
CHAPTER III

A COMPARATIVE STUDY OF THE CATALYTIC CONSTANTS OF
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INTRODUCTION

Electrophilic aromatic iodinations are known to be subject to general base catalysis¹⁻⁴. In particular the iodination of aniline in aqueous solution with iodine in potassium iodide in various buffer solutions was observed to be base catalysed by Berliner and others^{5,6}. Berliner studied the iodination of aniline with phosphate and acetate buffers in the pH range of 5.6 to 7.6. Mayberry-Bertoli³ qualitatively studied the base catalysis over the pH range of 5.4 to 9.8. Schutte and Havinga⁴ have used various bases as catalysts in the study of kinetics of iodination of p-cresol in aqueous solutions and tried to explain the effectiveness of catalysis on the basis of nucleophilicities and basicities. They, however, failed to consider the consequences of the changed pH in these kinetic studies.

In a quantitative study of the relationship between specific reaction rate of iodination of aniline and the percentage of aniline base in a buffer solution, we had observed that the specific reaction rate varied almost linearly with the percentage

of aniline base. Since the latter depends on the pH of the solution, any comparison of the effectiveness of different bases as catalysts for the reaction is meaningless unless the pH is maintained the same. Therefore the study of Berliner on the iodination of aniline in phosphate and acetate buffers in the pH range of 5.6 to 7.6 is of limited utility since the percentage of aniline base at these pH values ranges from 90 to 99. For a quantitative comparison of the catalytic effects of the various bases, a study of the reaction at a fixed pH is essential. Such a study is therefore undertaken to compare the catalytic activity of five typical bases.

Since at 25 °C the pK value of anilinium ion is 4.58, at pH 4.58 the percentage of aniline base and anilinium ion are 50 each. At pH 4.0, the percentage of aniline base is 20.8 while at pH 4.5 its percentage is 45.4. Therefore the present work is carried out at pH = 4.5 and 4.0 where the percentages of aniline base and anilinium ion are of comparable magnitudes so as to provide fair chance for each of these two species to react with iodine and also to indicate any difference in the catalytic activity of the bases at different proportions of the aniline base.

The bases selected for the present study at pH = 4.5 are formate, acetate, propionate, phthalate and oxalate ions.

The pK values of their conjugate acids are 3.75, 4.76, 4.87, 5.41 (second stage) and 4.27 (second stage) respectively⁷. These bases have been chosen because their pK values are different enough to show their effects on the catalytic constants and yet close enough to each other so that a pH value of 4.5 can be obtained by proper concentrations of the acids and bases. This study is repeated at pH 4.0 with the bases formate, acetate and propionate. Similar experiments with oxalate and phthalate solutions at pH 4.0 cannot be carried out due to limitations of the solubility of the buffer constituents.

For the comparison of the catalytic effects of these bases, it is proposed to maintain a fixed pH and yet vary the base concentration. This is possible by using Henderson's equation $\text{pH} = \text{pK} + \log \frac{[\text{base}]}{[\text{acid}]}$, by which the base concentration and the corresponding acid concentration are suitably varied. The specific reaction rates are determined at the various base concentrations. The graph of specific reaction rate versus the base concentrations is plotted, the slope of which is the catalytic constant for that particular base. Such catalytic constants have been determined at pH 4.5 at temperatures 35 °C and 40 °C for the five bases and at pH 4.0 at temperatures 35 °C and 40 °C for the three bases mentioned earlier.

This study has been carried out throughout with

potassium iodide at a concentration of ten times that of iodine for reasons mentioned in the preceding chapter.

For the determination of catalytic constant the concentration of the base is varied from 0.025 M to 0.125 M. In these studies it is important to maintain the ionic strength of the reaction system at a constant value. Hence in each case potassium chloride has been added in adequate concentration to maintain the ionic strength at 0.5 M, taking into consideration the concentration of the base and of potassium iodide already present in the solution.

EXPERIMENTAL

Chemicals :

Iodine, potassium iodide, potassium chloride, sodium thiosulphate, starch, formic acid, acetic acid, propionic acid, sodium oxalate, potassium hydrogen phthalate and sodium hydroxide of guaranteed reagent (G.R.) grade obtained from Sarabhai Chemicals, Wadi Wadi Baroda, India were used in the present study. The aniline was also obtained from the same source but was freshly distilled before use.

