CHAPTER - III

Kinetics and Mechanism of the Reaction Between cis-Diaquo-bis-Ethylenediamine Co(III) Ion and Phthalic Acid

INTRODUCTION

In the preceding chapter, we worked out the detailed mechanism of the reaction between cis-diaquo-bis-ethylenediamine cobalt(III) ion (Complex A) with malonic acid at 35°C and in the pH range 3.8 to 4.4. In the present chapter we have worked out the kinetics and mechanism of the reaction of A with phthalic acid at the same temperature 35°C and in the pH range 3.8 to 4.6; this study has facilitated us to compare the effects of a dibasic aromatic acid, namely phthalic acid and a dibasic aliphatic acid namely malonic acid on the mechanism of their reactions with the Complex A.

In aqueous solution phthalic acid forms the entities

\[ \text{H}_2 \text{phth}, \ \text{Hphth}^-, \ \text{phth}^{2-} \]

(henceforth to be termed respectively as \( \text{H}_2 \text{phth}, \ \text{Hphth}^- \) and \( \text{phth}^{2-} \)). Phthalic acid is a weak acid, the dissociation constants at 25°C are \( K_1 = 1.12 \times 10^{-3} \) (pK\(_1\) = 2.95) and \( K_2 = 3.89 \times 10^{-6} \) (pK\(_2\) = 5.41). The relative concentrations of the species of \( \text{H}_2 \text{phth}, \ \text{Hphth}^- \) and \( \text{phth}^{2-} \) in 0.05 mol dm\(^{-3}\) aqueous solution
of phthalic acid at 25°C and at pH 3.8, 4.0, 4.2, 4.4 and 4.6 have been calculated, using the $K_1$ and $K_2$ values, and the results have been given in Table 1. The rate of the reaction of phthalic acid with [Coen$_2$(H$_2$O)$_2$]$^{3+}$ at 35°C below pH 3.8 was too slow to be followed. The different pH values were adjusted by adding the requisite amount of ammonia solution to a solution of 0.05 mol of H$_2$phth in nearly one dm$^3$ of water and then making the volume up to one dm$^3$ exactly.

It will be seen from Table 1 that in 0.05 mol dm$^{-3}$ aqueous phthalic acid solution at 25°C and between pH 3.8 to pH 4.6, the entity [Hphth]$^-$ is overwhelmingly predominant compared to the entities H$_2$phth and phth$^{2-}$. At pH 3.8, the entity [H$_2$phth] and at pH 4.6 the entity [phth]$^{2-}$ are not quite negligible. We will therefore assume that at pH 4.0, 4.2 and 4.4, practically the only entity Hphth$^-$ is present in the reaction mixture; at pH 3.8 H$_2$phth is present in small amounts and at pH 4.6 the entity phth$^{2-}$ is present to some extent but even at these two pH's, the entity Hphth$^-$ is predominant.

In this chapter, using the same method as was adopted in the case of the reaction between A and malonic acid, we shall show that the stoichiometric mechanism of the reaction of phthalic acid with the complex [Coen$_2$(H$_2$O)$_2$]$^{3+}$ leading to the formation of the complex [Coen$_2$(phth$^{2-}$)$_4$] in the pH range 3.8 to 4.6 consists of two consecutive first order steps involving the formation of an intermediate D, e.g.,
In the reaction of the Complex A with malonic acid, the rate constants $k_1$ and $k_2$ were found to be pH dependent and the pH dependence of the rate constants was explained by adopting an ion-pair $\cdot$ cum $S_N$ CB mechanism. In this reaction with phthalic acid, the rate constants $k_2$ was found to be pH dependent, but the rate constant $k_1$ was found to be pH independent; therefore a mechanism involving the formation of an ion pair followed by outersphere, innersphere interchange was adopted for the first step $A \rightarrow D$ but the second step $D \rightarrow E$ was shown to follow two parallel paths - one $S_N$ CB and another slow dissociation of $H_2O$ leading to a pentacoordinate intermediate followed by rapid ring closure. The pH dependence of the rate constant, $k_2$, was due to the fact that a major part of this step proceeded through $S_N$ CB path.

Recently Bhattacharyya and Banerjee\textsuperscript{2} have studied the kinetics and mechanism of the reaction between $[\text{Co(NH}_3\text{)}_4(H_2O)_2]^{3+}$ and phthalic acid and have noted that the rate of the reaction increases with the increase of pH. They have adopted a mechanism
involving ion pair formation cum innersphere outersphere interchange in the ion pairs \([\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})_2]^{3+}\text{Hphth}^-\) and \([\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})_2]^{3+}\text{phth}^{2-}\). The authors have explained pH dependence of reaction by assuming that \([\text{R(}\text{H}_2\text{O})\text{phth}]^{1+}\) dissociates faster than \([\text{R(}\text{H}_2\text{O})\text{Hphth}]^{2+}\); this seems to be unlikely since it should be more difficult for the double negative phth\(^{2-}\) to come out the coordination sphere than the uninegative Hphth\(^-\) ion overcoming the attraction of the tripositive Co\(^{3+}\) ion.

Following the pioneering work of Bronsted\(^3\), who showed that the specific (OH\(^-\)) catalysed replacement of NO\(_3^-\) by H\(_2\)O in \([\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})(\text{NO}_3)]^{2+}\) proceeds at a measurable rate even below pH 3.0 and the rate increases with the increase of pH, it was established for all cobaltic complexes containing aquo or ammino groups in the coordination zone, the substitution reaction rate increases with the increase of pH and can be successfully explained by a specific (OH\(^-\)) catalysed substitution mechanism (S\(_N\)1 CB mechanism of Garrick\(^4\)). In our laboratory Ruj (Ph.D. thesis) has shown that the complex \([\text{Co(NH}_3\text{)}_4(\text{H}_2\text{O})_2]^{3+}\) is very much susceptible to anation reactions by specific (OH\(^-\)) catalysed \(S_N^1\) CB mechanism specially above pH = 3.0.

**EXPERIMENTAL SECTION**

i) **Instruments used** — The instruments used were the same as those used in the malonic acid reaction (Chapter-II).
ii) **Preparation of complex compounds required** - cis-[Coen$_2$(H$_2$O)$_2$](NO$_3$)$_3$ (Complex A) was prepared using the same method as described in Chapter-II and characterised by elemental analysis and absorption spectrum in the same way.

Phthalato bis-ethylenediamine cobalt(III) nitrate [Coen$_2$(phth)]NO$_3$.H$_2$O was prepared by heating on water-bath a mixture of Complex A and phthalic acid in the mol ratio (1:1.1); both Complex A and phthalic acid were dissolved separately in minimum volumes of water and pH of each of the solution were adjusted to 4.0 by adding requisite amount of ammonia solution. On mixing the solution the pH of the mixture decreased and if was adjusted once again to pH = 4.0. It was then heated on water-bath for about one hour and the concentrated liquid produced was then gradually cooled; dehydrated alcohol was added dropwise with stirring. The bright red crystals separated and the mixture was allowed to stand for complete precipitation (30 minutes). The product was separated by filtration, washed with a little alcohol and finally dried over calcium chloride. It was then characterised by elemental analysis [Found: Co 13.7, N 16.7; Calcd: Co 13.92, N 16.54 %]. The absorption spectrum for the complex in a 0.005 molar solution in water at pH 4.0 has been given in Fig.I; $\lambda_{\text{max}}$ at 505 nm ($E = 110.5$). It appears that this complex was prepared first time by us.
Fig-1

Absorption Spectra of Cis [Coen₂(H₂O)₂]³⁺ and [(Phth)Coen₂]⁺
(A and B respectively) in 0.005 mol dm⁻³ solution in water.

pH = 4.0; Cell length 2 Cms.
iii) **pH Control during the experiments** – In a preliminary study starting with a reaction mixture containing 0.005 mol dm$^{-3}$ of A and 0.05 mol dm$^{-3}$ of phthalic acid (pH was adjusted to 4.0), it was found that the pH of the mixture decreased during the course of the reaction and finally a value of pH 3.85 was reached at a stage at which no further observation on the course of the reaction was made. This increase in [H$^+$] during the reaction was due to the release of (H$^+$) from the intermediate, D, i.e. during the ring closure reaction D $\rightarrow$ E.

\[
\text{[Coen}_2(H_2O)(Hphth)]^{2+} \rightarrow \text{[Coen}_2(\text{phth})]^{1+} + \text{H}_3\text{O}^+
\]

D \hspace{2cm} E

(cf. reaction of complex A with malonic acid, Chapter-II)

The hydrogen ions produced during the reaction are not removed totally by the weak buffering action of ammonia-phthalic acid mixture, in the pH range of our study (pH 3.8 to 4.6). Hence pH decreased.

