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RESULTS

CHAPTER – III

RESULTS

KINETICS OF OXIDATION OF BENZOIC ACID AND 2-CHLORO BENZOIC ACID HYDRAZIDES

A detailed kinetic study of oxidation of benzoic acid and 2-chloro benzoic acid hydrazides is presented in this chapter. Requisite concentrations of thallium(III), hydrazide, hydrochloric acid, perchloric acid were used to prepare the reaction mixture and titration reading was measured as a function of time. Experiments were designed to include the following studies.

1. Effect of Thallium(III) concentration on the rate of the reaction.
2. Effect of hydrazide concentration on the reaction rate.
3. Effect of H^+ ion concentration
4. Effect of Cl^- ion concentration
5. Effect of temperature and evaluation of thermodynamic parameters.
6. Effect of dielectric constant of the medium.
7. End product analysis and free radical tests.

SECTION - A

KINETICS OF OXIDATION OF BENZOIC ACID HYDRAZIDE

Standard Kinetic Run :

Preliminary experiments were performed in order to decide the suitable temperature and concentrations of the reactants, it was observed that in the presence of 3×10^{-3} M thallium(III), 6.4×10^{-2} M hydrazide, 7×10^{-2} M hydrochloric acid, 1×10^{-1} M perchloric acid reaction proceeds with measurable velocity.

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

Table 3 : A : 1

Standard Run

[BAH] = 6.4×10^{-2} M   [$HClO_4$] = 1×10^{-1} M, μ = 0.3 M
[Tl(III)] = 3×10^{-3} M   [HCl] = 7×10^{-2}M,   Temp. = 25°C
[$Na_2S_2O_3$] = 1.111×10^{-3} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	25	0.005555	- 2.25531
10	23.1	0.0051328	- 2.28964
20	22	0.0048884	- 2.31083
30	21.1	0.0046884	- 2.32897
60	19.5	0.0043329	- 2.36322
90	17.0	0.0037774	- 2.42280
120	14.0	0.0031108	- 2.50712
150	11.9	0.0024418	- 2.57810
180	10.5	0.002331	- 2.632066
210	9.0	0.001998	- 2.69940
240	7.9	0.0017538	- 2.75601
270	7.2	0.0015984	- 2.7963
300	6.1	0.0013542	- 2.866831
By graph k = 9.21×10^{-5} sec^{-1}			

Here (a-x) is calculated by using the Equation

$$(a\text{-}x) = \frac{B.R. \times [S_2O_8]}{5}$$

where

a-x	-	concentration of thallium III in the reaction mixture.
B.R.	-	volume of sodium thiosulphate in ml.
$[S_2O_8]$	-	concentration of sodium thiosulphate.
5	-	volume of thallium solution in ml of the reaction mixture.

For example, for zero time,

$$(a\text{-}x) = \frac{25 \times 1.111 \times 10^{-3}}{5} = 0.00555$$

The value of k is obtained from the slope of plot of -log (a-x) against time [fig. 3 : A : 1] by using the relation

$$k = 2.303 \times slope$$

Effect of Thallium(III) concentration :

To study the effect of thallium(III) concentration on reaction rate and to determine the order of the reaction with respect to thallium(III), the reaction was carried out at five different initial concentrations of thallium(III) keeping the concentrations of hydrazide and perchloric acid constant. The concentration of HCl is varied to keep the ionic strength of the reaction mixture constant.

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

Table 3 : A : 2
Model Run

[BAH] = 5×10^{-2} M   [$HClO_4$] = 1×10^{-1} M, μ = 0.3 M
[Tl(III)] = 1×10^{-3} M   [HCl] = 9×10^{-2} M,   Temp. = 25°C
[$Na_2S_2O_3$] = 0.9765×10^{-3} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	9.3	0.0018162	- 2.74081
10	8.7	0.0016991	- 2.76977
20	8.2	0.00016014	- 2.79548
30	7.7	0.0015038	- 2.82280
60	7.1	0.0013866	- 2.85803
90	6.0	0.0011718	- 2.93114
120	4.2	0.0008202	- 3.08604
150	3.5	0.0006835	- 3.16522
180	3.0	0.0005859	- 3.23217
210	2.5	0.0004882	- 3.31135
240	2.1	0.0004101	- 3.38707
280	1.8	0.00035154	- 3.45402
By graph k = 7.31×10^{-5} sec^{-1}			

Similarly the reaction was carried out at the different initial concentrations of thallium(III) and results are tabulated as follows :

[BAH] = 5 x 10^{-2} M, [$HClO_4$] = 1 x 10^{-1}M,
[HCl] = 9x10^{-2} M, Temp. = 25°C.

[Tl(III)] M x 10^3	k x 10^5 sec^{-1}
1	7.31
3	7.67
5	7.67
7	7.31
10	7.67

A perusal of the data from the Table 3 : A : 2 shows that the rate of oxidation of Benzoic acid hydrazide remains practically constant at five different concentrations of thallium(III). So the rate of the reaction is independent of concentration of thallium(III). Since the pseudo first order plots were linear up to more than three half lives and the pseudo first order rate constants (Table 3 : A : 2) are fairly constant for all the concentration of Tl(III) studied hence the order in oxidant is unity.

Effect of Hydrazide concentration

In order to investigate the effect of hydrazide concentration, it was also considered necessary to employ the data of the kinetic runs to determine the order of the reaction with respect to hydrazide, keeping the concentrations of thallium(III) and acids constant. The results of these kinetic study have been embodied in Table 3 : A : 3 and represented graphically in Fig. 3 : A : 3.

Table 3 : A : 3
Model Run

[BAH] = 16 x 10^{-2} M [$HClO_4$] = 1 x 10^{-1} M, μ = 0.3 M
[Tl(III)] = 3 x 10^{-3} M [HCl] = 7 x 10^{-2}M, Temp. = 25°C
[$Na_2S_2O_3$] = 1.0548 x 10^{-3} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	25	0.005274	- 2.2778
10	22.5	0.0047466	- 2.3236
20	20.2	0.0042613	- 2.3704
30	17.6	0.0037128	- 2.4296
60	12.0	0.0025315	- 2.59661
90	9.2	0.0019408	- 2.7120
120	6.6	0.0013923	- 2.85625
150	4.0	0.00084384	- 3.07373
180	2.8	0.00090688	- 3.22864
210	2.0	0.00042192	- 3.37476
240	1.4	0.000295344	- 3.52967
270	0.9	0.000189864	- 3.72155
By graph k = 19.19 x 10^{-5} sec^{-1}			

Similarly, the experiments were performed at the five different concentrations of Benzoic acid hydrazide and results are tabulated as follows.

$[Tl(III)] = 3 \times 10^{-3}$ M, $[HClO_4] = 1 \times 10^{-1}$ M,

$[HCl] = 7 \times 10^{-2}$ M, Temp. = 25°C.

[BAH] M x 10^2	k x 10^5 sec^{-1}
1.6	3.83
3	6.14
6.4	9.21
12.8	15.35
16	19.19

An examination of the above results indicates that the value of rate constant (k) depends on initial concentration of hydrazide and it increases with increase in hydrazide concentration.

Effect of H^+ ion concentration

In order to study the effect of H^+ ion concentration on the rate of oxidation of Benzoic acid hydrazide, the concentration of HCl was varied and also different concentrations of NaCl were added in order to keep the ionic strength of the reaction mixture constant keeping the concentrations of other reactants constant. The results of these kinetic study are embodied in Table 3 : A : 4 and represented graphically in Fig. 3 : A : 4.

Table 3 : A : 4
Model Run

[BAH] = 3×10^{-2} M [NaCl] = 5×10^{-1} M, $\mu = 0.3$ M
[Tl(III)] = 3×10^{-3} M [HCl] = 2×10^{-2} M, Temp. = 25°C
[$Na_2S_2O_3$] = 1.9607×10^{-3} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	14.9	0.0058428	- 2.2344
30	13.5	0.0052938	- 2.2762
60	12.1	0.0047448	- 2.3238
90	10.7	0.0041958	- 2.3771
120	9.3	0.0036469	- 2.4354
150	8.0	0.0031371	- 2.50349
180	7.5	0.0029410	- 2.53149
220	6.4	0.0025096	- 2.60037
260	5.1	0.00199991	- 2.6989
300	4.5	0.0017646	- 2.75334
By graph k = 6.397×10^{-5} sec^{-1}			

Similarly, the reaction was carried out at the four different concentrations of H^+ ion and results are tabulated as follows.

$[BAH] = 3 \times 10^{-2}$ M, $[Tl(III)] = 3 \times 10^{-3}$ M,

Temp. = 25°C.

$[H^+]$ M x 10^2	k x 10^5 sec^{-1}
2.0	6.397
7.0	3.8
17.0	2.42
27.0	1.73

A perusal of the above data shows that the rate of oxidation of benzoic acid hydrazide decreases as the concentration of H^+ ion increases.

Effect of Cl^- ion concentration

In order to study the effect of Cl^- ion concentration on the rate of oxidation of benzoic acid hydrazide by thallium(III), the concentration of HCl . And $HClO_4$ were varied keeping the concentration of other reactant constant. The results of these runs are recorded in table 3:A:5.

Table 3 : A : 5
Example Run

[BAH] = 3×10^{-2} M
[Tl(III)] = 3×10^{-3} M
[$Na_2S_2O_3$] = 1.0416×10^{-3} M

[$HClO_4$] = 27×10^{-2} M,
Temp. = 25°C
$\mu = 0.3$ M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	24.5	0.0051038	- 2.29210
10	22	0.004583	- 2.33885
20	19.5	0.0040622	- 2.39123
30	17.1	0.0035622	- 2.44828
40	14.5	0.0030206	- 2.51990
50	11.9	0.002479	- 2.60572
60	9.4	0.0019582	- 2.70814
70	8.1	0.0016873	- 2.77278
80	7.0	0.0014582	- 2.83618
90	6.5	0.00135408	- 2.86835
100	5.9	0.0012290	- 2.91041
110	5.2	0.0010832	- 2.96526
120	4.8	0.0009999	- 3.00002
130	4.0	0.00083328	- 3.07920
By graph $k = 25.58 \times 10^{-5}$ sec^{-1}			

Similar type of the experiments were performed at the five different concentrations of perchloric acid and results are tabulated as follows.

$[Cl^-]$ M x 10^2	k x 10^5 sec^{-1}
3.0	25.58
5.0	6.9
10.0	2.84
20.0	1.8
30.0	0.73

From the above data it shows that the rate of oxidation of benzoic acid hydrazide decreases as Cl^- ion concentration decreases.

Effect of Temperature

In order to determine the temperature coefficient and thermodynamic parameters, the reaction was studied at four different temperatures ranging from 25°C to 55^{0}C and at five different initial concentrations of hydrazide. The results of these kinetic study have been tabulated. Table 3:A:6 to 3:A.10 gives the results of these experiments. Kinetic data from Table 3:A:8 has been represented graphically in Fig. 3:A:5.