Preparation of buffers :

By using the Henderson equation $\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$ and by knowing the pK_a values of acids, the concentration of acids was calculated for the desired, pH and the desired concentration of the base. In subsequent experiments the latter was varied from 0.025 M to 0.125 M and in each case the corresponding concentrations of acids were calculated.

Wherever possible, stock solutions of five times the final concentration of the buffer constituents were prepared. Calculated quantities of these solutions when mixed with the reactants and diluted to the final volume, yielded the desired pH.

In the case of oxalate buffer due to insufficient solubility, five times concentrated stock solution of buffer was not possible to be prepared. Hence the required amount of sodium oxalate was directly added to the reaction mixture. In the case of phthalate buffer due to inadequate solubility and also due to large catalytic effect, the base concentration was varied from 0.005 M to 0.025 M instead of from 0.025 to 0.125 M. As a typical example the following stock solutions of buffers were prepared :

<u>Stock solution</u>	<u>Solution</u>	<u>Dilution</u>
1	10.0 cm ³ of 0.89 M formic acid	100.0 cm ³
2	50.0 cm ³ of 1 M formic acid + 50.0 cm ³ of 1 M sodium hydroxide	100.0 cm ³

For a typical kinetic run at base concentration of 0.025 M, 2.5 cm³ of stock solution 1 plus 2.5 cm³ of stock solution 2 of buffers along with 10 cm³ of 0.025 M iodine and 10.0 cm³ of 0.025 M aniline were diluted to 50 cm³.

Similar reaction mixtures with different base concentrations were prepared by using the required quantities of stock solutions of the buffer.

Preparation of other solutions :

Stock solutions of aniline, iodine and potassium chloride were prepared separately at such concentrations that on five times dilution they yielded the desired concentration, the details of which are given in Chapter II.

Kinetic measurements :

From the stock solution of aniline, 10 cm^3 were pipetted out into 250 cm^3 glass stopped bottle. To this calculated quantities of buffer solutions were added so as to get the final desired pH along with the calculated quantity of the potassium chloride to obtain a final ionic strength of 0.5 and the whole mixture was diluted to 40 cm^3 . In another 250 cm^3 glass stoppered bottle, 10 cm^3 of stock iodine solution were pipetted out. Both the bottles were maintained at a temperature of $35 \pm 0.05 \text{ }^\circ\text{C}$ in a thermostat. When the solutions had attained the temperature of the thermostat, they were mixed and an aliquot of 5 cm^3 was immediately transferred into 20 cm^3 of 1 N sulphuric acid so as to arrest the reaction. The unreacted iodine was titrated against 0.01 N sodium thiosulphate solution from a 10 cm^3 semimicroburette reading to 0.02 cm^3 using freshly prepared starch as an indicator. Similarly, titrations were carried out at various time intervals.

From these measurements, the specific reaction rate for the reaction was determined as explained in the previous work. A typical set of results is presented in Table III.1 for the formate buffer.

Similar kinetic run was carried out at 35 °C and at pH 4.5 with various base concentrations namely 0.025, 0.05, 0.075, 0.10 and 0.125 M for all the bases. The results are given in Table III.2. The plot of specific reaction rates versus concentrations of base yields a straight line, the slope of which gives the catalytic constant for the base (Fig. III.D).

Similarly the catalytic constants for the five bases were determined at 40 °C at the same pH (Table III.6).

The catalytic constant determinations were extended in the case of formate, acetate and propionate to pH 4.0 and temperature 35.0 and 40.0 °C (Table III.3). The catalytic constants were evaluated under these conditions of pH and temperature and are presented in Table III.6.

From similar kinetic measurements, the specific reaction rates were obtained at various temperatures for formate, acetate and propionate bases. The results for typical case of formate is presented in Table III.4. From Arrhenious plot the energies of activation for the iodination of aniline catalysed by formate, acetate and propionate were determined which are given in Table III.5.

RESULTS AND DISCUSSION

In the iodination of aniline at any one fixed pH an increase of the concentration of the base constituent of the buffer is found to increase the specific reaction rate of the reaction, establishing that the reaction is base catalysed. The results are given in Table III.2 and III.3. This increase is not due to salt effect as the ionic strength of the reaction medium is kept constant throughout the study. Such an increase in the specific reaction rate is to be expected since iodination of aniline is known to be base catalysed.