As the rate constants of the reaction are very much pH sensitive, it was essential to maintain the pH of the reaction mixture constant throughout the course of the reaction. For this purpose, we adopted the same procedure as was followed in the reaction of Complex A with malonic acid (Chapter-II).
PART I

THE STUDY OF THE STOICHIOMETRIC MECHANISM OF THE REACTION OF PHTHALIC ACID WITH $[\text{Coen}_2(\text{H}_2\text{O})_2]^{3+}$

Kinetic Studies and Results:

The kinetic study of the reaction between Complex A and phthalic acid leading to the formation of the final ring closed product, E, was carried out in aqueous solution with $[\text{A}] = 0.005 \text{ mol dm}^{-3}$ and $[\text{Phthalic acid}] = 0.05 \text{ mol dm}^{-3}$ (complex : ligand mol ratio = 1:10, pseudo first order condition), at pH 4.0 and at 35°C. The reaction was followed spectrophotometrically, using $\lambda = 530 \text{ nm}$ where there is a substantial difference between the O.D. values of Complexes A and E (Fig.1).

The values of $\log \frac{d_\alpha - d_0}{d_\alpha - d_t}$ were plotted against time, $t$, (where $d_\alpha$, $d_0$, and $d_t$ are the O.D. values of pure E, pure A, and of the reaction mixture at time $t$ respectively) at 35°C at pH 4.0. The plot, shown in Fig.II, is a non-linear curve, and is very similar in nature to the non-linear curve in Fig.II (Chapter-II); both curves start with a near zero initial slope which increases continuously and ends in a straight line with its slope reaching a constant limiting value. This nature of the plot of $\log \frac{d_\alpha - d_0}{d_\alpha - d_t}$ vs $t$ indicates that the reaction goes through at least one intermediate step, subject to the condition that $d_\alpha > d_0$ and the O.D. value of the intermediate, D, lies between $d_\alpha$ and $d_0$. So we concluded that the formation
pH = 4.0, Temp = 35°C.

\( k_{2\text{obs}} = 3.23 \times 10^5 \text{ sec}^{-1}. \)

\( \lambda = 530 \text{ nm}. \)
of the product $E$, from Complex $A$ proceeds through the formation of an intermediate complex $D$ as shown in the reaction series $A \rightarrow D \rightarrow E$.

In analogy with the formula of the intermediate $B$ in the reaction of $[\text{Coen}_2(H_2O)_2]^{3+}$ with malonic acid (Chapter-II), we accepted the formula of the intermediate, $D$, in the reaction series $A \rightarrow D \rightarrow E$ to be $[\text{Coen}_2(H_2O)(\text{Hphth})]^{2+}$. However, in spite of repeated attempts, we could not isolate the intermediate complex, $D$ in the pure state.

It may be presumed that the straightline portion of the curve in Fig.II, representing the limiting constant slope starts from a time when practically all $A$ has been exhausted and the formation of $E$ occurs from the intermediate $D$ alone. Hence from the value of the limiting constant slope of this straightline we get the value of $k_2$, the rate constant of the step $D \rightarrow E$ of the reaction series, i.e. the rate constant of the ring closure reaction:

$$[\text{Coen}_2(H_2O)(\text{Hphth})]^{2+} \rightarrow [\text{Coen}_2(\text{phth})]^{1+} + H_3O^+$$

Also from the curve in Fig.II it is seen that initially $[D]$ is small and so $[E]$ is insignificant as $E$ is formed from $D$. Therefore in the initial period, $d_t$ is close to $d_0$. Hence the curve $(\log \frac{d_0 - d_t}{d_0 - d_0} \ vs \ t \ plot)$ had a near zero slope at
the beginning, but with increase of [E], the \( d_t \) value increased, the slope also increased continuously and reached a constant value when practically all A was exhausted.

In order to study the effect of variation of the concentration of \( \text{H}_2\text{phth} \) (ligand) on the rate constants of each of the steps of the reaction \( A \rightarrow D \rightarrow E \), we performed kinetic experiments on a series of reaction mixtures with \( [A] = 0.005 \) mol dm\(^{-3}\) in each of the mixtures and with \( [\text{H}_2\text{phth}] = 0.05 \) mol dm\(^{-3}\), 0.075 mol dm\(^{-3}\), 0.125 mol dm\(^{-3}\) in the successive mixtures (mol ratios of \( [A] : [\text{H}_2\text{phth}] = 1:10 \), 1:15 and 1:25 respectively) at 35°C and at pH 4.0, spectrophotometrically using \( \lambda = 530 \) nm. The plots of \( \log \frac{d\alpha - d_0}{d_\alpha - d_t} \) vs \( t \) have been drawn on the same scale for every mol ratio 1:10, 1:15 and 1:25 of \( [A] : [\text{H}_2\text{phth}] \) and all the three plots were curved lines with straightline end portions, fully coinciding with each other all throughout (Fig.III). Since the three plots of \( \log \frac{d\alpha - d_0}{d_\alpha - d_t} \) vs \( t \) obtained using very different mol ratios of \( [A] : [\text{H}_2\text{phth}] \) coincided each other from start to finish, we can safely conclude that the rates of both the first step and the second step of the reaction are ligand independent and are of the first order at the particular pH. The values of the rate constant \( k_2 \) for the second step \( D \rightarrow E \) of the reaction may be determined from the limiting slopes of the three coinciding curves, to be identical, namely \( 3.23 \times 10^{-5} \) sec\(^{-1}\). If the first step of the reaction was not of first order, the initial non-linear portions of the
Fig-III

[Coen$_2$(H$_2$O)$_2$]$^{3+}$ and Phthalic Acid at different mol. ratios,
pH=4.0; Temp = 35°C; $\lambda = 530$ nm.
Mol. ratio 1:10 $\circ$; 1:15 $\Delta$; 1:25 $\Box$.

![Graph showing reaction kinetics with time]
curves obtained at different mol ratios of A and H$_2$phth would have different curvatures not coinciding with each other; thus we would get not-coincident curved lines at the beginning and ending in parallel straightlines with same limiting slope. Thus we could make the definite conclusion that the rate of the first step of the reaction, A $\rightarrow$ D is independent of [H$_2$phth], and depending on [A] alone, therefore is of the first order at a constant pH.