Table 3 : A : 6

[BAH] = 1.6×10^{-2} M
[Tl(III)] = 3×10^{-3} M
[$Na_2S_2O_3$] = 0.8695×10^{-3} M
[HCl] = 7×10^{-2} M,
Temp. = 55°C μ = 0.3 M
[$HClO_4$] = 1×10^{-1} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	31	0.0053909	- 2.26833
10	27.1	0.0047126	- 2.32673
20	22.8	0.0039639	- 2.40176
30	19.0	0.0033041	- 2.48094
40	15.5	0.0026954	0 2,56937
50	13.0	0.0022604	- 2.64581
60	11.0	0.0019129	- 2.71830
70	9.5	0.00165205	- 2.78197
80	7.6	0.00132164	- 2.87888
90	6.3	0.00109557	- 2.96035
100	5.2	0.00090428	- 3.04369
By graph k = 30.7×10^{-5} sec^{-1}			

The results of four different temperatures for the same concentrated solutions are given below :

Temperature	k x 10^5 sec^{-1}
25°C	3.83
35°C	7.67
45°C	15.35
55°C	30.7

Table 3 : A : 7

[BAH] = 3×10^{-2} M
[HCl] = 7×10^{-2} M,
[Tl(III)] = 3×10^{-3} M
Temp. = 25°C
$\mu = 0.3$ M
[$Na_2S_2O_3$] = 1.25×10^{-3} M
[$HClO_4$] = 1×10^{-1} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	21.7	0.005424	- 2.26560
5	18.7	0.004675	- 2.33021
10	16.0	0.004	- 2.3979
15	13.0	0.00325	- 2.48811
20	11.1	0.002775	- 2.5565
25	9.0	0.00225	- 2.64781
30	7.9	0.001975	- 2.70443
35	6.5	0.001625	- 2.78914
40	5.4	0.00135	- 2.86966
45	4.2	0.00105	- 2.97881
50	3.7	0.000925	- 3.033858
55	3.0	0.00075	- 3.12493
60	2.6	0.00065	- 3.1870
65	2.3	0.000575	- 3.24033
70	2.0	0.0005	- 3.30102
By graph k = 47.97×10^{-5} sec^{-1}			

Similarly the concentration of hydrazide i.e. (BAH = 3×10^{-2}) is taken and the reaction was carried out at four different temperatures and the results are tabulated as follows.

Temperature	k x 10^5 sec^{-1}
25°C	6.14
35°C	12.79
45°C	23.03
55°C	47.97

Table 3 : A : 8
Example Run

[BAH] = 6.4 x 10^{-2} M
[Tl(III)] = 3 x 10^{-3} M
[$Na_2S_2O_3$] = 0.9615 x 10^{-3} M
[HCl] = 7 x 10^{-2} M,
Temp. = 45°C μ = 0.3 M
[$HClO_4$] = 1 x 10^{-1} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	27.4	0.005269	- 2.2783
10	24.2	0.004653	- 2.3322
20	21.0	0.004038	- 2.3938
30	17.1	0.003288	- 2.4830
40	14.2	0.002730	-2.5638
50	12.0	0.0023076	- 2.63683
60	10.7	0.002057	- 2.6862
70	8.8	0.0016922	- 2.77153
80	7.3	0.001403	- 2.8530
90	6.3	0.0012114	- 2.91668
100	5.8	0.00011534	-2.95259
120	4.0	0.0007692	- 3.11396
130	3.5	0.0006730	- 3.17195
By graph k = 38.38 x 10^{-5} sec^{-1}			

Similarly (BAH=6.4 x 10^{-2}M) the reaction was carried out at four different temperatures and the results are tabulated as follows :

Temperature	k x 10^{5} sec^{-1}
25°C	9.21
35°C	19.19
45°C	38.38
55°C	76.7

Table 3 : A : 9

[BAH] = 12.8 x 10^{-2} M
[Tl(III)] = 3 x 10^{-3} M
[$Na_2S_2O_3$] = 1.0548 x 10^{-3} M
[HCl] = 7 x 10^{-2} M,
Temp. = 35°C $\mu = 0.3$ M
[$HClO_4$] = 1 x 10^{-1} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	25	0.005274	- 2.27785
10	20.5	0.004324	- 2. 36405
20	17.0	0.003586	- 2.44535
30	14.7	0.0031011	- 2.50848
40	13.5	0.0028479	- 2.545466
50	11.4	0.0024049	- 2.61889
60	9.5	0.002004	- 2.69808
70	8.5	0.0017931	- 2.74638
80	7.5	0.0015822	- 2.800738
90	6.5	0.0013712	- 2.86289
120	3.5	0.0007383	- 3.13176
150	2.5	0.0005274	- 3.27785
By graph k = 30.7 x 10^{-5} sec^{-1}			

The results of rate constants at four different temperatures for the same concentrated Benzoic acid hydrazide i.e. (BAH=6.4×10^{-2}M) are given below.

Temperature	k x 10^5 sec^{-1}
25°C	15.35
35°C	30.7
45°C	61.49
55°C	122.8

Table 3 : A : 10

[BAH] = 1.6×10^{-2} M
[HCl] = 7×10^{-2} M,
[Tl(III)] = 3×10^{-3} M
Temp. = 45°C $\mu = 0.3$ M
[$Na_2S_2O_3$] = 1.0548×10^{-3} M
[$HClO_4$] = 1×10^{-1} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	25.0	0.005274	- 2.2778
5	20.9	0.004409	- 2.3556
10	16.7	0.003523	- 2.4530
15	13.9	0.0029324	- 2.53278
20	11.1	0.002341	- 2.6305
25	9.1	0.00191973	- 2.7167
30	7.5	0.001582	- 2.8007
35	6.5	0.0013712	- 2.8628
40	4.4	0.0009282	- 3.0323
45	3.7	0.0007805	- 3.10759
50	3.0	0.0006328	- 3.1987
55	2.5	0.0005274	- 3.27785
60	1.9	0.0004008	- 3.39704
By graph k = 76.76 x 10^{-5} sec^{-1}			

Similarly the reaction was carried out at four different temperatures and the results are tabulated as follows.

Temperature	k x 10^5 sec^{-1}
25°C	19.19
35°C	38.38
45°C	76.76
55°C	153.5

Perusal of the data in Table 3:A:6 to 3:A:10 clearly shows that the rate of the oxidation of Benzoic acid hydrazide are approximately doubled for 10°C rise 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°C rise in temperature was calculated in four pairs of temperature. The mean value of temperature coefficients of oxidation reaction for Benzoic acid hydrazide was found to be approximately 1.99.

Effect of $NaClO_4$ Concentration

In order to study the effect of $NaClO_4$ on the oxidation of Benzoic acid hydrazide, the concentration of $NaClO_4$ solution was varied keeping the concentration of the other reactants constant. The results of these runs are recorded in Table 3:A:11.

Table 3 : A : 11

[BAH] = 3×10^{-2} M
[HCl] = 7×10^{-2} M,
[Tl(III)] = 3×10^{-3} M
Temp. = 25°C
[$Na_2S_2O_3$] = 1.0526×10^{-3} M
[$HClO_4$] = 1×10^{-1} M
[$NaClO_4$] = 4.4×10^{-1}M
μ = 0.3 M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	24.9	0.0052419	- 2.28051
10	23.7	0.0049893	- 2.30196
20	22.2	0.0046735	- 2.31687
30	21.0	0.004420	- 2.35457
60	19.5	0.004105	- 2.38667
90	17.0	0.003578	- 2.4462
120	15.1	0.003178	- 2.4977
150	12.8	0.002694	- 2.56949
180	10.5	0.002210	- 2.65551
210	8.3	0.001742	- 2.75762
240	7.3	0.0015367	- 2.81336
270	5.4	0.0012631	- 2.89985
300	5.4	0.0012631	- 2.89985
By graph k = 6.14×10^{-5} x 10^{-5} sec^{-1}			

Following are the rate constants obtained at five different concentrations of $NaCl_4$

$[NaClO_4]$ $M \times 10^1$	$k \times 10^5\ sec^{-1}$
4.4	6.14
3.6	5.9
2.8	6.14
2.0	6.39
1.2	6.14

A perusal of the data from the Table 3:A:11 shows that the rate of oxidation of benzoic acid hydrazide remains practically constant at five different concentrations of sodium perchlorate.

Effect of Dielecrtric Constant

The effect of dielectric constant (D) of the medium on the rate of oxidation of benzoic acid hydrazide was studied by the addition of different volumes of ethanol (30% to 70%) to the reaction mixture, keeping the concentrations of other reactants constant. The results of these runs are recorded in Table 3:A:12.

Table 3 : A : 12

[BAH] = 3×10^{-2} M [HCl] = 7×10^{-2} M, $\mu = 0.3$ M
[Tl(III)] = 3×10^{-3} M Ethanol% (v/v) = 30,
[$Na_2S_2O_3$] = 1.058×10^{-3} M [$HClO_4$] = 1×10^{-1} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	25.1	0.0053111	- 2.27481
10	24.0	0.0050784	- 2.2942
20	22.8	0.0048224	- 2.31655
30	20.3	0.0042954	- 2.36699
60	17.5	0.003703	- 2.43144
90	14.2	0.0030047	- 2.52219
120	11.5	0.0024334	- 2.61378
150	8.5	0.0017986	- 2.74506
180	6.5	0.0013754	- 2.86157
210	5.4	0.0011426	- 2.94209
240	4.6	0.0009733	- 3.01172
300	4.0	0.0008464	- 3.07242
By graph $k = 7.67 \times 10^{-5}$ sec^{-1}			

Similarly the reaction was carried out at the different volumes of ethanol % (v/v) and results are tabulated as follows :

Ethanol % v/v	k x 10^5 sec^{-1}
30	7.67
40	6.97
50	6.14
60	5.68
70	5.11

A perusal of the data from the Table 3:A:11 shows that as dielectric constant of the reaction medium decreases rate of oxidation of benzoic acid hydrazide also decreases.

Effect of Acrylonitrile

In order to determine whether free radical formation takes place during the course of oxdidation it was necessary to determine the effect of Acrylonitrile concentration on the rate of oxidation, the reaction was carried out at five different initial concentrations of Acrylonitrile, keeping the concentrations of the other reactions constant. The results of these runs are recorded in Table 3:A:13.