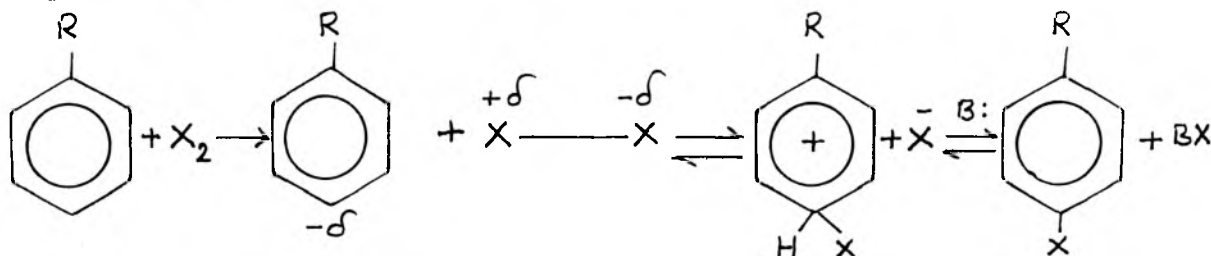
In our earlier work we have shown that the specific reaction rate of the iodination of aniline varied almost linearly with the percentage of aniline which depends on the pH of the solution. Hence for quantitative comparison of the effectiveness of different bases as a catalyst for the reaction, the pH should be maintained constant. Therefore the comparison of catalytic constants of the different bases has been carried out at a fixed pH and temperature.

The slope of the plot of specific reaction rates versus concentrations of base gives the catalytic constant for the base. The catalytic constants for formate, acetate, propionate, oxalate and phthalate ions were determined at the same pH and

temperature and it is observed that the various bases have different catalytic constants (Table III.6 and Fig. III.D).

The evaluation of catalytic constants for these bases is extended at the same pH but at a different temperature and at the same temperature but at a different pH. The results presented in Table III.6, clearly show that the catalytic constant varies with pH and temperature.

In the halogenation of aromatic substrates, the formation of the adduct is usually the rate determining step while the deprotonation is a fast reaction⁸



Iodination, however is an exception, in that the deprotonation step is the slow rate determining step which involves breakage of a C-H bond in the ring^{9,10}. It is because of this situation that the reaction is highly susceptible to base catalysis.

An examination of the results presented in Table III.6 shows that at a given pH and given temperature, the relative values of the catalytic constants of the various bases are such as to be expected from the Bronsted relation¹¹ $K_B = C_B(1/K_a)^\beta$

where K_B is catalytic constant for base and K_a the dissociation constant of the acid conjugate to the base B. G_B and β are constants for a series of similar catalysts but depends on the nature of the reaction and also on the solvent and the temperature.

Although belonging to the homologous series of the acetate and propionate ions, the formate ion has an exceptionally high catalytic constant which is about five to six times higher than that of acetate and propionate. Considering its pKa value of 3.75 its catalytic constant should have been lower than that of the acetate or the propionate ions. This is presumably because the lack of any alkyl group on the carboxylic carbon enables the formate ion to approach the reactive site and form the transition state more readily than the acetate or propionate ion. A similar situation had been observed in the case of aromatic bases, when the catalytic constants for primary, secondary and tertiary amines were compared, and in the iodination of ketones when the catalytic power of some Bronsted bases were studied¹²⁻¹⁵.

The energy of activation for the iodination of aniline at pH 4.5 is found to be the same in spite of the use of three different bases namely formate, acetate and propionate. This indicates that the mechanism of the base catalysis is almost the same in all three cases (Table III.5).

At higher pH values the catalytic constant for a given base is found to be more than at lower pH. This is presumably because at higher pH there is a higher percentage of aniline base. It is further observed that the catalytic constant is higher at higher temperatures than at lower temperatures. This is presumably because the deprotonation occurs much faster at higher temperatures.

Thus in the present study we have been able to make a quantitative evaluation of the catalytic constants of several bases in a typical aromatic electrophilic substitution reaction.