So far, the value of the rate constant, k$_2$, for the ring closure reaction has been found out (3.23 x 10$^{-5}$ sec$^{-1}$ at 35°C, at pH 4.0). Our next attempt was to calculate the value of the rate constant k$_1$ for the first step A $\rightarrow$ D at 35°C and at pH 4.0. The same trial and error method, which was used in the case of the reaction of A with malonic acid (Chapter-II), was employed in this case too. From the curve in Fig.II, it is seen that the straightline with limiting slope starts roughly at t = 300 minutes. It may be assumed that in 300 minutes the complex A is practically exhausted and after 300 minutes, only 1% of it (say) remains. From this time onwards, the final product E is formed practically from D alone so that a straight-line plot of $\log \frac{d\alpha - d_o}{d\alpha - d_t}$ vs t is obtained starting from this point. With this assumption, a rough value of k$_1$ (k$_1$ rough) in sec$^{-1}$ may be calculated from the equation:

$$\ln \frac{A_0}{A_t} = \ln \frac{100}{1} = k_1 \times 18000$$

(300 x 60 = 18000)
The value of $k_1$(rough) came out to be $2.6 \times 10^{-4}$ sec$^{-1}$. A set of values of $E_t$ ($E_t = \text{concentration of } E \text{ at time } t \text{ in the reaction mixture}$) was then calculated for different times $t$, using $k_2 = 3.23 \times 10^{-5}$ sec$^{-1}$ and arbitrary trial values of $k_1$, starting from a little lower side of $k_1$(rough) = $2.6 \times 10^{-4}$ sec$^{-1}$ to somewhat higher side of it and also using the following equation for two step first order consecutive reaction for the reaction series $A \xrightarrow{k_1} D \xrightarrow{k_2} E$:

$$E_t = A_0 \left[1 + \frac{1}{k_1 - k_2} \left( k_2 e^{-k_1 t} - k_1 e^{-k_2 t} \right) \right] \quad \ldots (1)$$

The values of $E_t$ for different times, $t$, thus calculated are shown in Table 2(a) against the corresponding arbitrary trial values of $k_1$.

The values of $E_t$ have also been determined spectrophotometrically at such times $t$ when all A is exhausted and only $D$ and $E$ remains; for this purpose, the following equation (2) was used. $E_t/A_0 = \text{fraction of the total amount of A converted into E at time, } t$.

$$E_t = A_0 \cdot \frac{d_t - d_o}{d_a - d_o} \quad \ldots (2)$$

d$^{-}_o$, d$^{-}_a$ and d$^{-}_t$ are the respective O.D. values of the solutions of pure A, pure E, and of the reaction mixture at time $t$ at $\lambda = 530 \text{ nm}$.
From Table 2(a), it will be found that the best fit for the calculated and experimental values of $E_t$ is observed when trial value of $k_1(\text{rough}) = 1.5 \times 10^{-4} \text{ sec}^{-1}$ at each of the reaction times $t = 300 \text{ min}, 360 \text{ min}, 420 \text{ min}$ and $480 \text{ min}$, and therefore the actual value of rate constant for the first step $A \rightarrow D$, at $35^\circ C$ and at pH 4.0 may be taken to be $1.5 \times 10^{-4} \text{ sec}^{-1}$. Also since the three curves in Fig.III coincide with each other, we may conclude that the values of $k_1$ for all the mol ratios 1:10, 1:15 and 1:25 plotted in Fig.III are nearly identical namely $1.5 \times 10^{-4} \text{ sec}^{-1}$. 
PART II

DETAILED MECHANISM OF THE ANATION REACTION $A \rightarrow E$ ; EFFECT OF pH VARIATION AND OF ION PAIR FORMATION

A. The Study of pH variation on the Rate Constants of the Reaction Series $A \rightarrow D \rightarrow E$ at $35^\circ C$ with pH varying between 3.8 to 4.6 and $[A] : [\text{Phthalic Acid}]$ mol Ratio = 1:10

The effect of pH variation on the rate constants $k_1$ and $k_2$ for the reaction series $A \rightarrow D \rightarrow E$ was studied in the same way as in Part I, using all reaction mixtures of the same mol ratio ( $[A] = 0.005$ mol dm$^{-3}$ ; $[H_2\text{phth}] = 0.05$ mol dm$^{-3}$ ) at the same temperature $35^\circ C$ using everytime the same wavelength $\lambda = 530$ nm; but pH values of the reaction mixtures were varied. Studies in different runs were made at pH 3.8, 4.0, 4.2, 4.4 and 4.6 respectively, keeping the pH constant throughout each run. The plots of $\log \frac{d\alpha - d_0}{d\alpha - dt}$ vs $t$ at each pH (i.e. 3.8, 4.0, 4.2, 4.4 and 4.6) drawn on the same scale in all cases, one given in Fig.IV.

By a comparison of the five curves i.e. A (pH = 4.0), B (pH = 3.8), C (pH = 4.2), D (pH = 4.4) and E (pH = 4.6) it is seen that all the curves obtained at different pH are similar in nature to the curve in Fig.II but each has a different initial curvature and a different limiting slope. From each such limiting slope at a particular pH we get the value of phthalic acid independent unimolecular ring closure rate constant $k_2$ at that pH. After the evaluation of $k_2$ the values of
Fig-IV

Plot of $\log \frac{d\alpha - d_0}{d\alpha d_t}$ vs. t at different pH

Temp 35°C  pH=3.8 Δ; pH=4.0 ○; pH=4.2 △; pH=4.4 ◊; pH=4.6 ●.

B  A  C  D  E
the first order rate constant $k_1$ for the first step were then determined for each of the pH values, adopting the same trial and error method used in the determination of $k_1$ at pH 4.0 at 35°C. Thus comparing the observed values with the (different) calculated values of $E_t$ using various trial values of $k_1$ (starting from a little higher side of $k_1$ (rough) value to a little lower side of it) the particular value of $k_1$ for which there is best agreement between the experimental and calculated values of $E_t$ for each plot has been determined. [Table 2(a) for pH 4.0, Table 2(b) for pH 3.8, Table 2(c) for pH 4.2, Table 2(d) for pH 4.4 and Table 2(e) for pH 4.6.]

The values of the rate constants $k_1$ and $k_2$ at the respective pH values stated above at 35°C are shown in Table 3. It is evident from the result that the rate constant for the first step, $k_1$, of the reaction series $A \rightarrow D \rightarrow E$ is independent of pH but $k_2$ i.e. the rate constant for the second step (ring closure) is pH dependent. This fact indicated the possibility of the play of $S_{N1}$ CB mechanism in the second step, $D \rightarrow E$ but not in the first step $A \rightarrow D$.

B. Specific $(OH)^-$ catalysed anation reaction: $S_{N1}$ CB mechanism:

In a specific $(OH)^-$ catalysed anation reaction of a Co(III) complex of the type

$$[T(H_2O)_2]^{3+} + X \xrightarrow{k_{CB \text{ slow}}} [T(H_2O)X]^{2+} + H_2O \quad \ldots \quad (3)$$
it has been shown in Part-II, Sec. B, Ch. II, that the rate of the overall reaction (3) is given by the rate of the slowest step i.e.,

$$\text{rate} = k_{CB}[CB]$$

where $k_{CB}$ is the unimolecular rate constant of the dissociation reaction of the conjugate base $[T(H_2O)(OH)^-]^{2+}$ i.e. CB to form the penta coordinate intermediate, $[T(OH)]^{2+}$.

It has also been shown in Part-II, Sec. B, Ch. II, that for a specific $OH^-$ catalysed reaction, the pseudo first order rate constant $k_{obs}$ of the net reaction (3) is given by

$$k_{obs} = \frac{K_A \cdot k_{CB}}{[H^+]}$$

(Equation 12 of Ch.II)

where $K_A$ is the acid dissociation constant of $[T(H_2O)_2]^{3+}$ ion.

Equation (4) implies that the plot of $k_{obs}$ vs $1/[H^+]$ should be a straightline passing through the origin. Again from equation (4) we may have,

$$\log k_{obs} = \log(K_A \cdot k_{CB}) - \log[H^+]$$

$$= \log(K_A \cdot k_{CB}) + pH$$

(Equation 13 of Ch.II)

The equation (5) predicts that the plot of $\log k_{obs}$ vs pH will yield a straightline with slope +1.0. Thus the unit
value of slope, (+1), provides the most convincing proof of the fact that the reaction under consideration proceeds through a specific \( \text{OH}^- \) catalysed \( S_{N1} \) CB mechanism.