Table 3 : A : 13

[BAH] = 3×10^{-2} M
[Tl(III)] = 3×10^{-3} M
[$Na_2S_2O_3$] = 0.9803×10^{-3} M
Acrylonitrile in ml = 2.
[HCl] = 7×10^{-2} M,
Temp. = 25°C $\mu = 0.3$ M
[$HClO_4$] = 1×10^{-1} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	27.0	0.0052936	- 2.27624
10	26.1	0.0051171	- 2.29097
20	25.3	0.0049603	- 2.30449
30	24.1	0.004725	- 2.32559
60	22.1	0.004332	- 2.36322
90	19.5	0.0038231	- 2.41758
120	17.4	0.0034114	- 2.46706
150	15.0	0.0029409	- 2.53151
180	12.9	0.0025291	- 2.59702
210	10.7	0.0020978	- 2.67822
240	8.6	0.0016861	- 2.77311
270	7.1	0.0013920	- 2.85635
300	5.8	0.0011371	2.94418
By graph k = 5.11×10^{-5} sec^{-1}			

Similarly the reaction was carried out at the different volumes of Acrtylonitrile and results are tabulated as follows.

Acrtylonitrile in ml	$k \times 10^5$ sec^{-1}
1	5.11
2	5.11
3	5.05
4	5.05
5	5.05

A perusal of the data from the Table 3:A:13 shows that the rate of oxidation of benzoic acid hydrazide remains practically constant at five different concentrations of Acrylonitrile. This shows that there is no formation of free radicals in the reaction.

FIG. 3·A·1- PLOT OF −Log (a−x) Vs TIME.

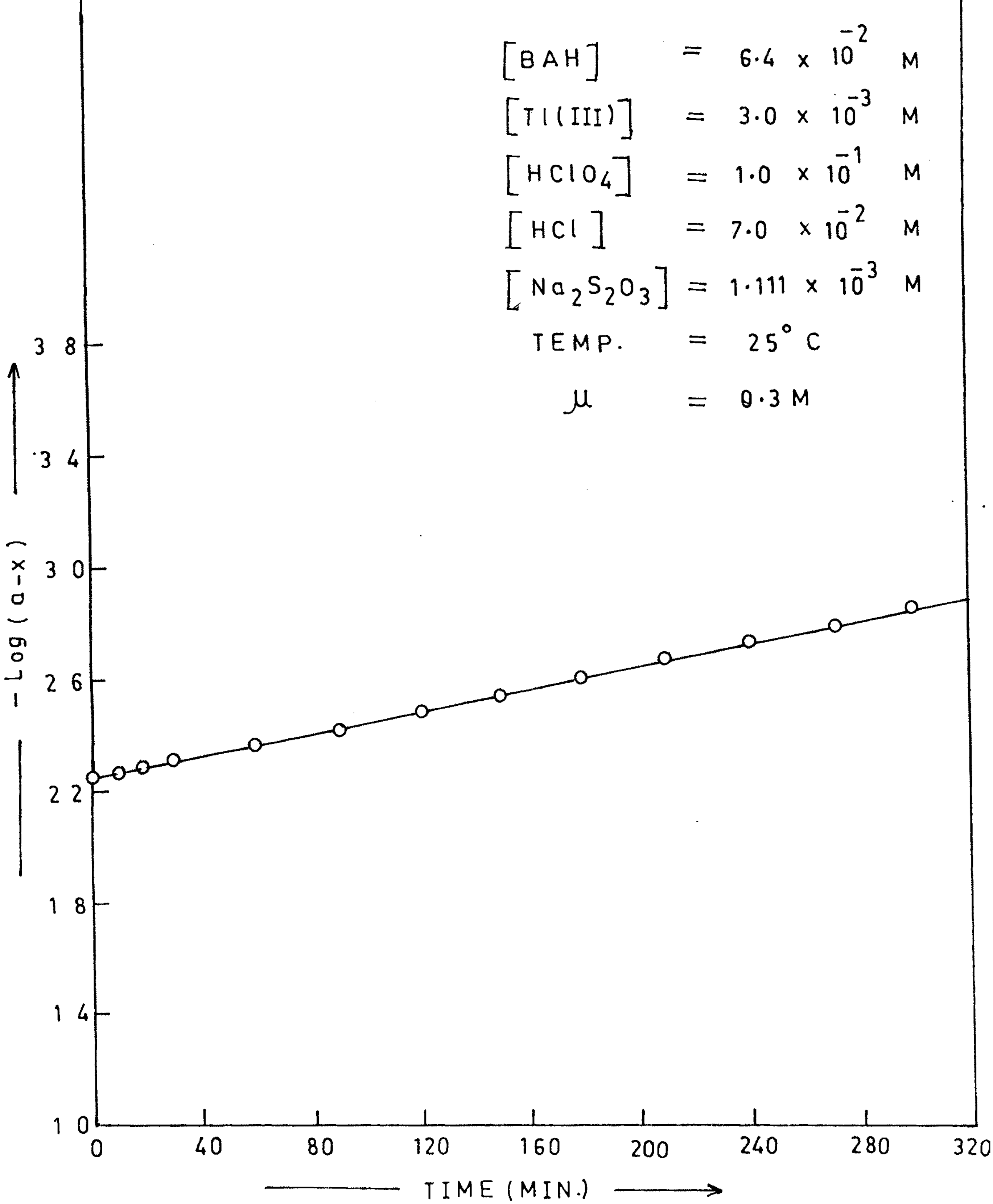
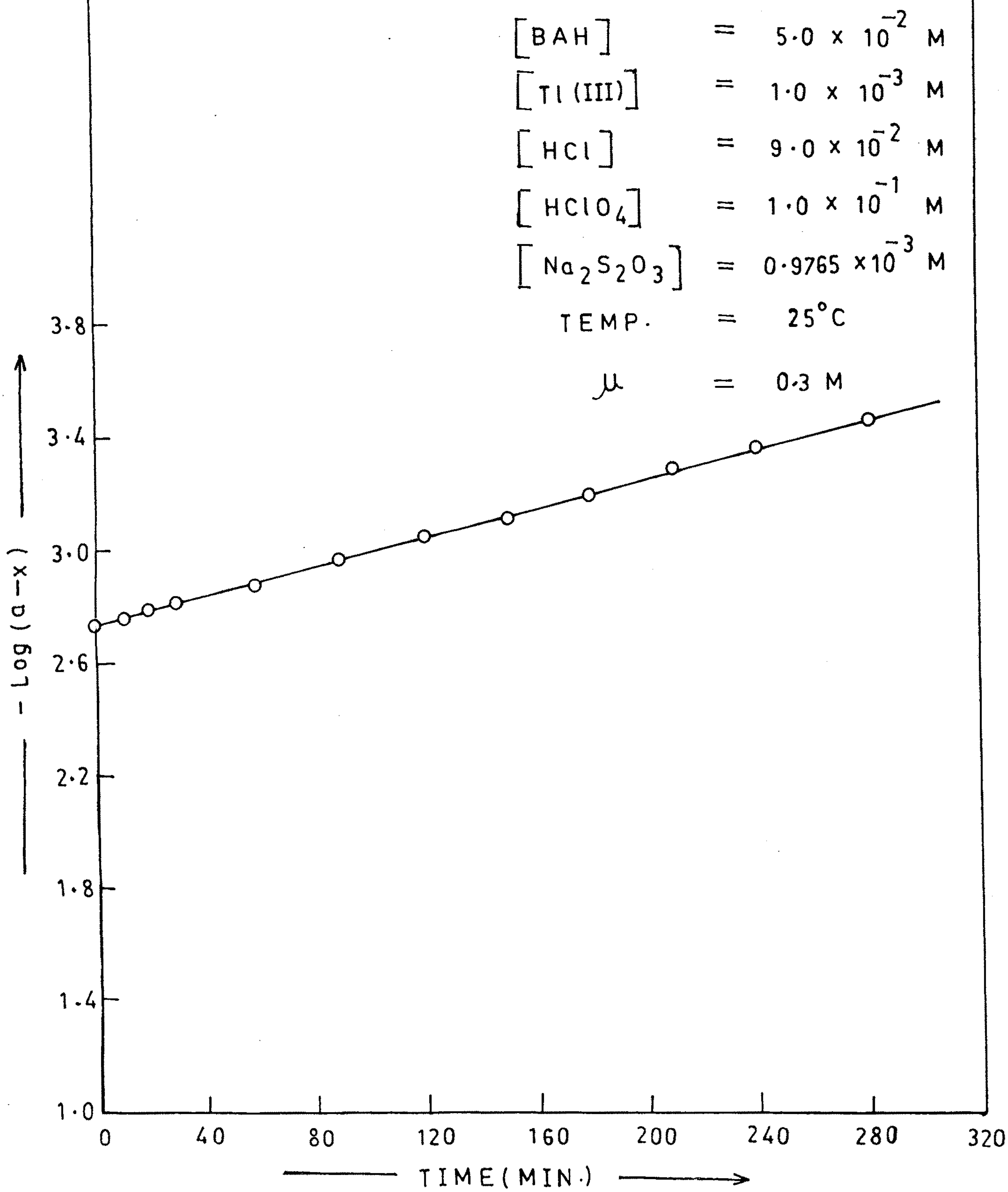


FIG. 3-A-2-PLOT OF -Log (a-x) Vs TIME.