Table III.1 : Kinetics of the iodination of aniline in formate buffer (Ref. Fig. III.A)

Initial concentration of aniline	: 5.0×10^{-3} M
Initial concentration of iodine	: 5.0×10^{-3} M
Concentration of potassium iodide	: 5.0×10^{-2} M
Concentration of sodium thiosulphate	: 1.0×10^{-2} M
Ionic strength of the medium	: 0.50 M
pH of formate buffer	: 4.50
Concentration of sodium formate	: 6.0×10^{-2} M
Concentration of formic acid	: 8.9×10^{-2} M
Volume of iodine pipetted out	: 5.0 cm^3
Temperature	: $35.0 \text{ }^\circ\text{C}$

Time/min	Volume of thiosulphate/ cm^3	Concentration of unreacted iodine $[\text{I}_2] / 10^{-3} \text{ M}$	$\frac{1}{[\text{I}_2]} \text{ M}^{-1}$
0	4.75	5.00	200
5	3.95	4.16	241
10	3.65	3.84	260
15	3.25	3.42	292
20	3.00	3.16	317
25	2.75	2.89	345
30	2.50	2.63	380
35	2.20	2.32	432

Slope of the graph of

$$\frac{1}{[\text{I}_2]} \text{ versus time} = \text{Specific reaction rate}$$

$$= 6.50 \text{ M}^{-1} \text{ min}^{-1}$$

Table III.2 : Specific reaction rates of the iodination of aniline in different buffers with various base concentrations at pH 4.5 (Ref. Fig. III.B)

Concentration of the base/M	Temp /°C	Specific reaction rate/M ⁻¹ min ⁻¹				
		Formate	Acetate	Propionate	Phthalate*	Oxalate
0.025	35.0	4.40	2.00	2.25	3.85	2.47
	40.0	8.00	3.45	4.31	6.16	3.45
0.050	35.0	6.50	2.85	3.00	4.71	2.70
	40.0	12.40	4.43	5.00	8.57	5.14
0.075	35.0	9.30	3.42	3.57	6.00	3.05
	40.0	19.00	6.30	6.20	11.00	6.70
0.100	35.0	12.40	4.05	4.15	7.16	3.80
	40.0	25.00	6.90	8.35	13.63	7.91
0.125	35.0	15.00	4.42	4.65	8.50	4.45
	40.0	31.50	8.36	9.50	16.80	8.35

* In the case of phthalate the range of base concentration is from 0.005 to 0.025 M, in steps of 0.005 M.

Table III.3 : Specific reaction rates of the iodination of aniline in different buffers with various base concentrations at pH 4.0

Concentration of the base/M	Temp /°C	Specific reaction rate/M ⁻¹ min ⁻¹		
		Formate	Acetate	Propionate
0.025	35.0	2.19	0.92	1.31
	40.0	4.35	1.83	2.27
0.050	35.0	3.77	1.28	1.50
	40.0	9.50	2.57	2.81
0.075	35.0	5.22	1.47	1.69
	40.0	13.00	3.10	3.20
0.100	35.0	6.73	1.81	1.92
	40.0	17.40	3.72	3.82
0.125	35.0	8.52	2.02	2.23
	40.0	20.70	4.15	4.50

Table III.4 : Variation of the specific reaction rate of the iodination of aniline in formate buffer with temperature (Ref. Fig. III.C)

Initial concentration of aniline : 5.0×10^{-3} M
 Initial concentration of iodine : 5.0×10^{-3} M
 Concentration of potassium iodide : 5.0×10^{-2} M
 pH of the formate buffer : 4.80
 Concentration of sodium formate : 5.0×10^{-2} M

Temp t/°C	Temp T/K	$\frac{1}{T} / 10^{-3} \text{ K}^{-1}$	Specific reaction rate $k_2 / \text{M}^{-1} \text{ min}^{-1}$	log k_2
25.0	298	3.356	1.33	0.124
30.0	303	3.300	2.50	0.398
33.0	306	3.268	4.20	0.623
36.0	309	3.236	6.87	0.837
39.0	312	3.205	10.90	1.037

Slope of the graph of log k_2 versus $\frac{1}{T} = -5900 \text{ K}$

$$\text{Energy of activation} = \frac{-2.303 \times 8.314 \times (-5900)}{1000}$$

$$= 113.0 \text{ kJ mole}^{-1}$$

Table III.6 : Energy of activation for the iodination of aniline catalysed by different bases at pH 4.5