C. Ion-pair Mechanism :

This mechanism involves, in the first step, an ion-pair formation which establishes rapidly an equilibrium with the constituent ions and this is followed by an outersphere – innersphere interchange reaction occurring at a slow rate whereby the product complex is formed.

The scheme is given below, \((X^-)\) is an entering anion):

\[
[M_{L6}]^{3+} + X \underset{\text{fast}}{\overset{K_i}{\rightleftharpoons}} [M_{L6}]^3 - X \overset{k_i}{\rightarrow} [M_{L5} X]^2 + L
\]

Ion-pair

\(K_i = \) ion-pair equilibrium constant, \(k_i = \) rate constant for the interchange reaction.

For a process involving such a mechanism, the \(k_{obs}\) value is given by the relation:

\[
k_{obs} = \frac{k_i K_i [X^-]}{1 + K_i [X^-]} \quad \ldots (6)
\]

The formulation and the characteristics of equation (6) have been mentioned in Chapter-II (Part II, Sec. C). Two limiting cases of equation (6) may arise.
(i) When \([X^-]\) is low and therefore the formation of the ion-pair is incomplete or when \([X^-]\) is large but \(K_i\) is low, the plot of \(k_{obs} vs [X^-]\) is a straight line with slope \(K_i k_i\) and \(k_{obs}\) varies linearly with \([X^-]\).

(ii) When \(K_i\) is high or when \([X^-]\) is high, the plot of \(k_{obs} vs [X^-]\) becomes curved but as \([X^-]\) goes on increasing there is continuous decrease in the slope of the curve and when \(K_i [X^-] \gg 1\),

\[
    k_{obs} = k_i = \text{a constant},
\]

\(k_{obs}\) becomes independent of \([X^-]\) and the plot becomes a straight line parallel to the abcissa. At this stage, the reaction rate shows a first order dependence on [Complex] only. This happens when the ion-pairing is complete.

D. Evidence of Ion-pair Formation in the Step \(A \rightarrow D\):

Kinetic studies in the Part-I of this chapter revealed that with \([A] : [Phthalic acid]\) ratios 1:10, 1:15 and 1:25 at 35°C and pH 4.0, both the rate constants in the reaction series \(A \xrightarrow{k_1} D \xrightarrow{k_2} E\) were independent of phthalic acid concentration and dependent only on the concentration of complex A in first step and that of D in the second. Thus under the conditions both reactions were of the first order. Yet, even in this case the possibility of the formation of ion pair in the first step cannot be ruled out, since [phthalic acid] in all
the reaction mixtures used in those experiments were high enough compared to \([A]\) i.e., \([A] : [H_2 phth]\) ratios were 1:10, 1:15 and 1:25. At such high concentrations of phthalic acid concentration the ion pair formation between \([A^{3+}]\) and \([Hphth]^-\) may be nearly complete and thus \(k_{obs}\) may be a constant \([\text{when } K_i[X] >> 1, k_{obs} = k_i = \text{constant ... (7)} ]\).

Since the Complex A is tripositive and the ligand Hphth is uninegative, the formation of an ion pair is quite possible; the ion formed may be reinforced in strength through hydrogen bonding between negative oxygen atom in coordinated water molecule of the complex \([\text{Coen}_2(H_2O)_2]^{3+}\) and positive hydrogen atom at the \(-COOH\) end of the ligand Hphth\(^-\) and complete ion-pairing at low temperatures such as 35°C is quite conceivable when phthalic acid concentration in the reaction mixture is high.

Hence we tried to get positive evidence of ion pair formation by repeating the experiments at 35°C and at pH 4.0, and the mol ratios of \([A] : [H_2 phth]\) as 1:3 and 1:5 keeping \([A]\) the same e.g. 0.005 mol dm\(^{-3}\). We repeated the experiments with a view to obtain curvature, if any, in the plot of \(k_{obs} vs [X^-]\) at lower phthalic acid concentration; such a curvature could provide positive evidence for ion-pair formation. But it was observed that with \([A] : [H_2 phth]\) mol ratio lower than 1:10 the rates of the reaction becomes too slow to be measured at 35°C.
Therefore, we decided to carry out the experiments at a higher temperature, viz. at 45°C and at pH 4.0, where the rates would be faster even at low phthalic acid concentration. We performed experiments at 45°C and at pH 4.0, keeping [A] the same i.e., 0.005 mol dm\(^{-3}\) in all reaction mixtures but varying phthalic acid concentration as 0.015 mol dm\(^{-3}\), 0.025 mol dm\(^{-3}\), 0.05 mol dm\(^{-3}\), 0.075 mol dm\(^{-3}\) and 0.10 mol dm\(^{-3}\) in the successive mixtures (Mol ratios of [A] : [H\(_2\)phth] were 1:3, 1:5, 1:10, 1:15 and 1:20 respectively). The pH of each of the reaction mixture was maintained constant at 4.0 (from beginning to end) and the wavelength used was \(\lambda = 530\) nm.

The plots of \(\frac{d\alpha - d_0}{d\alpha - d_t}\) vs t are shown in Fig.V. It is evident from the curves in Fig.V that each curve has a different initial curvature but all of them end in parallel straight lines with same limiting slope. Hence the ring closure rate constant, \(k_2\), (at 45°C and at pH 4.0) is of first order and has the same value for every mol ratio, thus being independent of phthalic acid concentration.

The respective value of \(k_2\) at each [A] : [phthalic acid] mol ratio at 45°C and at pH 4.0 are given in Table-5. The values of \(k_2\) are found to be constant within the range of the experimental error.

After calculating the constant value of \(k_2\), the respective values of \(k_1\) were found out by following the same procedure as

Temp = 45°C; pH = 4.0; 1:3 △; 1:5 ○; 1:10 ○; 1:15 ○; 1:20 ●.

λ = 530 nm.
described in Part-I i.e., by comparing the observed values of $E_t$ and corresponding calculated values of it using equation (1) with different trial values of $k_1$ (vide Table 2f to Table 2j for mol ratios $[A]^{3+} : [H_2\text{phth}] = 1:3, 1:5, 1:10, 1:15$ and $1:20$ respectively). The actual values of $k_1$ found out at different mol ratios of $[A] : [H_2\text{phth}]$ are given in Table 5. The plot of the rate constants $k_1$ vs $[\text{Phthalic acid}]$ at different mol ratios above and at $\text{pH} = 4.0$ and temperature $45^\circ\text{C}$ have been shown in Fig.VIa.

From Table-5 and Fig.VIa, it is observed that the rate constant, $k_1$ for step $A \rightarrow D$, increases with phthalic acid concentration and tends to reach a limiting value at high phthalic acid concentration. This provides the conclusive evidence that the ion pair mechanism is operative in the reaction, $A \rightarrow D$ (vide Sec. C).

Rearrangement of equation (6) gives

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{1}{k_1 K_1} \cdot \frac{1}{[X^-]}$$

Equation (8) implies that the plot of $\frac{1}{k_{obs}}$ vs $\frac{1}{[X^-]}$, at constant pH and temperature, should be linear with an intercept (on ordinate) $\frac{1}{k_1}$ and a slope $\frac{1}{k_1 K_1}$.

The value of $k_1$ found in our case for the stoichiometric mechanism $A \rightarrow D \rightarrow E$ should be regarded as $k_1(\text{obs})$. 
Fig VI a

Plot of $k_1$ Vs. [Phthalic acid].

