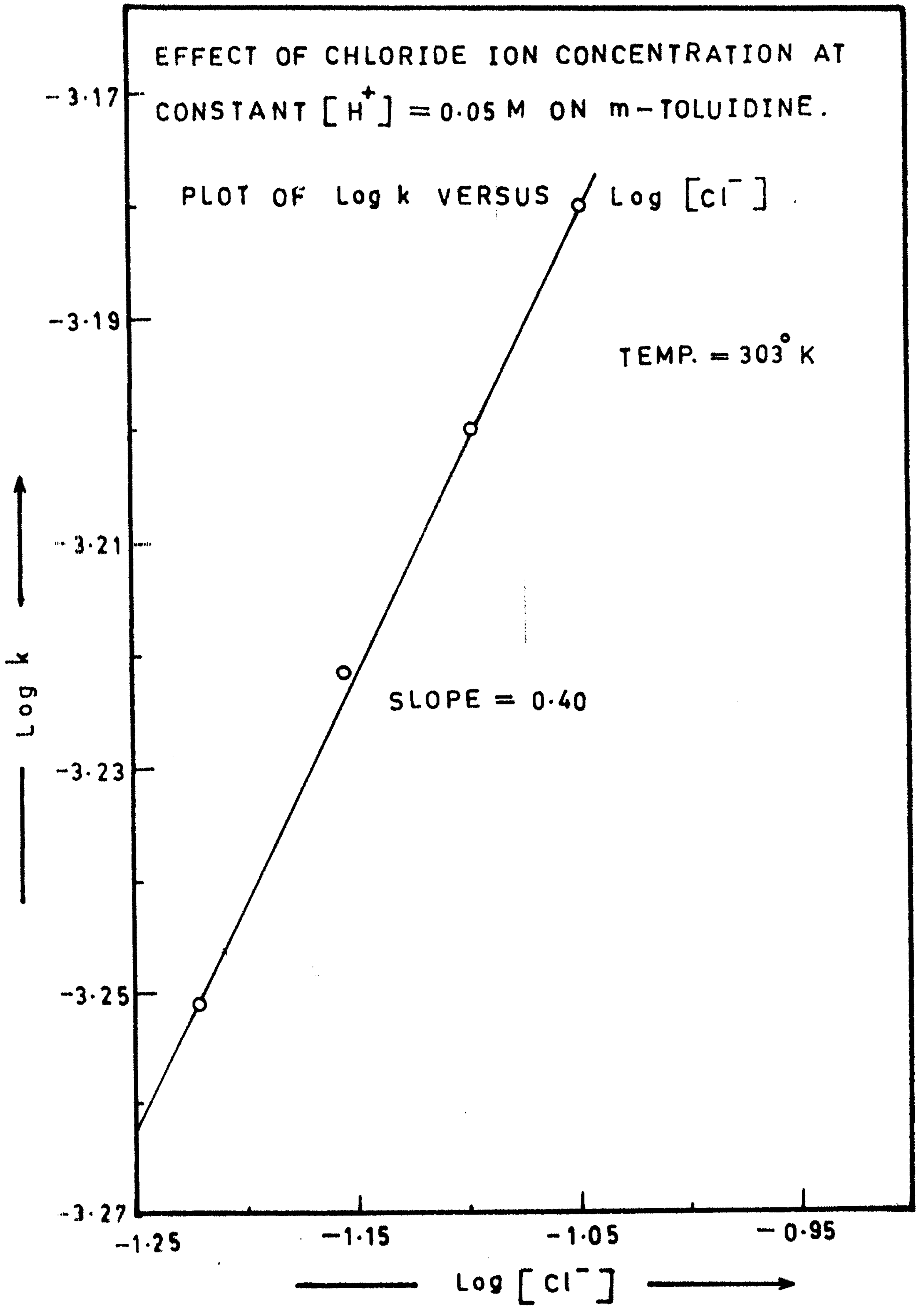

EFFECT OF CHLORIDE ION CONCENTRATION AT CONSTANT $[H^+] = 0.05$ M ON m-TOLUIDINE.
PLOT OF Log k VERSUS Log [Cl⁻]
TEMP. = 303°K
SLOPE = 0.40
-3.17
-3.19
-3.21
-3.23
-3.25
-3.27
Log k
-1.25
-1.15
-1.05
-0.95
Log [Cl⁻]

FIG. 3.2.9

VII) EFFECT OF IONIC STRENGTH :

The effect of ionic strength of the medium was studied using sodium perchlorate. It is found that the variation of ionic strength of the medium (0.5 to 1.0M) has no significant effect on the rate of chlorination of both the amines. This suggests that the reaction takes place between neutral species and not between the ionic species[1].

VIII) EFFECT OF CHANGE IN SOLVENT COMPOSITION :

The effect of change in solvent composition on the rate was studied by adding ethanol to the reaction mixture. The reaction was studied in 20% to 50% ethanol (V/V) medium. Then it is found that, variation of ethanol had a negligible effect on the rate, indicating the absence of dielectric constant effect.

IX) EFFECT OF END PRODUCT :

Addition of the reaction product, benezene sulphon-amide to the reaction mixture had no effect on the rate of reaction. The reactions were carried out in presence of 0.002 to 0.004M in benezene sulphonamide.

Thus, this result showed that the rate determining step is not reversible and product formed is not going to affect the reaction.

DISCUSSION

In order to discuss the possible mechanism for the chlorination of ortho toluidine and meta toluidine by chloramine-B it is necessary to summerise the results obtained.

Like chloramine-T, chloramine-B is a moderately strong electrolyte[74] in aqueous solution. In our kinetic study of chlorination of amines, hydrochloric acid is used as a medium in 50.0% ethanol (V/V) of ionic strength 0.5M. Therefore, the probable chlorinating species in the acid solutions of CAB are RNHCl, HOCl, RN^+H_2Cl and H_2OCl^+

To reach at suitable mechanism we have summarised our observations as follows.

1. The chlorination of ortho-toluidine and meta-toluidine is first order with respect to [CAB.] .
2. The chlorination of ortho-toluidine and meta-toluidine is fractional order with respect to [amine] .
3. Relatively low enthalpy of activation and high negative values of entropy of activation have been observed, the kinetic and thermodynamic parameters for both the amines studied and compared.
4. The rate of chlorination of aminnes increases with increase in concentration of hydrochloric acid medium at constant ionic strength. Order with respect to [HCl] was found, to be 1.36 for orthotoluidine and 1.06 for m-toluidine in the acid range of 0.03M to 0.07M.

5. Addition of sodium chloride at constant ionic strength and constant $[H^+]$ increase the rate of reaction. The order with respect to Cl^- is fractional in both the amines.
6. The rate of reaction increases with increase in $[H^+]$ at constant $[Cl^-]$ by addition of NaCl, when total ionic strength is constant.
7. The variation in the ionic strength of the medium does not influence the rate of chlorination of amines.
8. There is a negligible effect on the rate of reaction.
9. There is no effect on the rate of reaction by addition of the reaction product, benezene sulphonamide, to the reaction mixture.
10. Stoichiometry of the reaction was found to be 1:1.

The fractional order dependance on amine concentration and observation of change in colour before formation of products indicates the formation of reaction intermediate between the amine and the chlorinating species.

The small values of enthalpy ($\Delta H^{\neq}$) and high negative values of entropy ($\Delta S^{\neq}$) suggest the rigidity and solvation of activated complex. Relatively small values of frequency factor (A) also suggest the formation of rigid complex.

Addition of chloride ion increases the rate and a fractional order dependance on $[Cl^-]$ is observed. Such behaviour has been noted in the Orton rearrangement of N-haloamides[5].

Addition of benzene sulphonamide and ionic strength of the medium has no effect on the rate indicating that ~~either~~ neutral species ~~or ionic species~~ are involved in the rate determing step.

When the catalysis is effected simultaneously by $[H^+]$ and $[Cl^-]$ an order of 1.36 is observed in case of o-toluidine and 1.06 in case of m-toluidine. This may be traced to a mixed order kinetics.

Addition of acrylonitrile to the reaction mixture had no effect, indicating the absence of free radical species.

A fractional order dependance on amine clearly indicates complex formation between the substrate and chlorinating agent in an equilibrium prior to the rate determining step. The complex undergoes subsequent Orton rearrangement[5] to form nuclear chlorinated products in the presence of HCl.

Large negative entropies of activation and positive free energy of activation suggest the role of bond breaking in attaining the activated state.

Although the equilibria present in CAT solutions have been clearly established by the work of Bishop and Jenning[74] Morris and coworkers and Higuchi and Coworkers[13], no detail information is available about the species present in acidified CAB-solutions in literature.

Zilberg[8] has shown acidification of CAB by HCl, or H_2SO_4 gives dichloramine-B ($RNCl_2$) and benezene sulphonamide (RNH_2). Mogilevski and coworkers[9] have reported the presence of hypochlorous acid in acidified CAB solutions.

It is likely that equilibria[74,75,,13] similar to those of CAT exist in acidified CAB solutions.

To confirm this hypothesis conductometric and potentiometric titrations between aqueous solutions of CAB and HCl were performed. The conductometric behaviour of CAB solution is identical[76-78] with that of CAT, while pH titration curves observed were similar to those noted by Morris and coworkers[75] and Mahadevappa and Rangaswamy[76] in CAT-HCl titrations. Further pH measurements on aqueous solutions of CAB showed that a 0.05M CAB solution has a pH of 7.7 at 25°C. Hence a similar set of equilibria can be expected in CAB solutions. The work of Mukherjee and coworkers[26,27] indicates a similar set of equilibria.

The possible equilibria in aqueous CAB solutions are-

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \qquad .....(1)$$

$RNCl^-$ picks up proton in the acid medium to give conjugate acid RNHCl

$$RNCl^- + H^+ \rightleftharpoons RNHCl \qquad .....(2)$$

which in turn undergoes disproportion to $RNCl_2$,

$$2RNHCl \rightleftharpoons RNCl_2 + RNH_2 \qquad .....(3)$$

and hydrolyse to HOCl

$$RNHCl + H_2O \rightleftharpoons RNH_2^+ + HOCl \quad .....(4)$$

In strong acid solution, RNHCl may give RNH_2^+Cl,

$$RNHCl + H^+ \rightleftharpoons R\overset{+}{N}H_2Cl \quad .....(5)$$

which in turn undergoes hydrolysis to give H_2OCl^+,

Therefore, the probable chlorinating species in the acid solutions of CAB are RNHCl, HOCl, RN^+H_2Cl and H_2OCl^+

$RNCl_2$ can be ruled out as the chlorinating species[27] in view of the stirct first order dependance of rate on [CAB]. Effect of benzene sulphonamide on the rate also rules out the possibility of $RNCl_2$ and HOCl as chlorinating species.[27] If $RNCl_2$ were to be the active species, the rate law predicts a second order dependance of rate on [CAB] [42] but it is contrary to the experimental observations.

Therefore, RNHCl is the effective species in the present system.

The observed kinetics for the chlorination of o-toluidine and and m-toluidine in hydrochloric acid medium can be accounted as-

$$RNCl^- + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} RNHCl$$

where $R = C_6H_5SO_2$

$$RNHCl + H^+ \overset{K_2}{\rightleftharpoons} RNH_2Cl^+$$

$$RNH_2Cl^+ + S \overset{K_3}{\rightleftharpoons} X$$

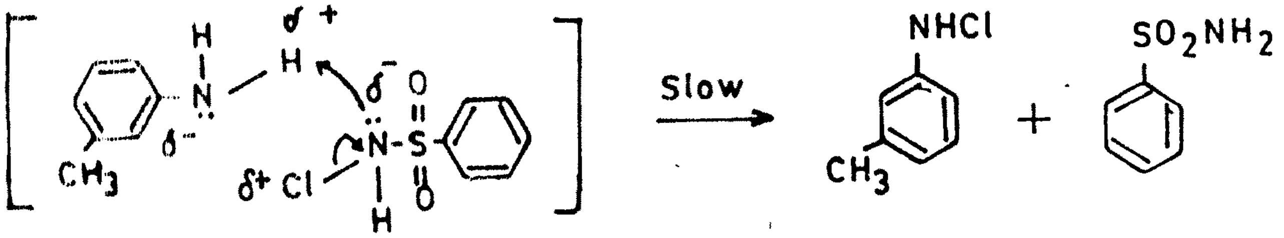
$$X \xrightarrow{k_4} X' \text{ (slow rate determining)}$$

$$X' \xrightarrow{k_5} \text{Products}$$

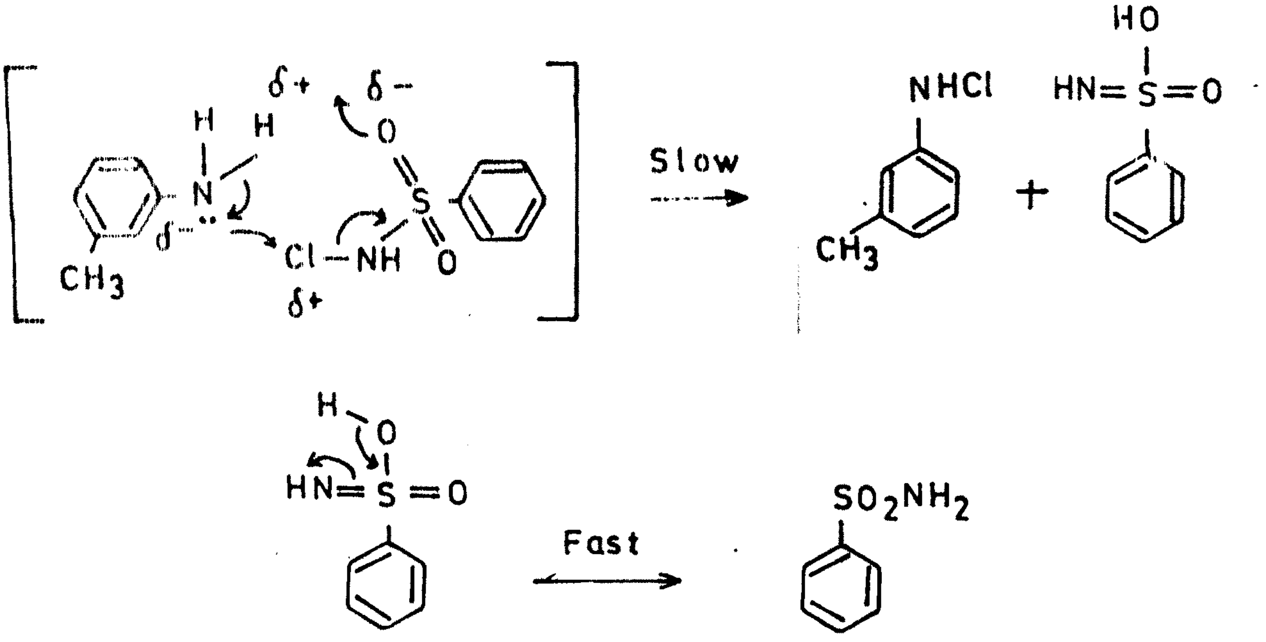
If $[CAB]_T = [RNCl^-] + [RNHCl] + [RNH_2Cl^+]$ then the rate law would be-

$$-\frac{d\log[CAB]}{dt} = \frac{k_4K_1K_2K_3[S][H^+]^2}{1+K_1[H^+]\{1+K_2[H^+]+K_2K_3[H^+][S]\}}$$

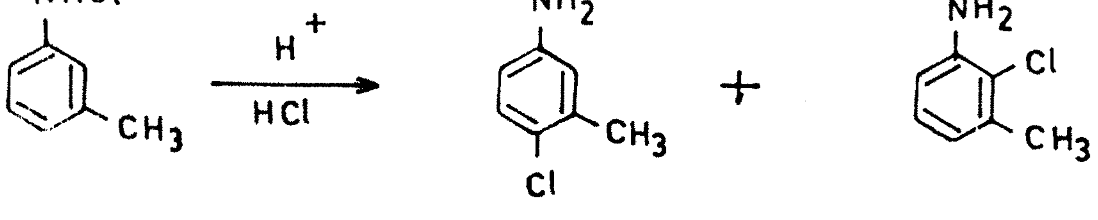
Different workers[61,62,66] have proposed the formation of N-chloramines in the chlorination of aromatic amines. The formation of ortho and para isomers in the halogenation of some aromatic amines have been reported[44,50] However, under the present experimental conditions the plausible mechanism has been proposed as described below.



SCHEME-1



SCHEME-2



Increase in the rate of reaction by the addition of chloride ion is similar to its effect observed in the Ortonrearrangement of N-haloamides. The latter refers to the migration of chlorine from the side chain of N-haloamines or a ring substituted derivative of chloroamide to the ring in the presence of H^+ and Cl^-. The present results can be explained by the following scheme, where a nucleophilic attack by Cl^- on RNH_2Cl^+ is assumed, accounting for catalytic effect of chloride ions.

$$RNCl^- + H^+ \xrightleftharpoons{K_1} RNHCl$$

$$RNHCl + H^+ \xrightleftharpoons{K_2} RNH_2Cl^+$$

$$RNH_2Cl^+ + S^- \xrightleftharpoons{K_6} X''$$

$$X'' \xrightarrow{k_7} X''' \quad \text{(slow rate determining)}$$

$$X''' \xrightarrow{k_8} \text{Products}$$

The rate law at constant $[H^+]$ can be derived as

$$\text{Rate} = \frac{K_1 K_2 K_6 k_7 \, [CAB]_T \, [H^+]^2 \, [S] \, [Cl^-]}{1 + K_1 [H^+] \{1 + K_2 [H^+] + K_2 K_6 [H^+][S][Cl^-]\}}$$

When catalysis is effected simultaneously by H^+ and Cl^- an order of 1.36 on the gross concentration of HCl is observed for ortho-toluidine while in case of meta toluidine it is 1.06. This may be traced to a mixed order kinetics following the rate law.

$$-\frac{d\,[CAB]}{dt} = k' \, [CAB] \, [H^+]^{0.97} \, [S]^{0.56} + k'' \, [CAB][Cl^-]^{0.39}[S]^{0.56}$$

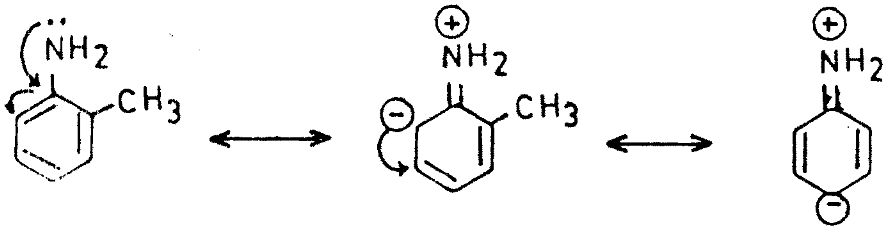
In the composite rate law, the first term accounts for H^+ catalysis and second for Cl^- catalysis. Similar observations were made in the chlorination of meta toluidine.

In the present study the reactivity of o-toluidine is slightly higher than m-toluidine since two nuclear positions are available for chlorination.

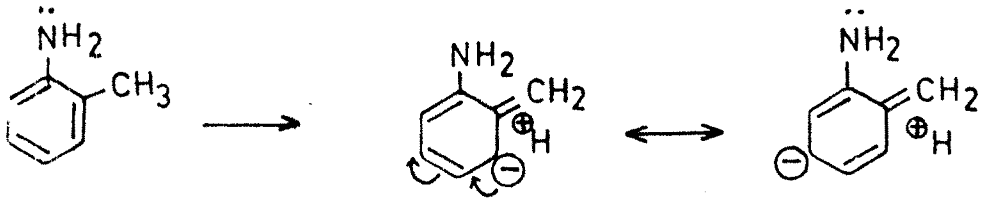
The electron relasing group enhance the rate in consonance with usual electronic effects. The number of nuclear positions available for chlorination in o-toluidine and m-toluidine is represented by mesomeric and hyper conjugation effect

i) In o-toluidine

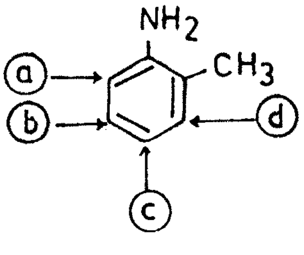
1. Mesomeric effect of - NH_2 group



2. Hyper conjugation effect of-CH_3 group



so total number of positions available for chlorination by electrophillic attack in o-toluidine will be



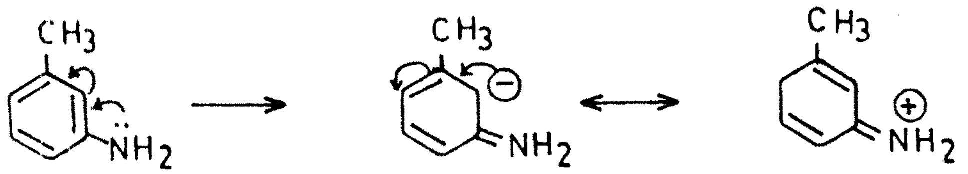
where

① ⓐ and ⓒ ⟶ nuclear positions available due to mesomeric effect of $\ddot{N}H_2$ group

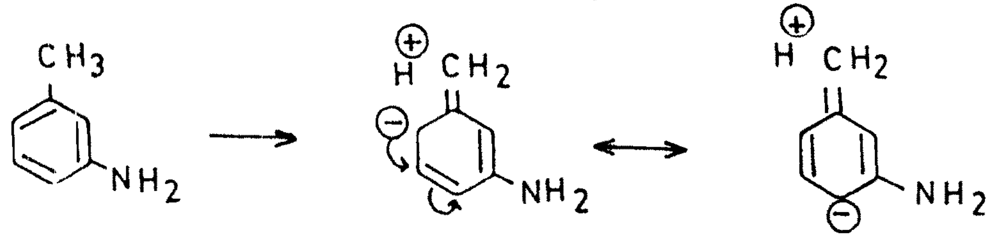
② ⓑ and ⓒ ⟶ nuclear positions available due to hyper conjugation effect of $-CH_3$ group.

II) In m-toluidine-

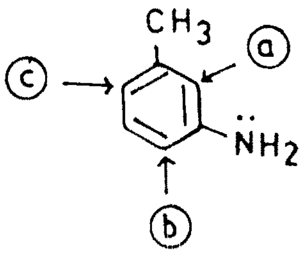
1 Mesomeric effect of $-\ddot{N}H_2$ group



2. Hyper conjugation effect of methyl group



so nuclear positions available for attack of electrophilic will be-



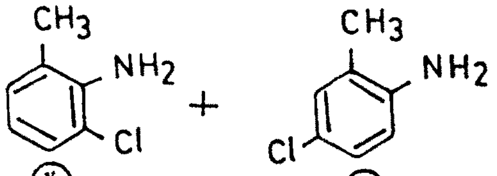
where

ⓐ and ⓑ → nuclear positions available due to mesomeric and hyper conjugation effect

ⓒ → nuclear position available due to mesomeric effect of $-NH_2$ group only

The products formed in the chlorination of o-toluidine and m-toluidine can be represented as-

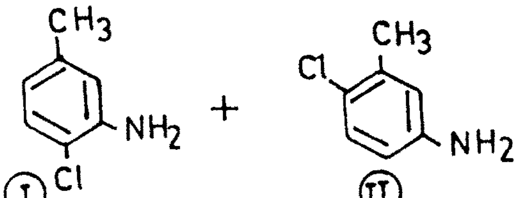
I) In o-toluidine



(I) 2-Chloro-6-methyl aniline

(II) 4-Chloro-6-methyl aniline

II) In m-toluidine



(I) 2-Chloro-5-methyl aniline

(II) 4-Chloro-5-methyl aniline

The chlorination of m-toluidine has been done by M.L.P. Rao and Padmanabha[61] by iodine monochloride. The values Ea, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for m-toluidine are found to be 14.55, 13.93 and -24.15 respectively and in our case these are shown in the Table 1 and 1'.

From the Table it is clear that the values of reaction rate constants in o-toluidine are slightly higher than those in m-toluidine.

TABLE (1)

Comparative study of rate constant-values for o-toluidine and m-toluidine.

[CAB] X 10^3M	k (sec^{-1}) X 10^4	
	o-T	m-T
2.0	4.10	3.77
2.5	4.08	3.60
3.0	4.10	3.62
[Substrate] X 10^2M		
2.0	3.44	3.42
3.5	5.05	4.80
4.0	5.39	5.37
Temperature $^{\circ}$K		
298	2.60	2.02
303	3.60	3.22
308	4.94	4.27
313	6.14	5.65
[HCl]		
0.04M	3.15	3.10
0.05M	4.11	3.83
0.06M	5.51	4.72
[H^+]		
0.04M	6.05	5.70
0.05M	7.42	6.55
0.06M	9.08	7.42

TABLE (1')

Thermodynamic parameters for O-toluidine and m-toluidine.

Amines	Ea k.cal	$\Delta H^{\neq}$ k.cal/mole	$\Delta S^{\neq}$ e.u	$\Delta G^{\neq}$ k.cal/mole
o-toluidine	11.56	10.91	−22.54	+38.36
m-toluidine	13.02	18.30	−22.68	+14.09