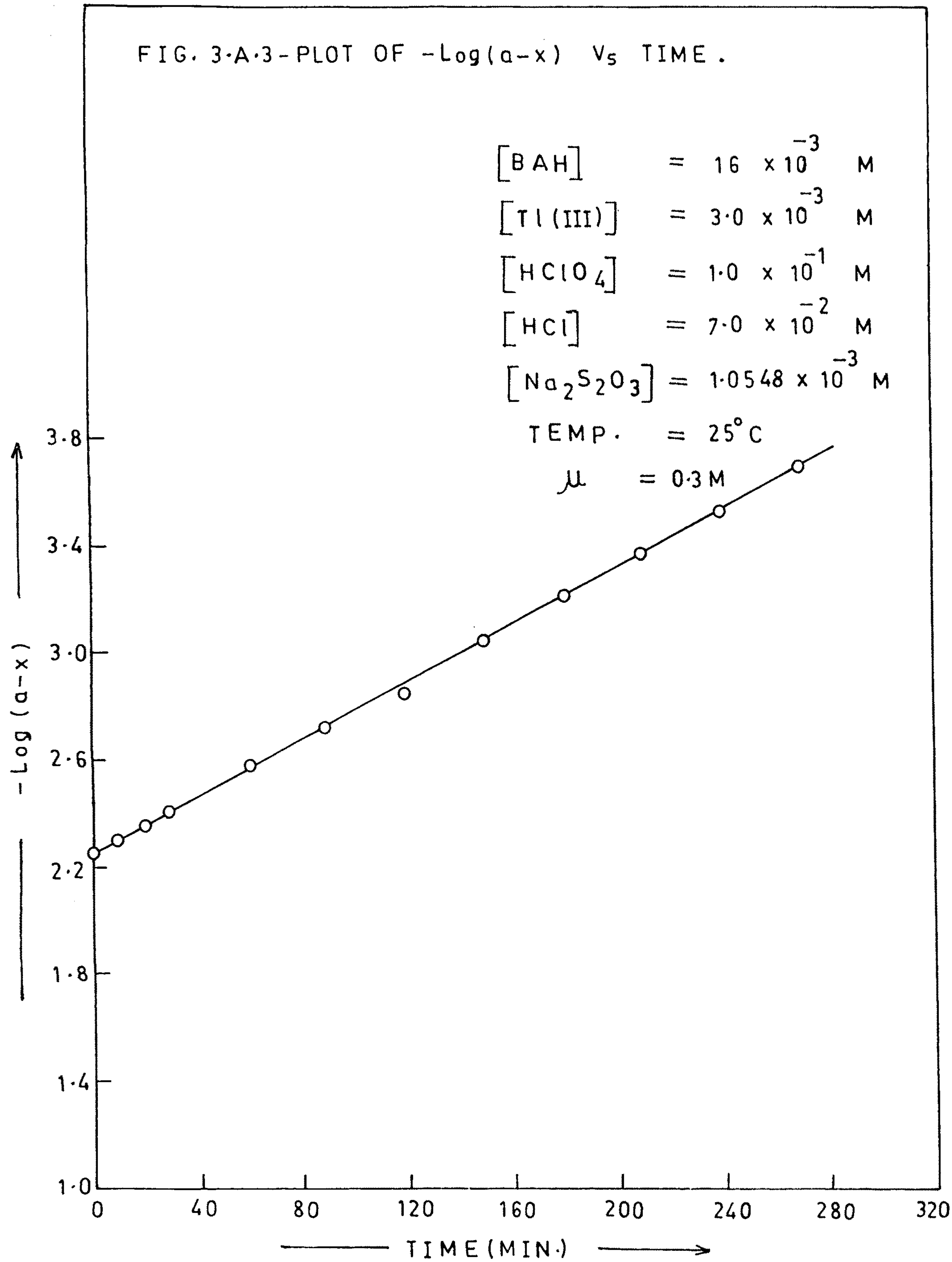


FIG. 3·A·3 - PLOT OF -Log(a-x) Vs TIME.
[BAH] = 16 x 10^-3 M
[Tl(III)] = 3·0 x 10^-3 M
[HClO4] = 1·0 x 10^-1 M
[HCl] = 7·0 x 10^-2 M
[Na2S2O3] = 1·0548 x 10^-3 M
TEMP. = 25°C
μ = 0·3 M
3·8
3·4
3·0
2·6
2·2
1·8
1·4
1·0
- Log (a-x)
0
40
80
120
160
200
240
280
320
TIME (MIN.)

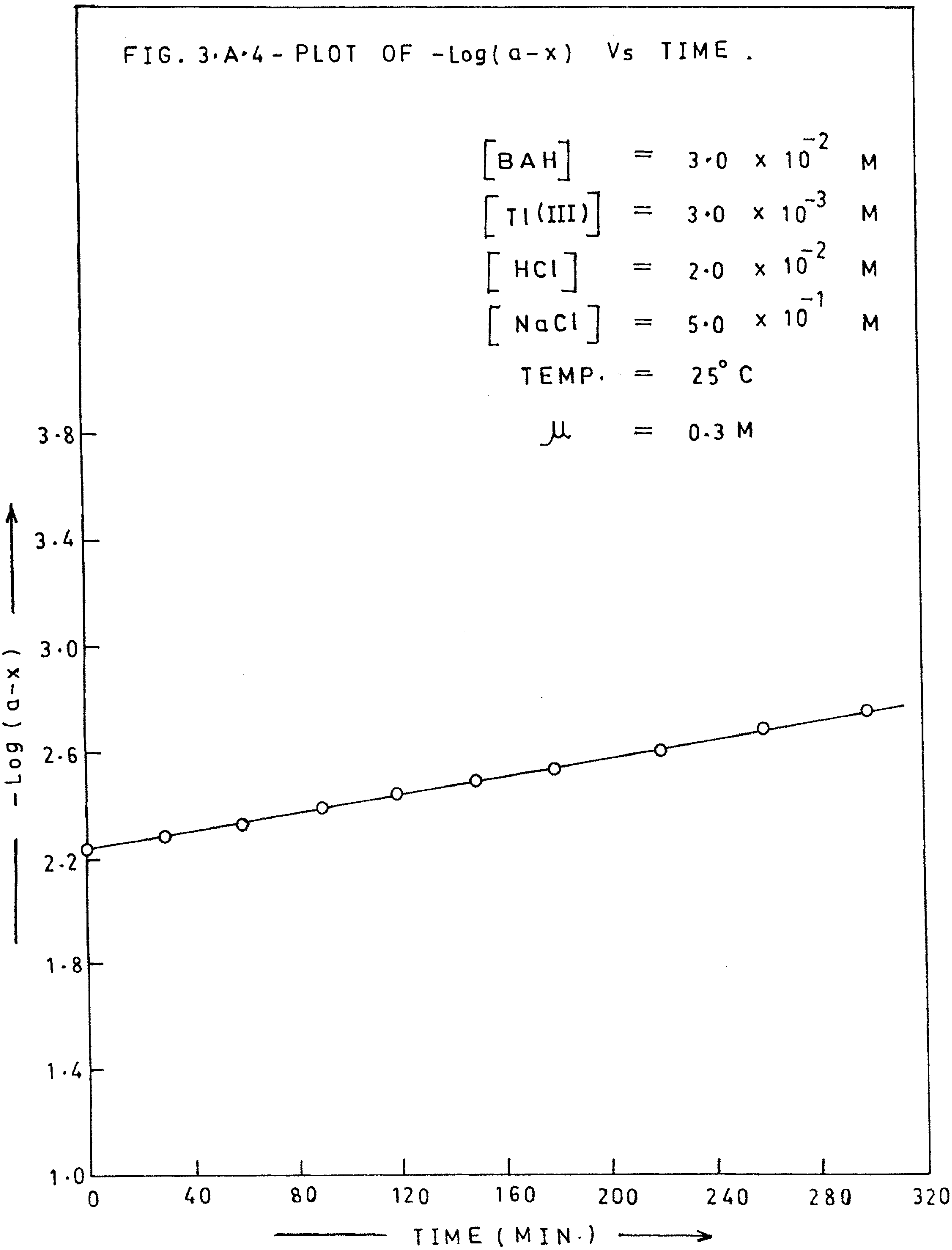


FIG. 3·A·4 - PLOT OF -Log(a-x) Vs TIME.
[BAH] = 3·0 x 10^-2 M
[Tl(III)] = 3·0 x 10^-3 M
[HCl] = 2·0 x 10^-2 M
[NaCl] = 5·0 x 10^-1 M
TEMP. = 25° C
μ = 0·3 M
-Log (a-x)
3·8
3·4
3·0
2·6
2·2
1·8
1·4
1·0
0
40
80
120
160
200
240
280
320
TIME (MIN.)

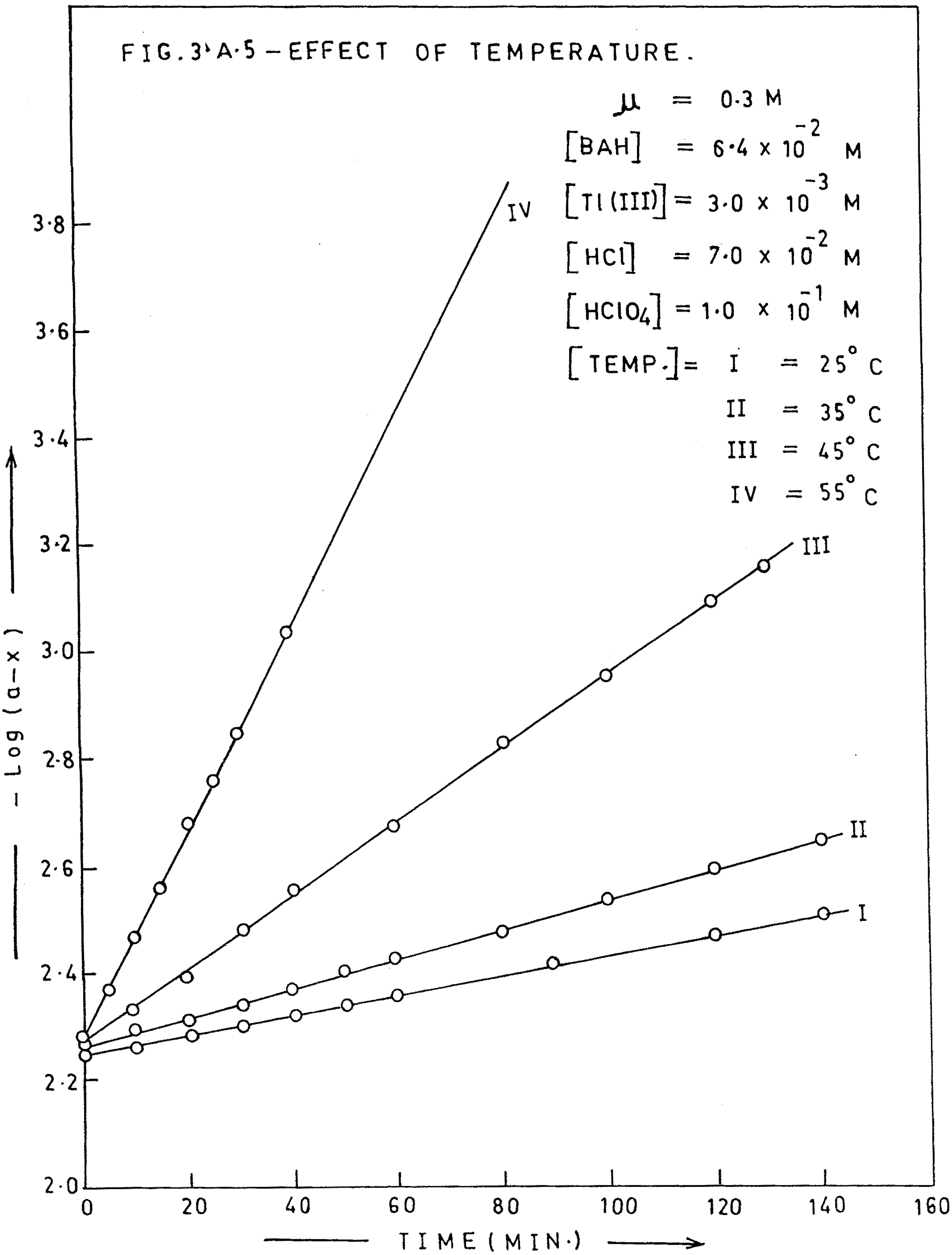


FIG. 3·A·5 – EFFECT OF TEMPERATURE.
μ = 0·3 M
[BAH] = 6·4 x 10^-2 M
[Tl(III)] = 3·0 x 10^-3 M
[HCl] = 7·0 x 10^-2 M
[HClO4] = 1·0 x 10^-1 M
[TEMP.] = I = 25° C
II = 35° C
III = 45° C
IV = 55° C
IV
III
II
I
3·8
3·6
3·4
3·2
3·0
2·8
2·6
2·4
2·2
2·0
– Log (a – x)
0
20
40
60
80
100
120
140
160
TIME (MIN.)