Temp = 45°C; pH = 4.0; [A] = 0.005 mol dm$^3$.
Fig. VI(b) shows the plot of $1/k_{i\text{obs}}$ vs $1/[H_2\text{phth}]$ for our case (at $45^\circ\text{C}$, pH = 4.0). The plot is found to be a straightline with an intercept and thus the formation of an ion pair as an intermediate in the first step of the reaction, $A \rightarrow D$ is definitely established. The values of $k_i$ and $K_i$ are obtained in the following way from the intercept and slope of the straightline in Fig. VI(b):

Slope = $1/k_i K_i = 41.49$; intercept = $1/k_i = 1700$

Hence, $k_i$ = rate constant for the interchange reaction

$= 5.88 \times 10^{-4}$ sec$^{-1}$ (at $45^\circ\text{C}$ and pH 4.0), and

$K_i$ = ion-pair equilibrium constant

$= 41.0$ (at $45^\circ\text{C}$ and pH 4.0).

[The rather high value of $K_i$ is indicative of hydrogen bonding between the ions paired.]

Hence in our reaction series:

(i) The reaction $A \rightarrow D$ occurs through the formation of ion-pair, and is independent of pH,

(ii) The ring closure step $D \rightarrow E$ involves an $S_{N1}$ CB mechanism and is unimolecular being independent of phthalic acid.

E. Discussion of the Detailed Mechanism:

(a) Mechanism of the substitution reaction $A \rightarrow D$ :- Table-1 (Introduction) shows that in a 0.05 mol dm$^{-3}$ of phthalic acid in aqueous solution at $25^\circ\text{C}$ and in the pH range 3.8 to 4.6,
Fig-VI b

Plot of $\frac{1}{k_1(\text{obs})}$ Vs. $\frac{1}{[L]}$

Temp = 45°C; pH = 4.0.

Slope = $\frac{1}{k_i} k_i = 41.49$.

Intercept = $\frac{1}{k_i} = 1700$
the species Hphth$^-$ is most predominant at every pH; hence Hphth$^-$ may be taken as the main reacting species. We shall therefore consider that the only ion pair present in the reaction mixtures is $[A]^{3+} [\text{Hphth}]^- \text{ except at pH } 3.8 \text{ where ion-dipole pair } [A]^{3+} [\text{H}_2\text{phth}]^0 \text{ and at pH 4.6 where the ion-pair } [A]^{3+} [\text{Phth}]^{2-} \text{ are present in small amounts. The intermediate D is formed from the complex, practically through the formation of the only ion pair } [A]^{3+} [\text{Hphth}]^- \text{ and the reaction route is being proposed in Scheme-I on this basis.}

(b) Mechanism of the Ring closure Reaction D $\rightarrow$ E: -- Table-3 shows that the first order rate constant $k_2$ for the ring closure reaction D $\rightarrow$ E is pH dependent between pH 3.8 and pH 4.6. This indicates the possibility of the play of $S_N^1$ CB mechanism in the second step of our reaction series. At first we shall assume that only an $S_N^1$ CB mechanism is operating in the ring closure reaction D $\rightarrow$ E, according to Scheme-IIA.
Reaction Scheme 1

\[
\left[ \text{en}_2 \text{Co(H}_2\text{O})_2 \right]^{3+} + \text{HPh}^\text{th} \xrightarrow{\text{fast}} \left[ \text{en}_2 \text{Co(H}_2\text{O})(\text{HPh}^\text{th}) \right]^{2+} + \text{H}_2\text{O}
\]
Scheme-IIA

\[
\begin{align*}
[D] & \xrightarrow{\text{fast}} [\text{enCo}^{3+}(C_2H_4N_2H_3)(H_2O)(Hphth)^-]^{1+} \\
& \xrightarrow{\text{slow}} k_{\text{CB}(D)}
\end{align*}
\]

For the pre-equilibrium step, the equilibrium constant is given by:

\[
\frac{[\text{CB}(D)]}{[D][OH^-]} = \frac{[\text{CB}(D)][H^+]}{[D]K_w} = \frac{K_D}{K_w} \quad \ldots (9)
\]

where \(K_D\) is the acid dissociation constant of \(D\) i.e., equilibrium constant of the following reaction:

\[
[D] \xrightarrow{\text{fast}} [\text{enCo}^{3+}(C_2H_4N_2H_3)(H_2O)(Hphth)^-]^{1+} + H^+
\]

Hence \(K_D = \frac{[\text{CB}(D)][H^+]}{[D]} \quad \ldots (10)\)

From (10), we have

\[
[\text{CB}(D)] = \frac{K_D}{K_w} \cdot [D][OH^-] = \frac{K_D \cdot [D]}{[H^+]} \quad \ldots (11)
\]
Since \[
\frac{[\text{OH}^-]}{K_W} = \frac{1}{[\text{H}^+]} \]

The rate of the ring closure reaction, \(D \rightarrow E\) = rate of its slowest step

\[
= k_{CB(D)} \cdot [CB(D)] \\
= \frac{k_{CB(D)} \cdot K_D \cdot [D]}{[\text{H}^+]} \]  

by equation (11).

Since the ring closure reaction, \(D \rightarrow E\) is unimolecular, its rate is proportional to \([D]\), so the rate of the reaction

\[
D \rightarrow E = k_2[D]  
\]  

... (13)

[In this case, \(k_2\) may be considered as \(k_{2 \text{obs}}\).]

Comparing equation (12) and equation (13), we get,

\[
k_2 = \frac{k_{CB(D)} \cdot K_D}{[\text{H}^+]} \]  

... (14)

The equation (14) predicts that the plot of \(k_2\) vs \(1/[\text{H}^+]\) should be a straight line passing through the origin and with a slope equal to \(k_{CB(D)} \cdot K_D\).

The observed values of \(k_2\) against the respective values of \(1/[\text{H}^+]\) have been given in Table-3; the plot of \(k_2\) vs \(1/[\text{H}^+]\) has been shown in Fig.VII(a). It will be seen therefrom (i.e. Fig.VIIa) that the plot is a straightline, but instead of passing through the origin, it makes an intercept (on the ordinate)
The plot of $k_2$ vs $1/[H^+]$. 
Temp = 35°C.

Intercept = $1.75 \times 10^{-5}$. 

$1 \text{ div.} = 0.1 \times 10^5$. 

$2 \text{ div.} = 1000$. 

$k_2 \times 10^5$ 

$1/[H^+] \times 10^{-3}$
\[ k' = 1.75 \times 10^{-5} \text{ sec}^{-1}. \] The rate constant \( k' \) is pH independent.

Equation (14) should therefore be corrected to the following form:

\[
k_2 = k' + \frac{k_{CB(D)} \cdot K_D}{[H^+]} \quad \ldots (15)
\]

where \( k' \) is the first order pH independent rate constant of the ring closure reaction; the slope of the straightline plot \((= 1.50 \times 10^{-9})\) represents the value of \( k_{CB(D)} \cdot K_D \) [vide equation (15)].

Again from equation (15), we get,

\[
\log(k_2 - k') = \log[k_{CB(D)} \cdot K_D] + \text{pH} \quad \ldots (16)
\]

This equation (16) predicts that the plot of \( \log (k_2 - k') \) vs pH will be a straightline with slope \( = +1.0 \). This plot, drawn from the experimental data (Table 4) has been shown in Fig.VIIb. It is found to be a straightline with slope \( +1.0 \). This provides a conclusive evidence of the fact that the ring closure reaction, \( D \rightarrow E \) involves an \( S_N1 \) CB path. The equation (15) suggests that the total reaction \( D \rightarrow E \) proceeds through two parallel paths - one simple unimolecular, pH independent ring closure path:

\[
[D: \text{Co}^{3+}\text{en}_2(H_2O)(\text{Hphth})^{2+}]^{2+} \xrightarrow{k'} \rightarrow [E: \text{Co}^{3+}\text{en}_2(\text{phth})^{2-}]^{1+} + \text{H}_3\text{O}^+
\]

and another \( S_N1 \) CB path.
Fig. VII b

Plot of $\log(k_2 - k')$ vs. pH.