Base	Energy of activation $E_a/\text{kJ mole}^{-1}$
Formate	113.0
Acetate	110.0
Propionate	108.0

Table III.6 : Catalytic constants for different bases at different pH and temperatures for the iodination of aniline

pH	Temp t/°C	Catalytic constant (K _p)				
		Formate	Acetate	Propio- nate	Oxalate	Phtha- late
4.5	35.0	110	22	24	16	240
	40.0	265	50	60	64	520
4.0	35.0	60	10	11	-	-
	40.0	145	22	24	-	-

FIG. III. A: KINETICS OF THE IODINATION OF ANILINE IN
FORMATE BUFFER AT pH 4.5

(REF. TABLE III 4)

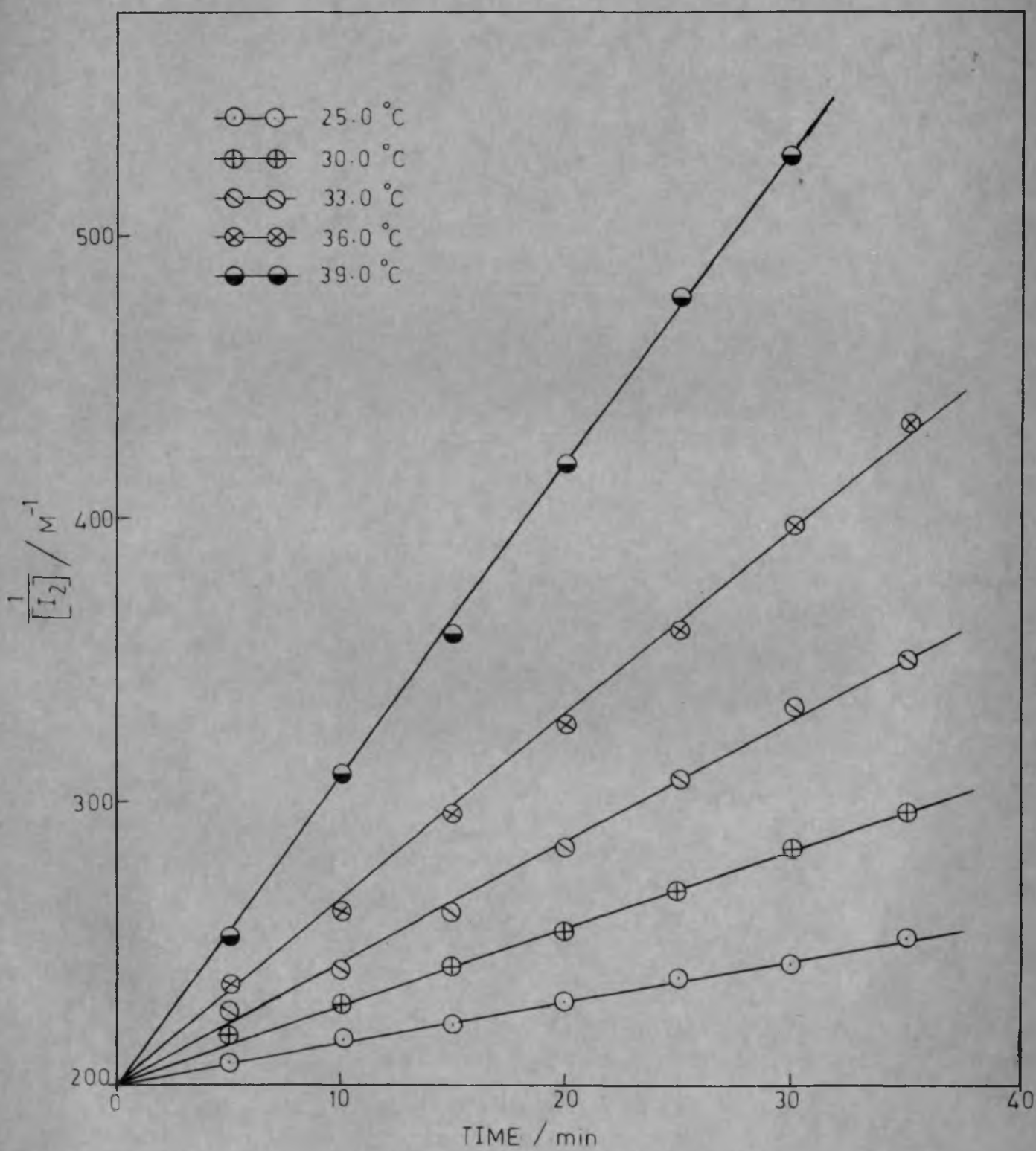


FIG. III. B: KINETICS OF THE IODINATION OF ANILINE IN FORMATE BUFFER AT VARIOUS BASE CONCENTRATIONS AT pH 4.5 AND 35.0°C.

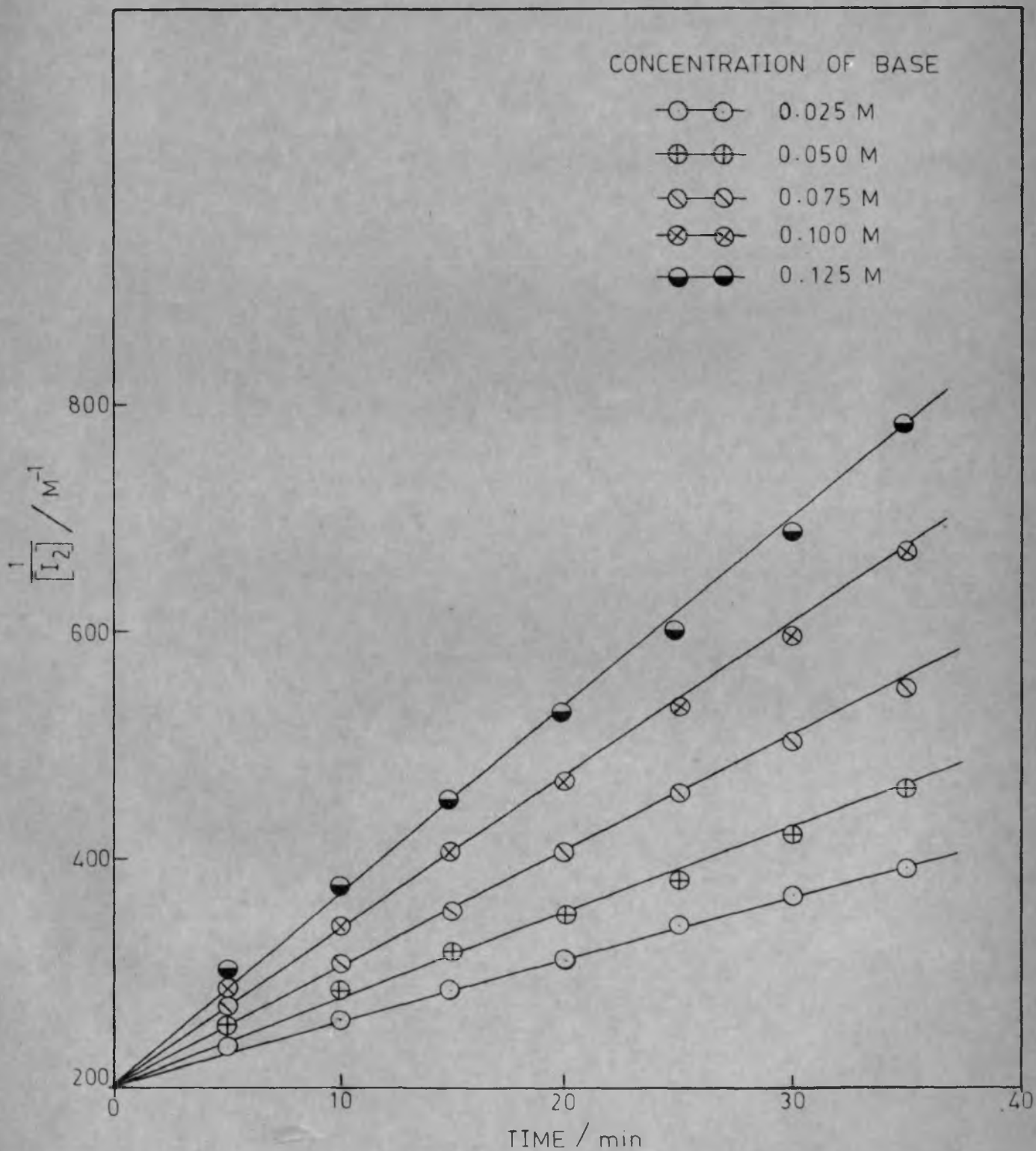


FIG. III.C: VARIATION OF THE SPECIFIC REACTION RATE OF THE IODINATION OF ANILINE WITH TEMPERATURE IN FORMATE BUEFER AT pH 4.5 (REF. TABLE. III. 4)

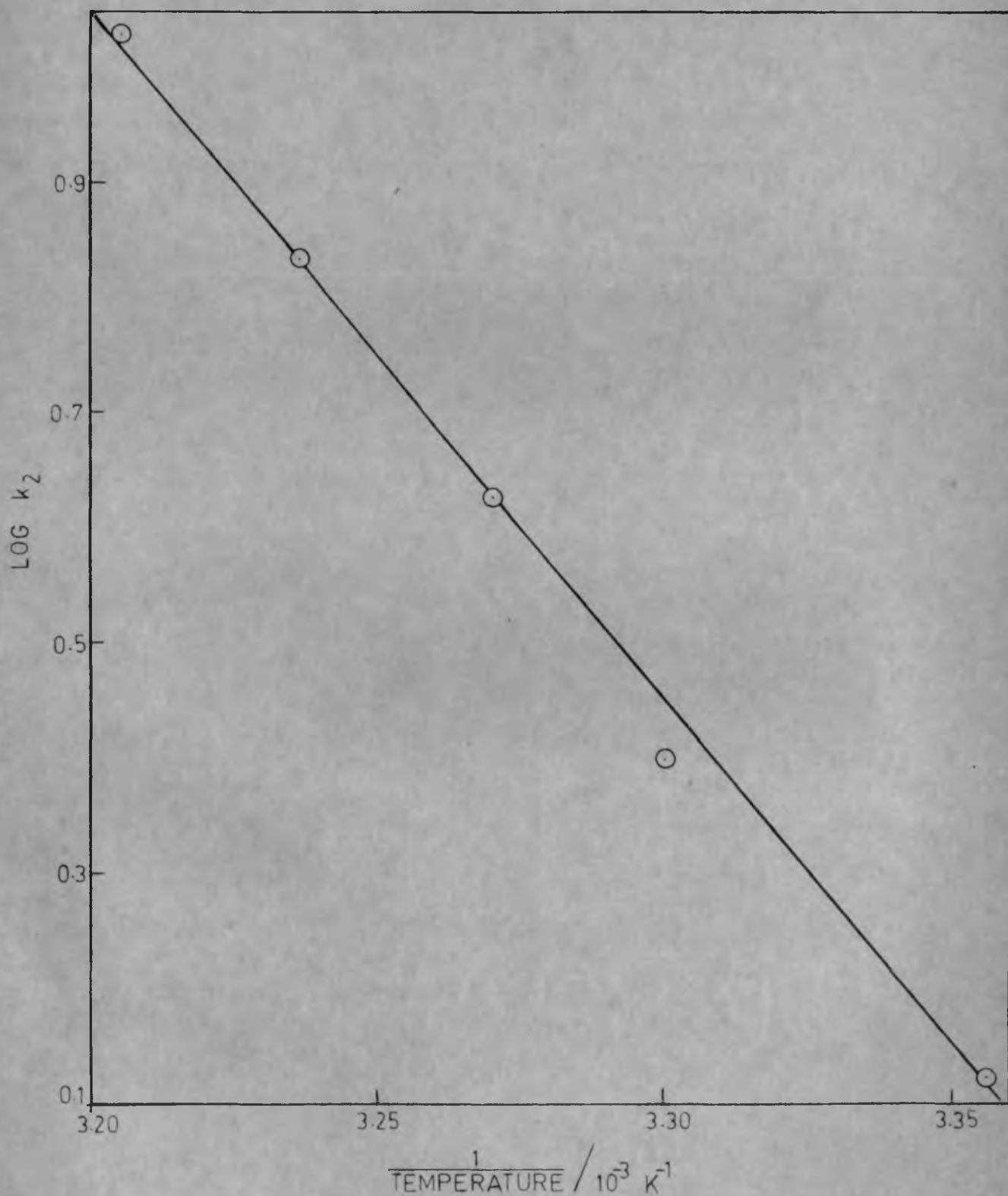
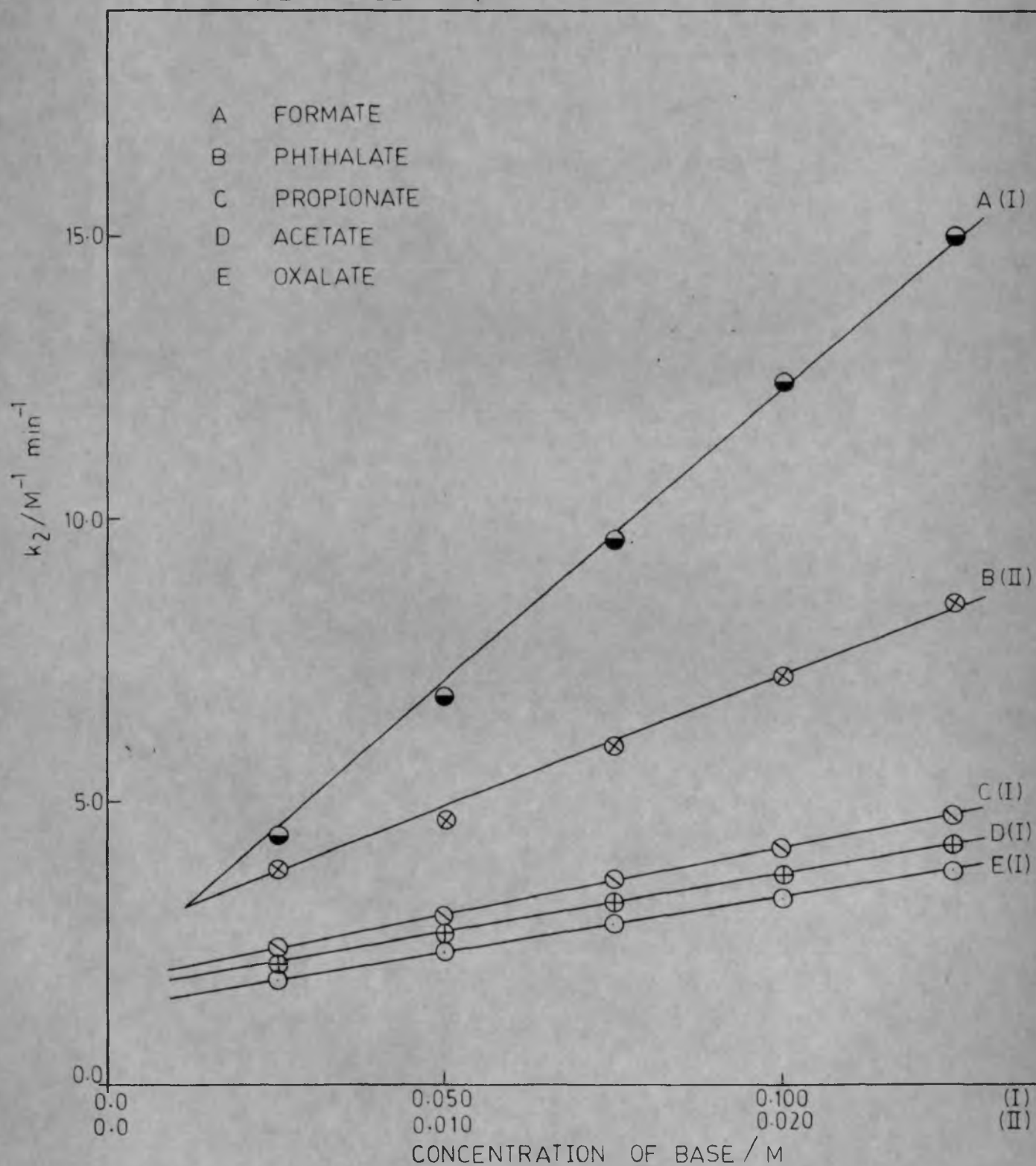


FIG. III.D: VARIATION OF THE SPECIFIC REACTION RATE OF THE IODINATION OF ANILINE WITH BASE CONCENTRATION AT pH 4.5 AND 35.0°C.
(REF. TABLE. III 2).



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