SECTION – B

KINETICS OF OXIDATION OF 2-CHLORO BENZOIC ACID HYDRAZIDE

Standard Kinetic Run

The preliminary experiments showed that the oxidation reaction under investigation proceeds with measurable velocity when concentrations of thallium (III), hydrazide, hydrochloric acid and perchloric acid were $3x10^{-3}$ M, $6.4x10^{-2}$ M, $7x10^{-2}$ M, and $1x10^{-1}$ M respectively.

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

Table 3:B:1

[2-Cl-BAH] = 6.4 x 10^{-2} M [$HClO_4$] = 1 x 10^{-1} M, μ = 0.3 M

[Tl (III)] = 3 x 10^{-3} M [HCl] = 7 x 10^{-2}M, Temp. = 35°C

[$Na_2S_2O_3$] = 0.9803 x 10^{-3} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	27.8	0.0054504	- 2.26375
10	26.0	0.0050975	- 2.29264
20	25.0	0.0049015	- 2.30967
30	23.9	0.0046858	- 2.32921
60	21.2	0.0041564	- 2.38128
90	18.0	0.003529	- 2.45234
120	15.5	0.0030389	- 2.51727
150	13.3	0.0026075	- 2.58375
180	11.1	0.0021762	- 2.66228
210	9.1	0.0017841	- 2.74856
240	8.0	0.0015684	- 2.80452
270	7.0	0.0013724	- 2.86251
300	6.1	0.0011959	- 2.92228
By graph k = 6.2 x 10^{-5} sec^{-1}			

Effect of Thallium (III) Concentration :-

To investigate the effect Thallium (III) concentration on the rate of oxidation, the reaction was carried out by using different initial concentrations of thallium (III) while concentration of hydrazide and perchloric acid were kept fixed. The kinetic data of this set of experiments is recorded in Table 3:B:2 and represented graphically by -log (a-x) Vs time plots (Fig. 3:B:2)

Table 3:B:2

[2-Cl-BAH] = 5×10^{-2} M [$HClO_4$] = 1×10^{-1} M, $\mu = 0.3$ M

[Tl (III)] = 5×10^{-3} M [HCl] = 5×10^{-2}M, Temp. = 35°C

[$Na_2S_2O_3$] = 1.865×10^{-3} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	24.9	0.0092877	- 2.032091
10	24.0	0.008952	- 2.048079
20	23.1	0.0086163	- 2.064694
30	22.3	0.0083179	- 2.07998
60	19.7	0.0073481	- 2.1338
90	17.0	0.006341	- 2.19784
120	15.0	0.005595	- 2.2521
150	12.2	0.0045506	- 2.34193
180	11.1	0.0041403	- 2.38296
210	9.3	0.0024689	- 2.45980
240	8.0	0.002984	- 2.52520
270	6.8	0.002536	- 2.59578
300	6.0	0.002984	- 2.6501399
By graph k = 5.48×10^{-5} sec^{-1}			

Similar reactions were carried out at the different initial concentrations of thallium (III) and results are tabulated as follows.

[Tl (III)] M x 10^3	k x 10^5 Sec^{-1}
1	5.29
3	5.11
5	5.48
7	5.48
10	5.29

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

Effect of Hydrazide Concentration :

To observe the effect of hydrazide concentration on the rate of reaction, the oxidation reaction was studied at five different initial concentrations of 2-chloro Benzoic acid hydrazide at 35°C, keeping concentrations of thallium (III) and acids unchanged. Table 3:B:3 contains the results of these experiments. These results are graphically represented in Fig 3:B:3.

Table 3:B:3

Kintetic data of one of the experiments

[2-Cl-BAH] = 16 x 10^{-2} M [$HClO_4$] = 1 x 10^{-1} M, μ = 0.3 M

[Tl (III)] = 3 x 10^{-3} M [HCl] = 5 x 10^{-2}M, Temp. = 35°C

[$Na_2S_2O_3$] = 0.9803 x 10^{-3} M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	27.5	0.0053916	- 2.26828
10	25.8	0.0050583	- 2.2959
20	24.3	0.0047642	- 2.3220
30	22.3	0.0044113	- 2.35546
60	19.0	0.003725	- 2.42887
90	16.0	0.0031369	- 2.50349
120	13.1	0.0025683	- 2.5903
150	10.2	0.0019958	- 2.69901
180	8.5	0.00166651	- 2.77819
210	7.3	0.0014312	- 2.844288
240	5.5	0.0010783	- 2.96724
270	4.5	0.00088227	- 3.05439
300	4.0	0.00078424	- 3.10555
By graph k = 12.7 x 10^{-5} sec^{-1}			

Similarly the reaction was carried out at the different initial concentrations of 2 chloro benzoic acid hydrazide and results are tabulated as follows.

[2-Cl BAH] M x 10^3	k x 10^5 Sec^{-1}
1.6	1.7
3	3.07
6.4	6.2
12.8	8.2
16	12.7

From the results, embodied in Table 3:B:3 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.

Effect of H^+ ion Concentration :

To observe the effect of H^+ ion concentration on the rate of the oxidation of 2-chloro benzoic acid hydrazide, the concentration of HCl was varied and also different concentrations of NaCl were added in order to keep the ionic strength constant keeping the concentrations of other reactants constant. The experimental conditions and results of this investigation are given in Table 3:B:4 and represented graphically in Fig. 3:B:4.

Table 3:B:4

[2-Cl-BAH] = 3 x 10^{-2} M   [Tl (III)] = 3 x 10^{-3} M

[HCl] = 2 x 10^{-2}M,   [NaCl] = 5 x 10^{-1}M

[$Na_2S_2O_3$] = 1.0 x 10^{-3} M   Temp. = 35°C μ = 0.3 M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	26.0	0.0052	- 2.2839
30	23.4	0.00468	- 2.3297
60	21.0	0.0042	- 2.3767
90	18.5	0.0037	- 2.4317
120	16.0	0.0032	- 2.4948
150	13.8	0.00276	- 2.55909
180	12.2	0.00245	- 2.6108
210	10.7	0.00214	- 2.6696
240	9.0	0.0018	- 2.74472
270	8.5	0.0016	- 2.79588
300	7.1	0.00142	- 2.84771
By graph k = 5.1 x 10^{-5} sec^{-1}			

Similar experiments were carried out at different concentrations of HCl and results are tabulated as follows.

$[H^+]$ M x 10^2	k x 10^5 Sec^{-1}
2	5.1
7	3.1
17	1.7
27	1.1

Perusal of the results in Table 3:B:4 it is seen that increase in the concentration of H+ ions, decreases the rate of oxidation of 2-chloro benzoic acid hydrazide.

<u>Effect of Cl^- ion concentration</u> :

In order to investigate the effect of Cl^- ion concentration on the rate of oxidation of 2-chloro benzoic acid hydrazide by thallium (III), the concentration of HCl and HCl04 were varied keeping the concentration of other reactants constant. The results of this investigation are embodied in Table 3:B:5.

Table 3:B:5

[2-Cl-BAH] = 3 x 10^{-2} M   [Tl (III)] = 3 x 10^{-3} M

[HCl] = 3 x 10^{-2}M, μ = 0.3 M

[$Na_2S_2O_3$] = 0.9803 x 10^{-3} M   Temp. = 35°C

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	27.5	0.0053916	- 2.26828
10	25.4	0.0049799	- 2.30285
20	23.1	0.0045289	- 2.34400
30	20.5	0.0040192	- 2.3958
40	18.2	0.0035682	- 2.4475
50	16.1	0.0031565	- 2.50086
60	14.5	0.002842	- 2.54242
90	11.0	0.0021566	- 2.6662
120	9.5	0.0018625	- 2.72988
140	6.3	0.0012357	- 2.90827
By graph k = 15.35 x 10^{-5} sec^{-1}			

Similar experiments were carried out at different concentrations of perchloric acid and results are tabulated as follows..

[Cl^-] M x 10^2	k x 10^5 Sec^{-1}
3	15.35
5	3.83
10	1.7
20	0.95
30	0.67

The perusal of the data in Table 3:B:5 shows that the rate of oxidation of 2-chloro benzoic acid hydrazide decreases as Cl^- ion concentration increases.

Effect of Temperature :

To investigate the effect of temperature and to determine thermodynamic parameters, the reaction was studied at four different temperatures ranging from 25°C to 55 °C. These experiments were repeated for five different concentrations of 2-chloro benzoic acid hydrazide and concentrations of other reactants were unchanged. The results of these experiments are tabulated in Tables 3:B:6 to 3:B:10. Kinetic data from Table 3:B:8 has been represented graphically in Fig. 3:B:5.

Table 3:B:6

Kinetic date of one of the Experiments

[2-Cl-BAH] = 1.6×10^{-2} M　　[HCl] = 7×10^{-2}M,

[$HClO_4$] = 1×10^{-1} M　　[Tl (III)] = 3 x 10-3M.

[$Na_2S_2O_3$] = 1.0204×10^{-3} M　　Temp. = 55°C,　　$\mu = 0.3$ M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	26.3	0.0053673	- 2.2702
10	25.6	0.0052244	- 2.2820
20	24.9	0.0050815	- 2.2940
30	24.2	0.0049387	- 2.3065
60	21.8	0.0044489	- 2.3518
90	19.8	0.0040407	- 2.3936
120	17.5	0.0035714	- 2.4472
150	15.0	0.0030612	- 2.51410
180	14.0	0.0028572	- 2.54407
210	12.0	0.0024489	- 2.6110
240	10.2	0.0020816	-2.68159
270	8.9	0.0018163	- 2.74080
300	7.8	0.001591824	- 2.798104
By graph k = 6.9×10^{-5} sec^{-1}			

Similarly the results of experiments at four different temperatures, keeping other conditions unchanged are embodied below.

Temperature	k x 10^5 Sec^{-1}
25°C	0.79
35°C	1.7
45°C	3.41
55°C	6.9

Table 3:B:7

Kinetic data of one of the Experiments

[2-Cl-BAH] = 3 x 10^{-2} M   [HCl] = 7 x 10^{-2}M,

[$HClO_4$] = 1 x 10^{-1} M   [Tl (III)] = 3 x 10^{-3}M.

[$Na_2S_2O_3$] = 1.0 x 10^{-3} Temp. = 55°C, μ = 0.3 M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	27.1	0.00542	- 2.2660
10	25.4	0.00508	- 2.2941
20	24.0	0.0048	- 2.3188
30	22.5	0.0045	- 2.3468
40	20.8	0.00416	- 2.3809
50	19.3	0.00386	- 2.4134
60	18.2	0.00364	- 2.4388
90	15.0	0.003	- 2.52287
120	11.8	0.00236	- 2.62708
150	9.0	0.0018	- 2.74472
180	6.2	0.00124	-2.90657
210	3.3	0.00066	- 3.18045
By graph k = 12.3 x 10^{-5} sec^{-1}			

Here the concentration of hydrazide i.e. (2-Cl BAH = 3 x 10^{-2}) is taken and the reaction was carried out at four different temperatures and the results are tabulated as follows.

Temperature	k x 10^5 Sec^{-1}
25°C	1.53
35°C	3.07
45°C	6.14
55°C	12.3

Table 3:B:8

[2-Cl-BAH] = 6.4 x 10^{-3} M [HCl] = 7 x 10^{-2}M,

[$HClO_4$] = 1 x 10^{-1} M [Tl (III)] = 3 x 10^{-3}M.

[$Na_2S_2O_3$] = 1.0204 x 10^{-3} Temp. = 55°C, μ = 0.3 M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	26.1	0.0053264	- 2.2735
10	23.6	0.004816	- 2.3173
20	21.2	0.004326	- 2.3639
30	19.0	0.003877	- 2.4115
40	16.6	0.003387	- 2.47018
50	14.1	0.002877	- 2.5410
60	11.5	0.002346	- 2.6296
90	9.1	0.001857	- 2.73115
120	6.3	0.001285	- 2.89085
150	3.5	0.0007142	- 3.146131
By graph k = 23.98 x 10^{-5} sec^{-1}			

Similarly the concentration of hydrazide i.e. (2-Cl BAH = 6.4 x 10^{-3}) is taken and the reaction was carried out at four different temperatures and the results are tabulated as follows.

Temperature	k x 10^5 Sec^{-1}
25°C	3.13
35°C	6.29
45°C	12.38
55°C	23.98

Table 3:B:9

[2-Cl-BAH] = 12.8 x 10^{-3} M [HCl] = 7 x 10^{-2}M,

[$HClO_4$] = 1 x 10^{-1} M [Tl (III)] = 3 x 10^{-3}M.

[$Na_2S_2O_3$] = 0.9523 x 10^{-3} Temp. = 55°C, μ = 0.3 M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	28.0	0.0053328	- 2.27304
10	24.8	0.0047234	- 2.32574
20	21.2	0.0040377	- 2.39386
30	17.9	0.0034092	- 2.46734
40	15.2	0.0028949	- 2.53836
50	13.6	0.0025902	- 2.58666
60	11.9	0.0022664	- 2.64466
90	7.5	0.0014284	- 2.84513
120	3.8	0.00072374	- 3.140412
By graph k = 31.98 x 10^{-5} sec^{-1}			

Similarly the concentration of hydrazide i.e. (2-Cl BAH = 12.8 x 10^{-3}) is taken and the reaction was carried out at four different temperatures and the results are tabulated as follows.

Temperature	k x 10^5 Sec^{-1}
25°C	4.38
35°C	8.16
45°C	16.14
55°C	31.98

Table 3:B:10

[2-Cl-BAH] = 16 x 10^{-2} M [HCl] = 7 x 10^{-2}M,

[$HClO_4$] = 1 x 10^{-1} M [Tl (III)] = 3 x 10^{-3}M.

[$Na_2S_2O_3$] = 1.0204 x 10^{-3} Temp. = 55°C μ = 0.3 M

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	26.2	0.0053468	- 2.2720
5	22.1	0.0045101	- 2.34580
10	18.0	0.0036734	- 2.4449
15	15.1	0.0030816	- 2.51122
20	12.5	0.002551	- 2.5033
25	10.5	0.0021428	- 2.66901
30	8.4	0.0017142	- 2.7660
40	5.5	0.0011224	- 2.9500
50	4.0	0.0008163	- 3.0881
60	2.8	0.0005714	- 3.2431
By graph k = 51.1 x 10^{-5} sec^{-1}			

The concentration of 2-chlorobenzoic acid hydrazide 16.0 x 10^{-2} M is taken and the reaction was carried out at four different temperatures and the results are tabulated as follows.

Temperature	k x 10^5 Sec^{-1}
25°C	6.39
35°C	12.79
45°C	25.58
55°C	51.1

Perusal of the data in Table 3:A:6 to 3:A:10 clearly shows that the rate of the oxidation of 2-ClBAH is approximately doubled for 10°C rise in temperature.

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

Temperature coefficient : The ratio of first order rate constants for 10°C rise in temperature was calculated in four pairs of temperature. The mean value temperature coefficients of oxidation reaction for 2-chloro benzoic acid hydrazide was found to be 1.99.

Effect of $NaClO_4$ concentration

To study the effect of $NaClO_4$ on the oxidation of 2-chloro benzoic acid hydrazide, the concentration of sodium perchlorate solution was varied keeping the concentration of the other reactants constant. The results of these runs are recorded in Table 3:B:11.

Table 3:B:11

[2-Cl-BAH] = 3 x 10^{-2} M   [HCl] = 7 x 10^{-2}M, μ = 0.3 M
[$HClO_4$] = 1 x 10^{-1} M   [Tl (III)] = 3 x 10^{-3}M.   Temp. = 35°C,
[$NaClO_4$] = 3.6 x 10^{-1} M,   [$Na_2S_2O_3$] = 1.0204 x 10^{-3}

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	26.3	0.0053673	- 2.27024
10	25.9	0.0052856	- 2.27690
20	25.4	0.0051836	- 2.28536
30	24.9	0.0050815	- 2.29400
60	22.9	0.0046734	- 2.33036
90	20.7	0.0042242	- 2.37423
120	19.1	0.0038979	- 2.40916
150	17.5	0.0035714	- 2.44716
180	16.0	0.0032652	- 2.48609
210	14.4	0.0029387	- 2.53183
240	13.0	0.002653	- 2.57625
270	11.6	0.0023673	- 2.62574
300	10.1	0.0020612	- 2.68587
By graph k = 3.01 x 10^{-5} sec^{-1}			

Similarly the reaction was carried out at the different initial concentrations of $NaClO_4$ and results are tabulated as follows :

$[NaClO_4]$ M x 10	k x 10^5 Sec^{-1}
4.4	6.14
3.6	5.9
2.8	6.14
2.0	6.39
1.2	6.14

A perusal of the data from the Table 3:B:11 shows that the rate of oxidation of 2-chloro benzoic acid hydrazide remains practically constant at five different concentrations of sodium perchlorate.

Effect of Dielectric Constant

In order to investigate the effect of dielectric constant (D) of the medium on the rate of oxidation of 2-chlorobenzoic acid hydrazide, the reaction was studied by the addition of different volumes of ethanol (30% to 70%) to the reaction mixture, keeping the concentrations of the reactants constants. The kinetic data of this study is recorded in Table 3:B:12.

Table 3:B:12

[2-Cl-BAH] = 3 x 10^{-2} M
[HCl] = 7 x 10^{-2}M, Temp. = 35°C,
[$HClO_4$] = 1 x 10^{-1} M
[Tl (III)] = 3 x 10^{-3}M. μ = 0.3 M
Ethanol% (v/v) = 30
[$Na_2S_2O_3$] = 1.0548 x 10^{-3}

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	25.3	0.0053372	- 2.27268
10	24.0	0.005063	- 2.29559
20	23.0	0.004852	- 2.31407
30	22.1	0.004662	- 2.33140
60	20.2	0.0042613	- 2.37045
90	18.4	0.0038816	- 2.41098
120	17.0	0.0035863	- 2.44535
150	15.1	0.0031854	- 2.49683
180	13.5	0.0028479	- 2.54546
210	12.1	0.0025526	- 2.59301
240	10.7	0.002257	- 2.64641
270	9.4	0.00198302	- 2.702672
300	8.0	0.00168768	- 2.77270
By graph k = 4.38 x 10^{-5} sec^{-1}			

Similarly the reaction was carried out at the different volumes of ethanol% (v/v) and results are tabulated as follows :

Ethanol % (v/v)	k x 10^5 Sec^{-1}
30	4.38
40	3.83
50	3.07
60	2.79
70	2.55

A perusal of the data from the Table 3:B:12 shows that as dielectric constant of the reaction medium decreases rate of oxidation of 2-chlorobenzoic acid hydrazide also decreases.

Effect of Acrylonitrile :

In order to study whether free radical formation takes place during the course of oxidation, it was necessary to determine the effect of Acrylonitrile concentration on the rate of oxidation; the reaction was carried out at five different initial concentrations of Acrylonitrile, keeping the concentrations of the other reactants constant. The results of this study recorded in Table 3:B:13.

Table 3:B:13

[2-Cl-BAH] = 3×10^{-2} M   [HCl] = 7×10^{-2}M,   Temp. = 35°C
$[HClO_4]$ = 1×10^{-1} M   [Tl (III)] = 3×10^{-3}M. μ = 0.3 M
Acrylonitrile in ml = 3, $[Na_2S_2O_3]$ = 1.0548×10^{-3}

Time in min	Vol. (in ml) of $Na_2S_2O_3.5H_2O$ used	(a – x)	Log (a-x)
0	25.2	0.0053161	- 2.27440
10	24.5	0.0051685	- 2.28663
20	24.0	0.005063	- 2.29559
30	23.5	0.0049575	- 2.30473
60	22.0	0.0046411	- 2.3337
90	20.3	0.0042824	- 2.36831
120	19.0	0.0040082	- 2.39705
150	17.3	0.0036496	- 2.43775
180	15.6	0.0032909	- 2.48267
210	14.3	0.0030167	- 2.52046
240	13.0	0.0027424	- 2.56185
260	11.6	0.0024471	- 2.61134
300	10.3	0.0021728	- 2.66296
By graph k = 2.51×10^{-5} sec^{-1}			

Similarly the reaction was carried out at the different volumes of Acrylonitrile and results are tabulated as follows :

Acrylonitrile in ml	k x 10^5 Sec^{-1}
1	5.11
2	5.11
3	5.05
4	5.05
5	5.05

A perusal of the data from the Table 3:B:13 shows that the rate of oxidation of 2-chlorobenzoic acid hydrazide remains practically constant at five different concentrations of Acrylonitrile. This shows that their is no formation of free radicals in the reaction.

End Product Analysis :

For identification of products the reaction was carried out by using aqueous solution of Hydrazide, Thallium(III), HCl and $HClO_4$. The flask containing reaction mixture was kept in thermostated water bath maintained at 50°C for 24 hours to complete the reaction. After completion of reaction, the residue obtained after filtration was analysed for acid as follows :

(i) The presence of carboxylic acid group was detected by testing with bicarbonate

(ii) The formation of acid was confirmed by TLC and its melting point.

Benzoic acid : M.P. = 122°C.

2-chlorobezoic acid : M.P. = 140°C

Nitrogen was detected by lime test.[11]

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 nitrogen as the end product.

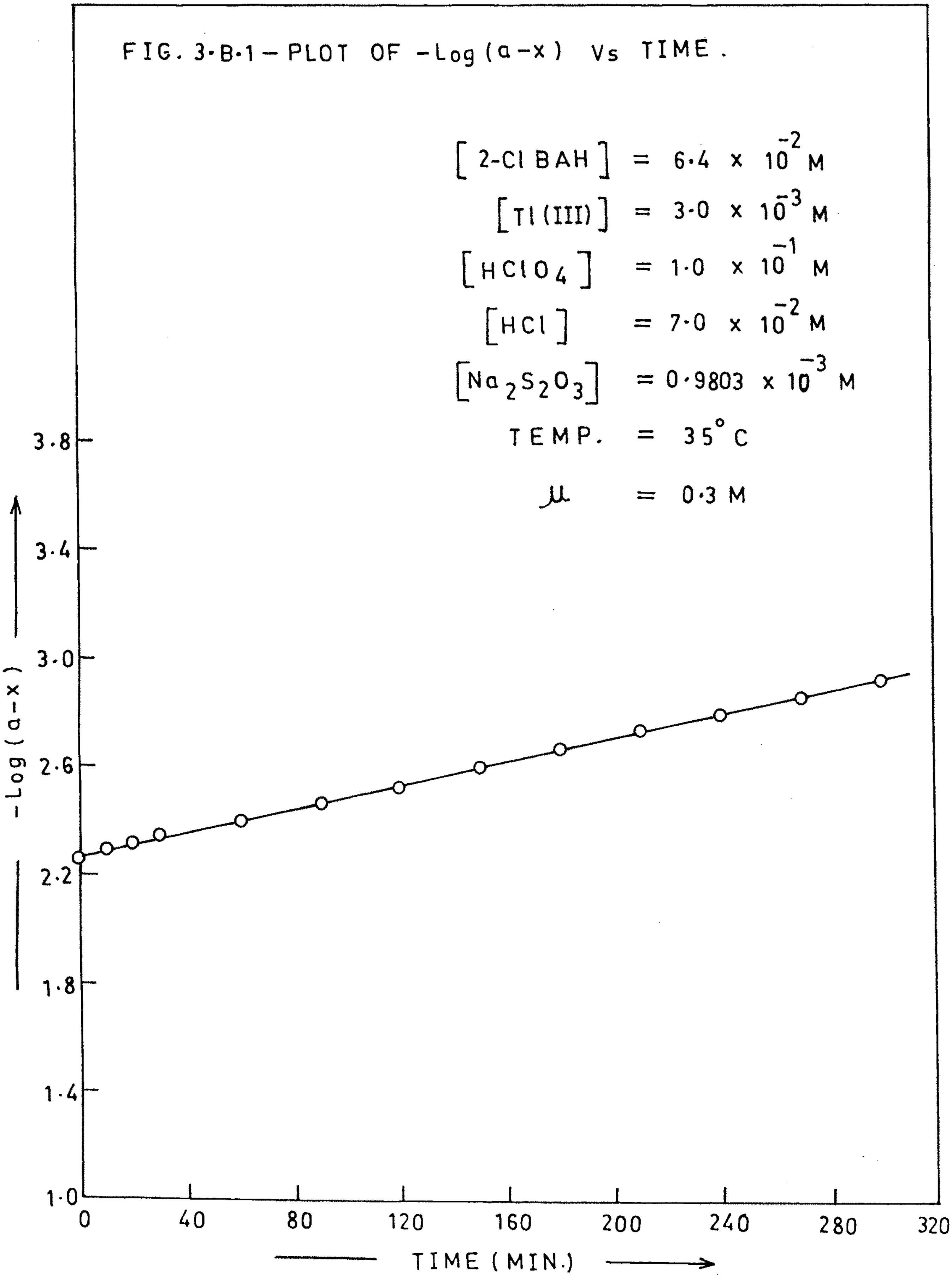


FIG. 3·B·1 — PLOT OF −Log (a−x) Vs TIME.
[2-Cl BAH] = 6·4 x 10^-2 M
[Tl (III)] = 3·0 x 10^-3 M
[HClO4] = 1·0 x 10^-1 M
[HCl] = 7·0 x 10^-2 M
[Na2S2O3] = 0·9803 x 10^-3 M
TEMP. = 35°C
μ = 0·3 M
−Log (a−x)
3·8
3·4
3·0
2·6
2·2
1·8
1·4
1·0
0
40
80
120
160
200
240
280
320
TIME (MIN.)

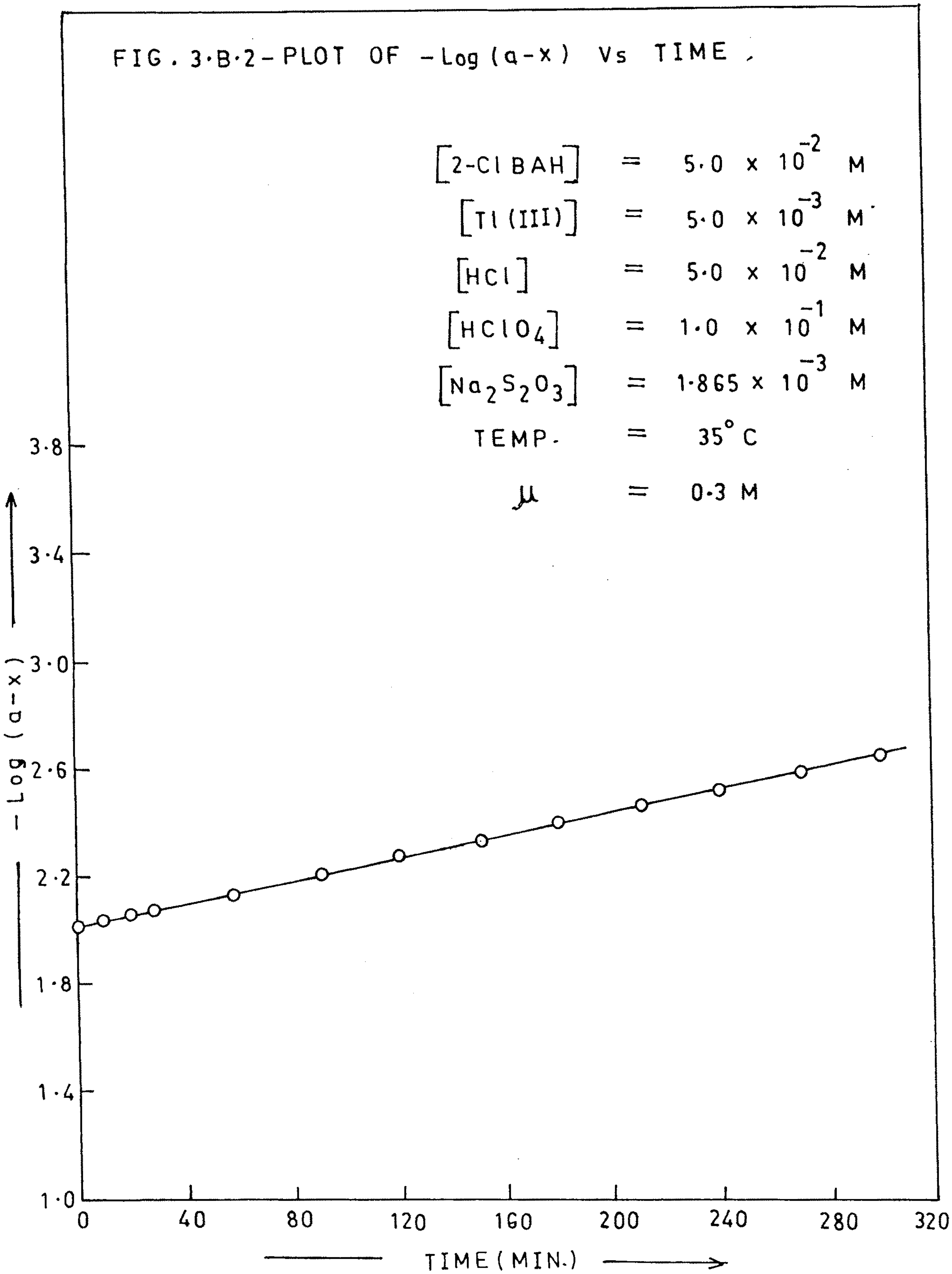


FIG. 3·B·2 - PLOT OF -Log (a-x) Vs TIME.
[2-Cl BAH] = 5·0 x 10^-2 M
[Tl(III)] = 5·0 x 10^-3 M
[HCl] = 5·0 x 10^-2 M
[HClO4] = 1·0 x 10^-1 M
[Na2S2O3] = 1·865 x 10^-3 M
TEMP. = 35° C
μ = 0·3 M
3·8
3·4
3·0
2·6
2·2
1·8
1·4
1·0
- Log (a-x)
0
40
80
120
160
200
240
280
320
TIME (MIN.)

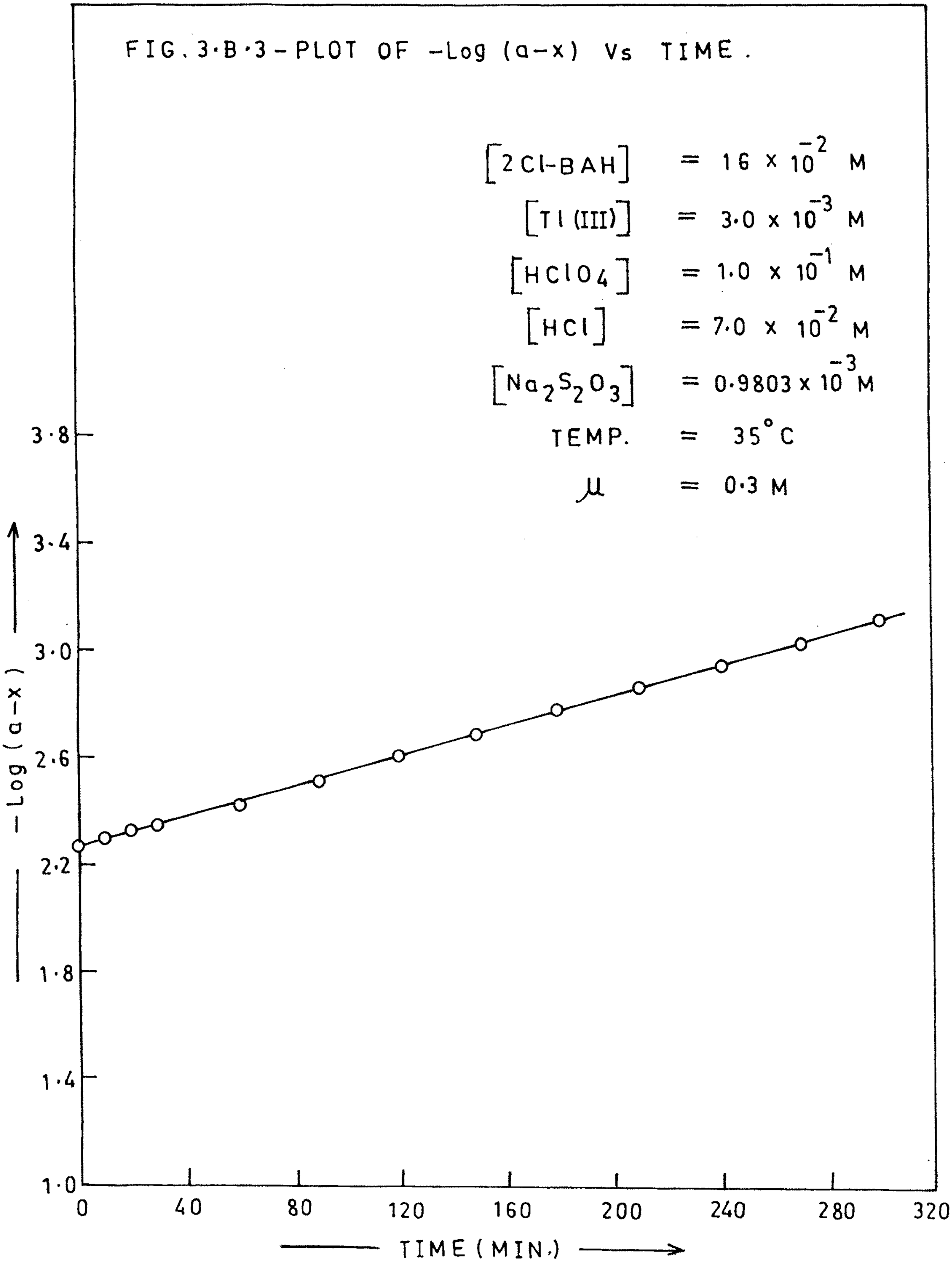


FIG. 3·B·3 - PLOT OF -Log (a-x) Vs TIME.
[2 Cl-BAH] = 16 x 10^-2 M
[Tl (III)] = 3·0 x 10^-3 M
[HClO4] = 1·0 x 10^-1 M
[HCl] = 7·0 x 10^-2 M
[Na2S2O3] = 0·9803 x 10^-3 M
TEMP. = 35°C
μ = 0·3 M
- Log (a-x)
3·8
3·4
3·0
2·6
2·2
1·8
1·4
1·0
0
40
80
120
160
200
240
280
320
TIME (MIN.)

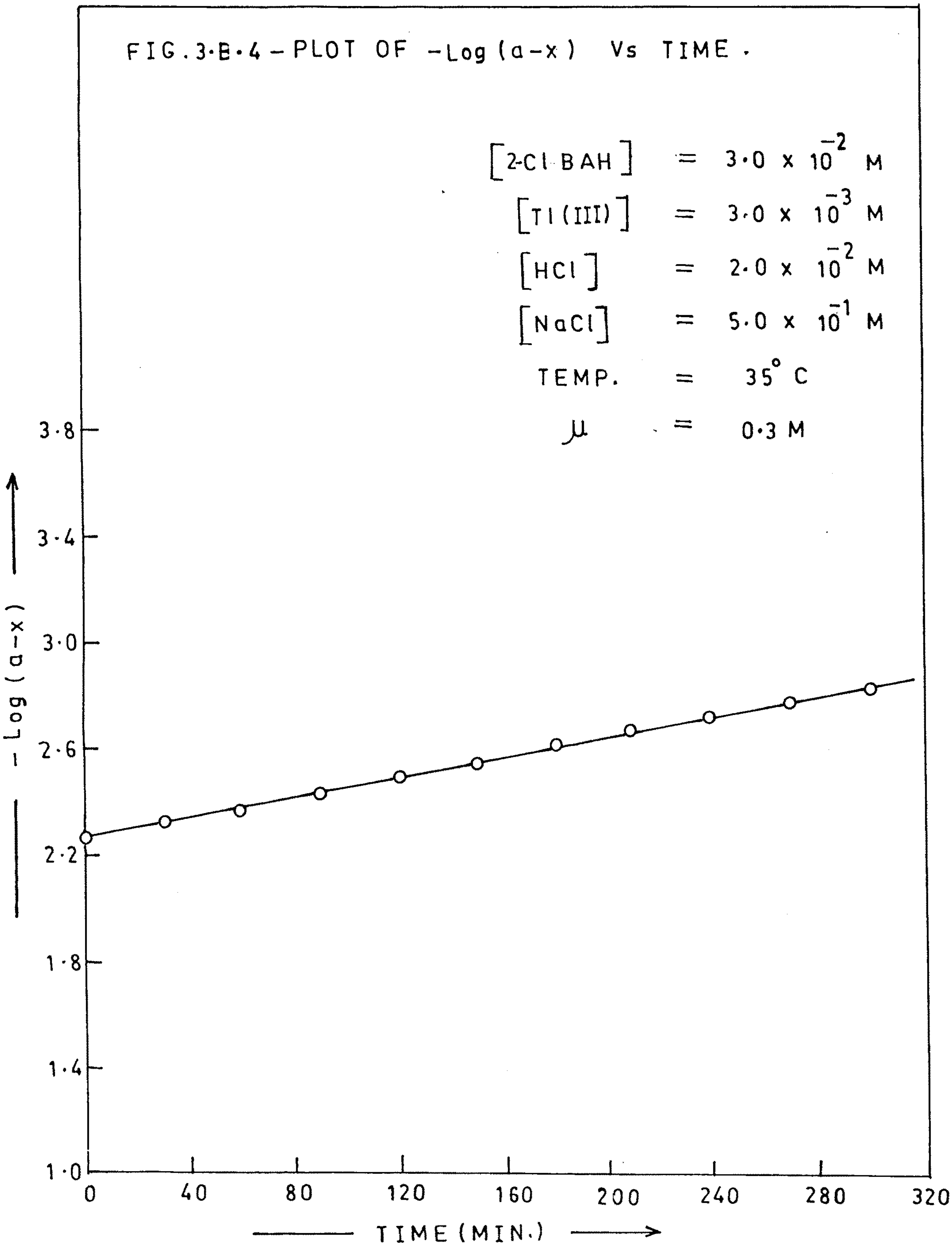


FIG.3·B·4 – PLOT OF –Log (a–x) Vs TIME.

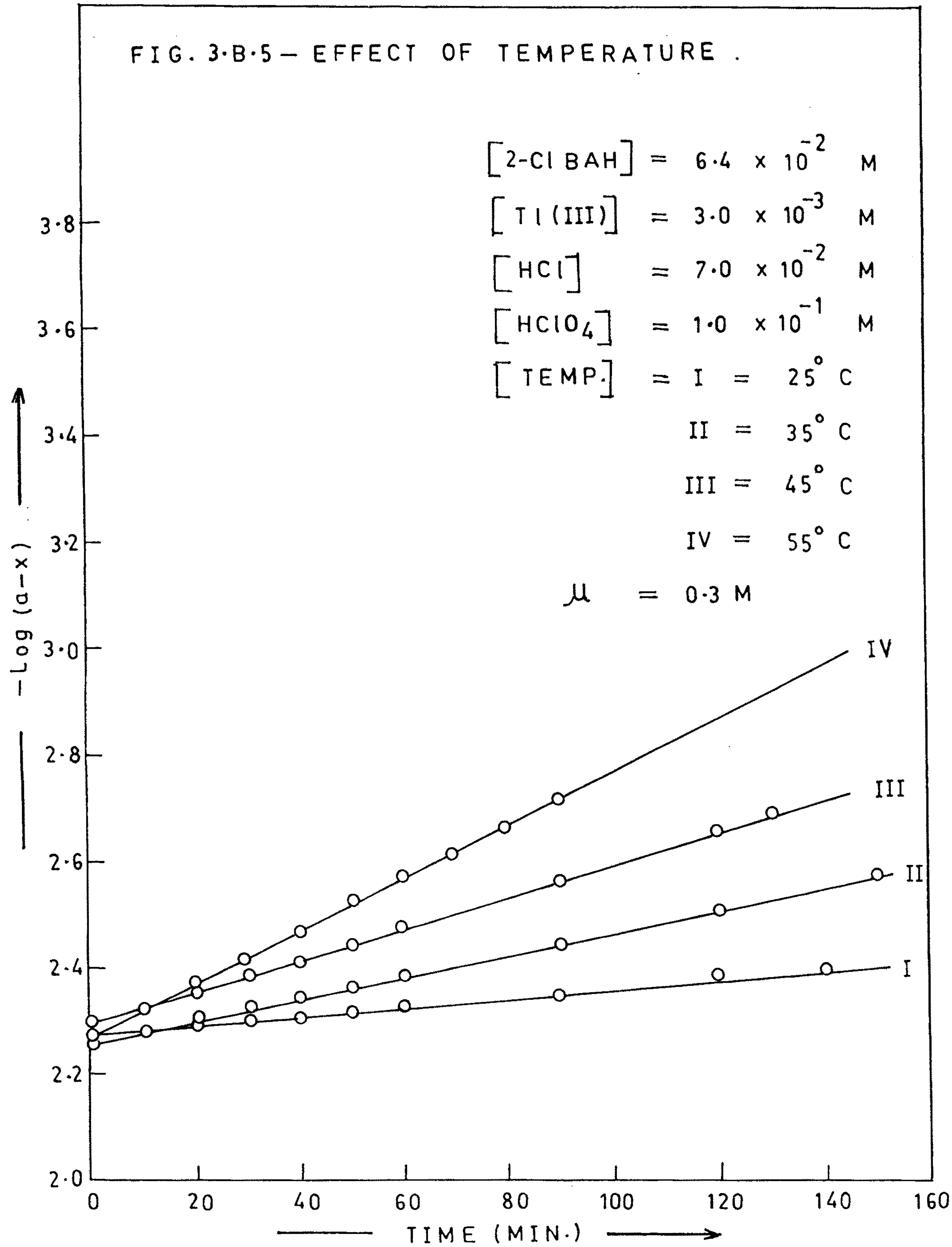


FIG. 3·B·5 — EFFECT OF TEMPERATURE.
[2-Cl BAH] = 6·4 x 10^-2 M
[Tl (III)] = 3·0 x 10^-3 M
[HCl] = 7·0 x 10^-2 M
[HClO4] = 1·0 x 10^-1 M
[TEMP.] = I = 25° C
II = 35° C
III = 45° C
IV = 55° C
μ = 0·3 M
IV
III
II
I
3·8
3·6
3·4
3·2
3·0
2·8
2·6
2·4
2·2
2·0
— Log (a—x)
0
20
40
60
80
100
120
140
160
TIME (MIN.)