Temp = 35°C.

Slope = +1.0
Hence the complete reaction mechanism for the ring closure reaction D → E is given below in Reaction Scheme IIB.

**Reaction Scheme IIB**

\[
\text{[enCo}^{3+}(C_2H_4N_2H_4)(H_2O)(Hphth^-)]^{2+} + \text{OH}^- \\
\xrightarrow{\text{H}_3\text{O}^+} \text{slow unimolecular} \\
\text{[enCo}^{3+}(C_2H_4N_2H_3)^-(H_2O)(Hphth)^-]^{1+} + \text{H}_2\text{O} \\
\xrightarrow{k_{\text{CB}(D)}} \text{fast ring closure} \\
\text{[Co}^{3+}\text{en}_2(\text{phth})^{2-}]^{1+} \xrightarrow{\text{Dissociation of H}_2\text{O}} \text{Pentacoordinate}
\]

At pH = 3.8, the little amount of the ion-dipole pair \([\text{en}_2\text{Co(H}_2\text{O})_2]^{3+}\text{H}_2\text{phth}\) formed may react through a path similar to Route I of Reaction Scheme-I described in Section E of Ch. II to form a same intermediate \([\text{(en)}_2\text{Co(H}_2\text{O})(\text{Hphth})^-]^{2+}\) which may then close the ring to form \([\text{Coen}_2(\text{phth})^{2-}]^{1+}\) according to Reaction Scheme IIB above.

At pH = 4.6, the small amount of the ion-pair \([\text{en}_2\text{Co(H}_2\text{O})_2]^{3+}\text{phth}^{2-}\) formed may react according to Scheme-III and ultimately form the ring closed compound \([\text{Coen}_2(\text{phth})^{2-}]^{1+}\)
Scheme-III

\[
[\text{Coen}_2(H_2O)_2]^{3+} \cdot \text{phth}^{2-} \xrightarrow{\text{Interchange}} [\text{Coen}_2(\text{phth})^{2-}(H_2O)]^1 + H_2O
\]

Ion-pair

\[
[\text{Co}^{3+}\text{en(C}_2\text{H}_4\text{N}_2\text{H}_4)(\text{phth})^{2-}(H_2O)]^+ + \text{OH}^-
\]

\[
\xleftrightarrow{\text{Conjugate base CB}} [\text{Coen(C}_2\text{H}_4\text{N}_2\text{H}_3)^-\text{(phth)}^{2-}(H_2O)]^0 + H_2O
\]

Slow unimolecular ring closure

\[
- H_2O \xrightarrow{\text{slow dissociation of } H_2O} [\text{Coen(C}_2\text{H}_4\text{N}_2\text{H}_3)^-\text{(phth)}^{2-}]^0 + H_2O
\]

Penta coordinate

\[
\xrightarrow{\text{Rapid ring closure}} [\text{Coen}_2(\text{phth})^{2-}]^1 + \text{OH}^-
\]

Ring closed complex

* phth = Singly linked Ph < \[
\begin{array}{c}
\text{COO}^- \\
\text{COO}^-
\end{array}
\]
Table 1 - Relative concentration of H$_2$phth, Hphth$^-$ and phth$^{2-}$ in 0.05 mol dm$^{-3}$ solution of phthalic acid at different pH values at 25°C

<table>
<thead>
<tr>
<th>pH</th>
<th>[H$^+$]</th>
<th>[H$_2$phth]</th>
<th>[Hphth$^-$]</th>
<th>[phth$^{2-}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>1.58 x 10$^{-4}$</td>
<td>0.0061</td>
<td>0.0429</td>
<td>0.0011</td>
</tr>
<tr>
<td>4.0</td>
<td>1.0 x 10$^{-4}$</td>
<td>0.0040</td>
<td>0.0443</td>
<td>0.0017</td>
</tr>
<tr>
<td>4.2</td>
<td>6.31 x 10$^{-5}$</td>
<td>0.0025</td>
<td>0.0447</td>
<td>0.0028</td>
</tr>
<tr>
<td>4.4</td>
<td>3.98 x 10$^{-5}$</td>
<td>0.0016</td>
<td>0.0441</td>
<td>0.0043</td>
</tr>
<tr>
<td>4.6</td>
<td>2.51 x 10$^{-5}$</td>
<td>0.0010</td>
<td>0.0425</td>
<td>0.0066</td>
</tr>
</tbody>
</table>
Table 2(a) - Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 3.23 \times 10^{-5}$ sec$^{-1}$.

$[A] = 0.005$ mol dm$^{-3}$, $[H_2$phth$] = 0.05$ mol dm$^{-3}$,

Temp. = $35^\circ$C, pH = 4.0

The value of $k_1$(rough) = $2.6 \times 10^{-4}$ sec$^{-1}$

<table>
<thead>
<tr>
<th>Trial values of $k_1 \times 10^4$ sec$^{-1}$</th>
<th>Calculated values of $E_t \times 10^3$ using eqn.(1) (in mol dm$^{-3}$)</th>
<th>300 min.</th>
<th>360 min.</th>
<th>420 min.</th>
<th>480 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>1.39, 1.73, 2.06, 2.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>1.49, 1.84, 2.16, 2.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>1.53, 1.88, 2.21, 2.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>1.57, 1.92, 2.25, 2.54</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>1.64, 1.99, 2.31, 2.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>1.81, 2.16, 2.47, 2.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental values of $E_t \times 10^3$ (mol dm$^{-3}$)

|                                      | 1.51, 1.86, 2.19, 2.50 |

It will be seen that the calculated values of $E_t$ are not very much sensitive to small changes in the trial values of $k_1$; however the best agreement for the experimental and calculated values of $C_t$ is for $k_1 = 1.5 \times 10^{-4}$ sec$^{-1}$. 
Table 2(b) - Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 2.80 \times 10^{-5}$ sec$^{-1}$.

$[A] = 0.005$ mol dm$^{-3}$, $[H_2phth] = 0.05$ mol dm$^{-3}$, Temp. = 35°C, pH = 3.8

The value of $k_1$(rough) = $3.2 \times 10^{-4}$ sec$^{-1}$

<table>
<thead>
<tr>
<th>Trial values of $k_1 \times 10^4$ sec$^{-1}$</th>
<th>Calculated values of $E_t \times 10^3$ using eqn.(1) (in mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 min.</td>
</tr>
<tr>
<td>1.2</td>
<td>1.24</td>
</tr>
<tr>
<td>1.3</td>
<td>1.28</td>
</tr>
<tr>
<td>1.4</td>
<td>1.32</td>
</tr>
<tr>
<td>1.5</td>
<td>1.36</td>
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<tr>
<td>1.6</td>
<td>1.40</td>
</tr>
<tr>
<td>1.8</td>
<td>1.46</td>
</tr>
<tr>
<td>3.2</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Experimental values of $E_t \times 10^3$ (mol dm$^{-3}$)

1.35  1.70  2.01  2.28

It will be seen that the calculated values of $E_t$ are not very much sensitive to small changes in the values of $k_1$; however the best agreement for the experimental and calculated values of $E_t$ is for $k_1 = 1.5 \times 10^{-4}$ sec$^{-1}$
Table 2(c)- Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 3.90 \times 10^{-5}$ sec$^{-1}$.

$[A] = 0.005$ mol dm$^{-3}$, $[H_2$ phth$] = 0.05$ mol dm$^{-3}$, Temp. $35^\circ$C, pH = 4.2

The value of $k_1$(rough) = $3.2 \times 10^{-4}$ sec$^{-1}$

<table>
<thead>
<tr>
<th>Trial values of $k_1 \times 10^4$ (sec$^{-1}$)</th>
<th>Calculated values of $E_t \times 10^3$ (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(in mol dm$^{-3}$)</td>
</tr>
<tr>
<td></td>
<td>300 min. 360 min. 420 min. 480 min.</td>
</tr>
<tr>
<td>1.4</td>
<td>1.72 2.11 2.46 2.78</td>
</tr>
<tr>
<td>1.5</td>
<td>1.77 2.16 2.51 2.83</td>
</tr>
<tr>
<td>1.6</td>
<td>1.81 2.21 2.55 2.87</td>
</tr>
<tr>
<td>1.7</td>
<td>1.85 2.24 2.59 2.90</td>
</tr>
<tr>
<td>3.2</td>
<td>2.18 2.55 2.87 3.15</td>
</tr>
</tbody>
</table>

Experimental values of $E_t \times 10^3$ (mol dm$^{-3}$)

<p>| |</p>
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80</td>
</tr>
<tr>
<td>2.21</td>
</tr>
<tr>
<td>2.57</td>
</tr>
<tr>
<td>2.88</td>
</tr>
</tbody>
</table>

The best agreement for the experimental and calculated values of $E_t$ is for $k_1 = 1.6 \times 10^{-4}$ sec$^{-1}$. [Also see the foot note of Table 2(a)].
Table 2(d) - Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 5.47 \times 10^{-5}$ sec$^{-1}$.

$[A] = 0.005$ mol dm$^{-3}$, $[H_2$phth$] = 0.05$ mol dm$^{-3}$, Temp. $35^\circ C$, pH = 4.4.

The value of $k_1(\text{rough}) = 3.2 \times 10^{-4}$ sec$^{-1}$

<table>
<thead>
<tr>
<th>Trial values of $k_1 \times 10^4$ sec$^{-1}$</th>
<th>Calculated values of $E_t \times 10^3$ using eqn.(1) (in mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>240 min.</td>
</tr>
<tr>
<td>1.4</td>
<td>1.69</td>
</tr>
<tr>
<td>1.5</td>
<td>1.75</td>
</tr>
<tr>
<td>1.6</td>
<td>1.80</td>
</tr>
<tr>
<td>1.7</td>
<td>1.85</td>
</tr>
<tr>
<td>1.8</td>
<td>1.90</td>
</tr>
<tr>
<td>3.2</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Experimental values of $E_t \times 10^3$ (mol dm$^{-3}$)

| 1.78 | 2.30 | 2.76 | 3.16 |

The best agreement for the experimental and calculated values of $E_t$ is for $k_1 = 1.6 \times 10^{-4}$ sec$^{-1}$. [See also the foot note of Table 2(a)].
Table 2(e) - Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 7.64 \times 10^{-5} \text{ sec}^{-1}$, $[A] = 0.005 \text{ mol dm}^{-3}$, $[\text{H}_2\text{phth}] = 0.05 \text{ mol dm}^{-3}$, Temp. $35^\circ \text{C}$, pH = 4.6

The value of $k_1(\text{rough}) = 2.6 \times 10^{-4} \text{ sec}^{-1}$

<table>
<thead>
<tr>
<th>Trial values of $k_1 \times 10^4 \text{ sec}^{-1}$</th>
<th>Calculated values of $E_t \times 10^3$ using eqn.(1) (in mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>240 min.</td>
</tr>
<tr>
<td>1.2</td>
<td>1.98</td>
</tr>
<tr>
<td>1.3</td>
<td>2.06</td>
</tr>
<tr>
<td>1.4</td>
<td>2.14</td>
</tr>
<tr>
<td>1.5</td>
<td>2.21</td>
</tr>
<tr>
<td>1.6</td>
<td>2.27</td>
</tr>
<tr>
<td>2.6</td>
<td>2.69</td>
</tr>
</tbody>
</table>

Experimental values of $E_t \times 10^3$ (mol dm$^{-3}$)

2.19 2.76 3.26 3.64 3.96

The best agreement for the experimental and calculated values of $E_t$ is for $k_1 = 1.5 \times 10^{-4} \text{ sec}^{-1}$. [See also footnote of Table 2(a)].
Table 2(f)- Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 2.21 \times 10^{-4} \text{ sec}^{-1}$.

$[A] = 0.005 \text{ mol dm}^{-3}$, $[H_2\text{phth}] = 0.015 \text{ mol dm}^{-3}$, Temp. $45^\circ\text{C}$, pH $= 4.0$.

The value of $k_1(\text{rough}) = 5.1 \times 10^{-4} \text{ sec}^{-1}$

<table>
<thead>
<tr>
<th>Trial values of $k_1 \times 10^4$ (in $\text{mol dm}^{-3} \text{ sec}^{-1}$)</th>
<th>Calculated values of $E_t \times 10^3$ using eqn. (1) (in $\text{mol dm}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>210 min.</td>
</tr>
<tr>
<td>2.2</td>
<td>3.83</td>
</tr>
<tr>
<td>2.3</td>
<td>3.88</td>
</tr>
<tr>
<td>2.4</td>
<td>3.93</td>
</tr>
<tr>
<td>2.5</td>
<td>3.97</td>
</tr>
<tr>
<td>2.6</td>
<td>4.01</td>
</tr>
<tr>
<td>5.1</td>
<td>4.46</td>
</tr>
</tbody>
</table>

Experimental values of $E_t \times 10^3$ (mol dm$^{-3}$)

|                             | 3.93     | 4.22     | 4.44     |

The best agreement for the experimental and calculated values of $E_t$ is for $k_1 = 2.4 \times 10^{-4} \text{ sec}^{-1}$. [See also the foot note of Table 2(a)].
Table 2(g) - Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 2.28 \times 10^{-4}$ dm$^{-3}$. 

$[A] = 0.005$ mol dm$^{-3}$, $[H_2$phth$] = 0.025$ mol dm$^{-3}$, Temp. $45^\circ$C, pH = 4.0

The value of $k_1$(rough) = $6.4 \times 10^{-4}$ sec$^{-1}$

<table>
<thead>
<tr>
<th>Trial value of $k_1 \times 10^4$ sec$^{-1}$</th>
<th>Calculated value of $E_t \times 10^3$ using eqn.(1) (in mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150 min.</td>
</tr>
<tr>
<td>2.4</td>
<td>3.11</td>
</tr>
<tr>
<td>2.6</td>
<td>3.21</td>
</tr>
<tr>
<td>2.8</td>
<td>3.30</td>
</tr>
<tr>
<td>3.0</td>
<td>3.39</td>
</tr>
<tr>
<td>3.2</td>
<td>3.46</td>
</tr>
<tr>
<td>3.4</td>
<td>3.53</td>
</tr>
<tr>
<td>6.4</td>
<td>4.01</td>
</tr>
</tbody>
</table>

Experimental value of $E_t \times 10^3$ (mol dm$^{-3}$) 

3.28 3.74 4.09 4.38

The best agreement for the experimental and calculated values of $E_t$ is for $k_1 = 2.8 \times 10^{-4}$ sec$^{-1}$. [See also the foot note of Table 2(a)].
Table 2(h) - Comparison of the calculated and experimental values of \( E_t \) taking \( k_2 = 2.33 \times 10^{-4} \text{ sec}^{-1} \).

\([A] = 0.005 \text{ mol dm}^{-3}, [H_2\text{phth}] = 0.05 \text{ mol dm}^{-3}, \]

Temp. 45\(^\circ\)C, pH = 4.0

The value of \( k_1(\text{rough}) = 8.5 \times 10^{-4} \text{ sec}^{-1} \)

<table>
<thead>
<tr>
<th>Trial values of ( k_1 \times 10^{4} \text{ sec}^{-1} )</th>
<th>Calculated value of ( E_t \times 10^{3} ) using eqn. (1) (in mol dm(^{-3}))</th>
<th>120 min.</th>
<th>135 min.</th>
<th>150 min.</th>
<th>180 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td></td>
<td>3.02</td>
<td>3.33</td>
<td>3.60</td>
<td>4.03</td>
</tr>
<tr>
<td>3.7</td>
<td></td>
<td>3.08</td>
<td>3.39</td>
<td>3.66</td>
<td>4.08</td>
</tr>
<tr>
<td>3.8</td>
<td></td>
<td>3.11</td>
<td>3.42</td>
<td>3.68</td>
<td>4.10</td>
</tr>
<tr>
<td>3.9</td>
<td></td>
<td>3.14</td>
<td>3.45</td>
<td>3.71</td>
<td>4.12</td>
</tr>
<tr>
<td>4.0</td>
<td></td>
<td>3.17</td>
<td>3.47</td>
<td>3.73</td>
<td>4.14</td>
</tr>
<tr>
<td>4.5</td>
<td></td>
<td>3.29</td>
<td>3.58</td>
<td>3.83</td>
<td>4.22</td>
</tr>
<tr>
<td>8.5</td>
<td></td>
<td>3.73</td>
<td>3.97</td>
<td>4.17</td>
<td>4.45</td>
</tr>
</tbody>
</table>

Experimental value of \( E_t \times 10^{3} \) (mol dm\(^{-3}\))

|                                                     |                                                                                  | 3.10    | 3.42    | 3.68    | 4.11    |

The best agreement for the experimental and calculated values of \( E_t \) is for \( k_1 = 3.8 \times 10^{-4} \text{ sec}^{-1} \). [See also the foot note of Table 2(a)].
Table 2(i) - Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 2.34 \times 10^{-4} \text{ sec}^{-1}$.

$[A] = 0.005 \text{ mol dm}^{-3}$, $[H_2\text{phth}] = 0.075 \text{ mol dm}^{-3}$,

Temp. $45^\circ\text{C}$, $pH = 4.0$.

The values of $k_1(\text{rough}) = 6.4 \times 10^{-4} \text{ sec}^{-1}$

<table>
<thead>
<tr>
<th>Trial value of $k_1 \times 10^4 \text{ sec}^{-1}$</th>
<th>Calculated value of $E_t \times 10^3$ using eqn. (1) (in $\text{mol dm}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120 min.</td>
</tr>
<tr>
<td>4.0</td>
<td>3.16</td>
</tr>
<tr>
<td>4.2</td>
<td>3.21</td>
</tr>
<tr>
<td>4.3</td>
<td>3.24</td>
</tr>
<tr>
<td>4.4</td>
<td>3.26</td>
</tr>
<tr>
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<td>3.28</td>
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<tr>
<td>4.6</td>
<td>3.30</td>
</tr>
<tr>
<td>6.4</td>
<td>3.57</td>
</tr>
</tbody>
</table>

Experimental value of $E_t \times 10^3$ (mol $\text{dm}^{-3}$)

<table>
<thead>
<tr>
<th></th>
<th>120 min.</th>
<th>150 min.</th>
<th>180 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>3.80</td>
<td>4.19</td>
<td>4.47</td>
</tr>
</tbody>
</table>

The best agreement for the experimental and calculated values of $E_t$ is for $k_1 = 4.4 \times 10^{-4} \text{ sec}^{-1}$ [See also the foot note of Table 2(a)].
Table 2(j) - Comparison of the calculated and experimental values of $E_t$ taking $k_2 = 2.33 \times 10^{-4}$ sec$^{-1}$.

$[A] = 0.005$ mol dm$^{-3}$, $[H_2 \text{phth}] = 0.10$ mol dm$^{-3}$, Temp. $45^\circ$C, pH = 4.0

The values of $k_1(\text{rough}) = 1.0 \times 10^{-3}$ sec$^{-1}$

<table>
<thead>
<tr>
<th>Trial value of $k_1 \times 10^4$ sec$^{-1}$</th>
<th>Calculated value of $E_t \times 10^3$ using eqn.(1) (in mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>90 min.</td>
</tr>
<tr>
<td>4.2</td>
<td>2.45</td>
</tr>
<tr>
<td>4.6</td>
<td>2.55</td>
</tr>
<tr>
<td>4.8</td>
<td>2.59</td>
</tr>
<tr>
<td>5.0</td>
<td>2.63</td>
</tr>
<tr>
<td>5.1</td>
<td>2.65</td>
</tr>
<tr>
<td>5.2</td>
<td>2.67</td>
</tr>
<tr>
<td>10.0</td>
<td>3.15</td>
</tr>
</tbody>
</table>

Experimental value of $E_t \times 10^3$ (mol dm$^{-3}$)

|                                           | 2.60    | 3.00     | 3.35     | 3.89     |

The best agreement for the experimental and calculated values of $E_t$ is for $k_1 = 4.8 \times 10^{-4}$ sec$^{-1}$. [See also the foot note under Table 2(a)].
Table 3 - Values of Rate Constants at different pH
complex concentration 0.005 mol dm\(^{-3}\),
phthalic acid concentration 0.05 mol dm\(^{-3}\),
Temp. 35°C

<table>
<thead>
<tr>
<th>pH</th>
<th>1/[H(^+)]</th>
<th>(k_1 \times 10^4) sec(^{-1})</th>
<th>(k_2 \times 10^5) sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>.6310</td>
<td>1.5</td>
<td>2.80</td>
</tr>
<tr>
<td>4.0</td>
<td>10000</td>
<td>1.5</td>
<td>3.23</td>
</tr>
<tr>
<td>4.2</td>
<td>15849</td>
<td>1.5</td>
<td>3.90</td>
</tr>
<tr>
<td>4.4</td>
<td>25119</td>
<td>1.6</td>
<td>5.47</td>
</tr>
<tr>
<td>4.6</td>
<td>39811</td>
<td>1.5</td>
<td>7.64</td>
</tr>
</tbody>
</table>
Table 4 - Values of log\((k_2 - k')\) at different pH.

Temp. 35°C, \(k' = 1.75 \times 10^{-5} \text{ sec}^{-1}\)

<table>
<thead>
<tr>
<th>pH</th>
<th>log((k_2 - k'))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>-4.98</td>
</tr>
<tr>
<td>4.0</td>
<td>-4.83</td>
</tr>
<tr>
<td>4.2</td>
<td>-4.67</td>
</tr>
<tr>
<td>4.4</td>
<td>-4.43</td>
</tr>
<tr>
<td>4.6</td>
<td>-4.23</td>
</tr>
</tbody>
</table>

Table 5 - Values of \(k_1\) and \(k_2\) at 45°C

pH = 4.0, \([A] = 0.005 \text{ mol dm}^{-3}\)

<table>
<thead>
<tr>
<th>([H_2m]) \text{ mol dm}^{-3}</th>
<th>(k_1 \times 10^4) \text{ sec}^{-1}</th>
<th>(k_2 \times 10^4) \text{ sec}^{-1}</th>
<th>(1/k_1) \text{ sec}</th>
<th>(1/[H_2m]) \text{ mol}^{-1} \text{ dm}^{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>2.4</td>
<td>2.21</td>
<td>4167.0</td>
<td>66.7</td>
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<tr>
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<td>2.28</td>
<td>3571.4</td>
<td>40.0</td>
</tr>
<tr>
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<td>2.35</td>
<td>2632.0</td>
<td>20.0</td>
</tr>
<tr>
<td>0.075</td>
<td>4.4</td>
<td>2.34</td>
<td>2273.0</td>
<td>13.3</td>
</tr>
<tr>
<td>0.100</td>
<td>4.8</td>
<td>2.33</td>
<td>2083.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>
References:


