www.ThePharmaJournal.com

The Pharma Innovation

Yogeshwar Sharma
Associate Professor, Department
of Chemistry, Motilal Nehru
College, Benito Juarez Marg,
University of Delhi South
Campus, New Delhi, India

Kinetics and mechanism of complexation of Co (II) with 2-aminobenzoic acid

Yogeshwar Sharma

Abstract
The kinetics of the complexation of Co (II) with 2-aminobenzoic acid has been investigated at 25, 30, 35 and 40± 0.05 °C in the pH range 2.10-4.62 using Aminco Morrow Stopped Flow Spectrophotometer. The ionic strength was maintained at 0.1 M KNO_3. The anionic form of 2-aminobenzoic acid is more reactive and the protonated form interacts only to a small extent. Kinetic results indicate that the ligand is not involved in the rate determining step which is, in fact, associated with the release of a water molecule from the shell of the metal ions prior to complexation with the ligand. Enthalpy, entropy of activation, energy of the molecule and heat of formation were also calculated. A mechanism consistent with the kinetic data has been suggested.

Keywords: Kinetics, complexation, metal ions, biochemical ligand, rate constant, activation parameters, energy of the molecule, heat of formation

Introduction

2-Aminobenzoic acid is an important B - complex factor. It has been used for dogs as a protective agent against sensitization of their skins. It also finds applications in rheumatic fever and in a couple of other diseases. Cobalt (II) - 2 - aminobenzoic acid complex is used as an anti - inflammatory drug in which tissue repairs and the repair process reestablishes normal function. This complex is used as an antiulcer, anticancer and antiepileptic drugs and emphasize the need for more research in the area of metal ligand complexation. The predominant form of the 2 - aminobenzoic acid in solution is
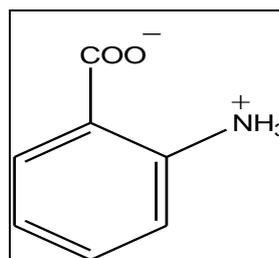

(2-aminobenzoic acid) Zwitterion

It can also be assumed that due to intramolecular hydrogen bonding between the protonated amino group and carboxylate group of the zwitterion, the zwitterionic species should be unreactive towards Co (II). In order to check the reactivity of zwitterion and to know the different binding steps, their corresponding rate constants and activation parameters, kinetics of Co (Il) with 2 aminobenzoic acid was initiated. The kinetics of complexation of metal ions Co (II) by 2-aminobenzoic acid would no doubt give important information regarding the types of interaction of these ions with 2-aminobenzoic acid and the clearance of 2-aminobenzoic acid or metal ions in the form of metal – ligand complex through the animal body[1-7]. With the hope that these anomalies might have rational explanation and to understand the biological processes clearly, a comprehensive kinetic study has been undertaken on the reaction of Co (II) with 2-aminobenzoic acid. Such investigations are further desired for determining some important parameters, e.g. binding steps, rate constants corresponding to the binding steps Kos (outer sphere complex formation constant), ko (Rate constant of water exchange) and activation parameters corresponding to the interaction of various reactive forms of the 2-aminobenzoic acid.

Correspondence
Yogeshwar Sharma
Associate Professor, Department
of Chemistry, Motilal Nehru
College, Benito Juarez Marg,
University of Delhi South
Campus, New Delhi, India

Materials and Methods

2-aminobenzoic acid (B.D.H.), KNO$_3$ (B.D.H.) were used as such. Other chemicals used were of A.R. grade. The pH of ligand solution and metal ion solution was adjusted to same value using 2, 6-lutidine (Merck Schuchardt) and HCl. However, a slight change in pH value (~ 0.05 units) was observed after mixing of two solutions. The final pH was recorded from Radiometer pH meter, *pH* M26. pH's reported are those of reaction mixtures. The temperature of the system was maintained by immersion type thermostat (German NBE model). The kinetic runs were made on Aminco Morrow stopped flow spectrophotometer under pseudo first order conditions, i.e., [M(II)] >>[2-aminobenzoic acid] *(M= Co)* at 620nm.
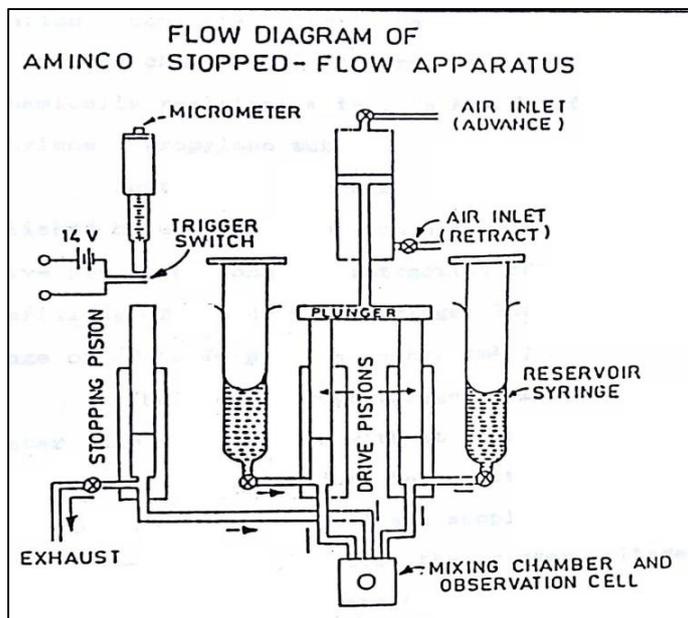
Cobalt nitrate, 10^{-2}M, buffer 10^{-2}M Lutidine and, μ= 0.1 M KNO$_3$ was mixed with ligand solution and the traces from the oscilloscope gave excellent first order plots, from which second order rate constants *(k$_{obs}$)* were computed by the relation

$$k_{obs} = k'_{obs}[M(II)]$$ --------------- (1)

where k'$_{obs}$ is the pseudo first order rate constant.

Results and Discussion

Co (II)- 2-aminobenzoic acid Complexation

The kinetics of complexation of Co (II) – 2-aminobenzoic acid was found to be of first order in cobalt ion, which was taken in large excess over ligand to ensure pseudo-first order conditions and complete formation of mono complex only [8-9]. As protonated form of the ligand predominates in the pH range 2-4 (pKa$_1$ = 2.14, pKa$_2$ = 4.95) [19], the kinetic study of interaction has been made in the pH range 2.10-4.62 at ionic strength 0.1M KNO$_3$ and at temperatures 25, 30, 35 and 40± 0.05 °C, under the condition [Co (II)] >> [2-aminobenzoic acid]. Oscilloscope traces of voltage versus time were used to determine the values of pseudo-first order rate constants (k'$_{obs}$), and these were further utilized to evaluate the values of second order rate constants (k$_{obs}$), using equation (i). These rate constants are tabulated in Table 1.

Table 1: First order and Second order rate constants for the complexation of Co (II) with 2-aminobenzoic acid at different pH's and temperatures I = 0.10 M KNO$_3$
[Co (II)] = 1.66 x 10^{-2} M
[2-aminobenzoic acid] = 1.66 x 10^{-3} M

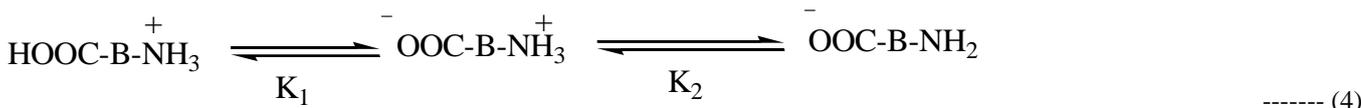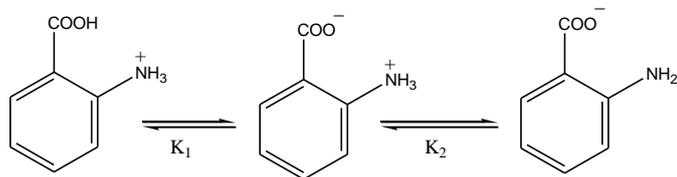| Temp. (±0.05 °C)	pH	k'$_{obs}$ x 10^2(s^{-1})	k$_{obs}$ x 10^{-1}(M^{-1}s^{-1})	Temp. (±0.05 °C)	pH	k'$_{obs}$10^2(s^{-1})	k$_{obs}$10^{-1}(M^{-1}s^{-1})
25	2.10	7.05	4.25	35	2.10	50.9	30.7
25	2.58	7.65	4.61	35	2.71	60.6	36.5
25	3.38	8.10	4.88	35	3.28	78.3	47.2
25	3.66	41.9	25.3	35	3.70	198	119
25	4.03	69.3	41.8	35	4.10	322	194
25	4.28	117	70.5	35	4.38	413	249
25	4.59	164	98.7	35	4.61	493	297
30	2.11	20.0	12.1	40	2.10	103	62.3
30	2.56	26.9	16.2	40	2.71	110	66.5
30	3.38	31.0	18.7	40	3.22	131	78.8
30	3.70	86.7	52.2	40	3.68	287	173
30	3.98	127	76.7	40	4.03	429	259
30	4.30	201	121	40	4.14	526	317
30	4.63	256	154	40	4.62	662	399

The rate equation for Co (II) – 2-aminobenzoic acid interaction can be written as

Rate = -d/dt[Co (II)]

= -d/dt[2-aminobenzoic acid]

= k_{obs} [2-aminobenzoic acid] [Co (II)]   ------ (2)

= k'_{obs} [2-aminobenzoic acid]   ------ (3)

Where $k'_{obs}= k_{obs}$ [Co (II)]

The dissociation equilibria of 2-aminobenzoic acid can be represented as

$$HOOC\text{-}B\text{-}\overset{+}{N}H_3 \underset{K_1}{\rightleftharpoons} {}^{-}OOC\text{-}B\text{-}\overset{+}{N}H_3 \underset{K_2}{\rightleftharpoons} {}^{-}OOC\text{-}B\text{-}NH_2$$

       ------- (4)

From equation (4), equation (3) reduces to

$$Rate = k'_{obs} \left\{ \left[HOOC\text{-}B\text{-}\overset{+}{N}H_3 \right] + \left[{}^{-}OOC\text{-}B\text{-}\overset{+}{N}H_3 \right] \left[{}^{-}OOC\text{-}B\text{-}NH_2 \right] \right\}$$

       ------- (5)

Where $HOOC\text{-}B\text{-}\overset{+}{N}H_3$, ${}^{-}OOC\text{-}B\text{-}\overset{+}{N}H_3$ and ${}^{-}OOC\text{-}B\text{-}NH_2$ represent the diprotonated, monoprotonated and deprotonated form of the ligand respectively. If it is assumed that only two forms i.e., monoprotonated and deprotonated form of the ligand participate in the reaction according to scheme given by Malhotra and Sharma [10-13], then the plots of $k_{obs} \{1 + K_3 / [H^+]\}$ versus $[H^+]^{-1}$ should be linear. However, these plots at 25, 30, 35 and 40±0.05 °C were found to be nonlinear (Fig 1).
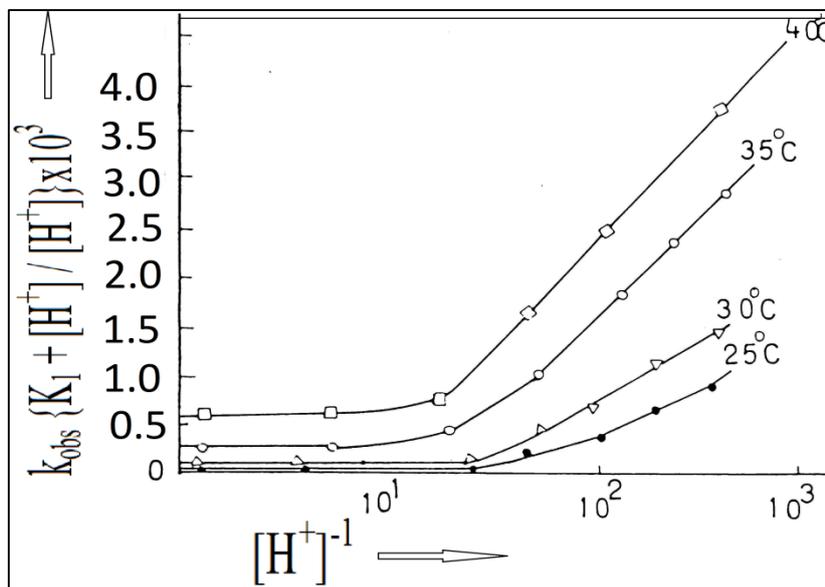
Fig 1: Variation of $k_{obs} \{1 + K_3 / [H^+]$ versus $[H^+]^{-1}$ for Co (II) 2-aminobenzoic acidinteraction at different temperatures

The rate equation for Co (II) – 2-aminobenzoic acid interaction can be written as

Rate   = -d/dt[Co (II)]

       = -d/dt[2-aminobenzoic acid]

       = k_{obs} [Co (II)] [2-aminobenzoic acid]   ----------------(2)

= k'_{obs} [2-aminobenzoic acid]   --------------- (3)

Where $k'_{obs}= k_{obs}$ [Co (II)]

The interaction of monoprotonated and deprotonated forms of the ligand was visualised by earlier workers [7-9] through

$$LH^+ \quad + \quad M^{2+} \longrightarrow ML^{2+} \quad + \quad H^+$$
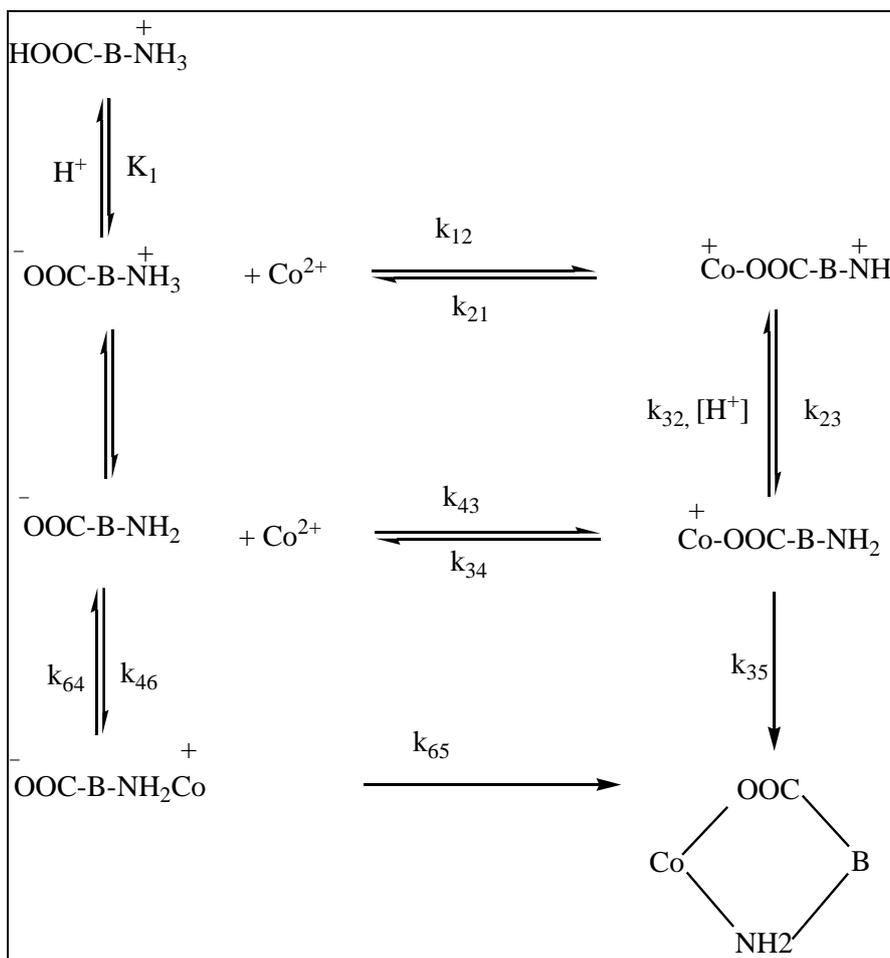
$$H^+ \Updownarrow K_1$$

$$L \quad + \quad M^{2+} \longrightarrow ML^{2+}$$
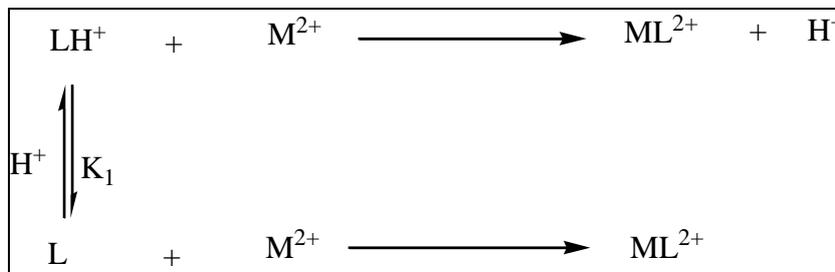
Scheme 1

According to Scheme 1, the plots of k_{obs} {K_1 + [H+]} / [H+] versus [H+]$^{-1}$ should be a straight lines. These plots at 25, 30, 35 and 40 °C, shown in Fig 1 were found to be non-linear. It is observed that curves become non-linear at high pH. Thus it is obvious that complexation of Co (II) by 2 - aminobenzoic acid cannot be explained by Scheme 1. This scheme was therefore modified (Scheme 2) to give the best fit with the experimental data.

The following scheme 2 for complexation of Co (II) with 2-aminobenzoic acid, which could explain non linearity of the curves was suggested:

$$HOOC\text{-}B\text{-}\overset{+}{N}H_3$$

$$H^+ \Updownarrow K_1$$

$$^-OOC\text{-}B\text{-}\overset{+}{N}H_3 \quad + Co^{2+} \overset{k_{12}}{\underset{k_{21}}{\rightleftharpoons}} \overset{+}{C}o\text{-}OOC\text{-}B\text{-}\overset{+}{N}H_3$$

$$k_{32,}[H^+] \Updownarrow k_{23}$$

$$^-OOC\text{-}B\text{-}NH_2 \quad + Co^{2+} \overset{k_{43}}{\underset{k_{34}}{\rightleftharpoons}} \overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2$$

$$k_{64} \Updownarrow k_{46} \qquad\qquad k_{35} \downarrow$$

$$^-OOC\text{-}B\text{-}NH_2\overset{+}{C}o \overset{k_{65}}{\longrightarrow}$$

Co diamond OOC / B / NH2

Scheme 2

The rate from scheme 2 can be given as

$$\text{Rate} = \quad k_{35} \left[\text{M-OOC-B-}\overset{+}{N}H_2 \right] + k_{65} \left[^-\text{OOC-B-}NH_2\overset{+}{M} \right]$$

\------------ (5)

Steady state approximations for non-chelated species

$$\left[\overset{+}{C}o\text{-OOC-B-}\overset{+}{N}H_3 \right], \left[\overset{+}{C}o\text{-OOC-B-}NH_2 \right]_{\text{and}} \left[^-\text{OOC-B-}NH_2\overset{+}{C}o \right]_{\text{can be given as}}$$

$$\frac{d}{dt}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}\overset{+}{N}H_3\right] = k_{12}\left[\overset{-}{}OOC\text{-}B\text{-}\overset{+}{N}H_3\right]\left[Co^{2+}\right] + k_{32}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2\right]\left[H^+\right]$$

$$- k_{21}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}\overset{+}{N}H_3\right] - k_{23}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}\overset{+}{N}H_3\right] = 0 \quad \text{---------- (6)}$$

$$\frac{d}{dt}\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\text{-}\overset{+}{C}o\right] = k_{46}\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\right]\left[Co^{2+}\right] - k_{64}\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\overset{+}{C}o\right]$$

$$- k_{65}\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\overset{+}{C}o\right] = 0 \quad \text{---------- (7)}$$

$$\frac{d}{dt}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2\right] = k_{43}\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\right]\left[Co^{2+}\right] + k_{23}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}\overset{+}{N}H_3\right]$$

$$- k_{32}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2\right]\left[H^+\right] - k_{35}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2\right]$$

$$- k_{34}\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2\right] = 0 \quad \text{---------- (8)}$$

Using equations 6, 7 and 8, it can be shown that

$$\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\overset{+}{C}o\right] = k_{46}\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\right]\left[Co^{2+}\right] / (k_{64} + k_{65}) \quad \text{---------- (9)}$$

$$\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2\right] = \frac{(k_{21} + k_{23}) k_{43}\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\right]\left[Co^{2+}\right] + k_{23} k_{12}\left[\overset{-}{}OOC\text{-}B\text{-}\overset{+}{N}H_3\right]}{(k_{34} + k_{35})(k_{21} + k_{23}) + k_{21} k_{32}[H^+]} \quad \text{---------- (10)}$$

Substituting the value of $\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\right]$ and $\left[\overset{-}{}OOC\text{-}B\text{-}\overset{+}{N}H_3\right]$ from equation 4,

$$\left[\overset{-}{}OOC\text{-}B\text{-}\overset{+}{N}H_3\right] = K_1\left[HOOC\text{-}B\text{-}\overset{+}{N}H_3\right] / [H^+] \quad \text{---------- (11)}$$

$$\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\right] = K_1 K_2\left[HOOC\text{-}B\text{-}\overset{+}{N}H_3\right] / [H^+]^2 \quad \text{---------- (12)}$$

We get equation 13

$$\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\overset{+}{C}o\right] = k_{46}K_1 K_2\left[HOOC\text{-}B\text{-}\overset{+}{N}H_3\right]\left[Co^{2+}\right] / (k_{64} + k_{65})[H^+]$$

$$\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2\right] = \frac{(k_{21} + k_{23}) k_{43} K_1 K_2 + k_{23}k_{12}K_1[H^+]}{(k_{34} + k_{35})(k_{21} + k_{23}) + k_{21} k_{32}[H^+]} \times \frac{\left[HOOC\text{-}B\text{-}\overset{+}{N}H_3\right]\left[Co^{2+}\right]}{[H^+]^2} \quad \text{-------- (13)}$$

Substituting for $\left[\overset{-}{}OOC\text{-}B\text{-}NH_2\overset{+}{C}o\right]$ and $\left[\overset{+}{C}o\text{-}OOC\text{-}B\text{-}NH_2\right]$ in equation (5), the rate law becomes:

$$\text{Rate} = \left\{\frac{k_{35}(k_{21} + k_{23}) k_{43} K_1 K_2 + k_{23}k_{12}K_1[H^+]}{(k_{34} + k_{35})(k_{21} + k_{23}) + k_{21} k_{32}[H^+]} + \frac{k_{46}k_{65}K_1 K_2}{k_{64} + k_{65}}\right\} \times \frac{\left[HOOC\text{-}B\text{-}\overset{+}{N}H_3\right]\left[Co^{2+}\right]}{[H^+]^2} \quad \text{-------- (14)}$$

The expected behaviour of the reaction of Co (II) and 2-aminobenzoic acid could be best described by using limiting forms of equation (14). If the reaction goes to completion and at high pH, we can make the following assumptions:
$k_{23} \gg k_{21}$, $k_{65} > k_{64}$ and $k_{35} > k_{34}$
Equation 14, after rearrangement gives:

$$\text{Rate} = \left\{\frac{k_{43} K_1 K_2 + k_{12}K_1[H^+] + k_{46}K_1 K_2 + k_{46}K_1 K_2 k_{21}k_{32}[H^+]/k_{23}k_{35}}{1 + k_{21} k_{32}[H^+] / k_{23}k_{35}}\right\} \times \frac{\left[HOOC\text{-}B\text{-}\overset{+}{N}H_3\right]\left[Co^{2+}\right]}{[H^+]^2} \quad \text{------- (15)}$$

Since the product K_1K_2 is very small and k_{23} and k_{35} are very large, therefore, the term in equation (15) can be ignored under our experimental conditions. The final form of the equation becomes,

$$\text{Rate} = \left\{ \frac{(k_{43} + k_{46})K_1K_2 + k_{12}K_1[H^+]}{1 + k_{21}\,k_{32}[H^+]\,/\,k_{23}k_{35}} \right\} \times \frac{\left[HOOC\text{-}B\text{-}\overset{+}{N}H_3 \right]\left[Co^{2+} \right]}{[H^+]^2} \qquad \text{---------------- (16)}$$

For Co (II) - 2 - aminobenzoic acid complexation reaction equation 2 can be written as

$$\text{Rate} = k_{obs} \left\{ [H^+]^2 + K_1[H^+] + K_1K_2 \right\} \frac{\left[HOOC\text{-}B\text{-}\overset{+}{N}H_3 \right]\left[Co^{2+} \right]}{[H^+]^2} \qquad \text{---------------- (17)}$$

On comparing equations (16) and (17) we get equation (18)

$$k_{obs}\left\{ [H^+]^2 + K_1[H^+] + K_1K_2 \right\} = \left\{ \frac{(k_{43} + k_{46})K_2 + k_{12}[H^+]}{1 + k_{21}\,k_{32}[H^+]\,/\,k_{23}k_{35}} \right\} K_1 \qquad \text{---------------- (18)}$$

$$k_{obs} = \left\{ \frac{(k_{43} + k_{46})K_2 + k_{12}[H^+]}{1 + k_{21}\,k_{32}[H^+]\,/\,k_{23}k_{35}} \right\} \times \frac{K_1}{\left\{ [H^+]^2 + K_1[H^+] + K_1K_2 \right\}} \qquad \text{---------------- (19)}$$

Equation (19) can be rearranged to give equation (20)

$$k_{obs} = \frac{A + B[H^+]}{C[H^+] + 1} \times \frac{K_1}{\left\{ [H^+]^2 + K_1[H^+] + K_1K_2 \right\}} \qquad \text{-------------- (20)}$$

Where
A = $(k_{43} + k_{46})\, K_2$ -------------- (21)
B = k_{12} -------------- (22)
C = $k_{21}\,k_{32}\,/\,k_{23}\,k_{35}$ -------------- (23)

In order to calculate the values of A, B and C a non-linear least-square analysis was used. The values of A, B and C at 25, 30, 35 and 40 °C are given in Table 2. Also from Scheme 2, K_{23} may be defined as

$$K_{23} = k_{23}/k_{32} = \frac{\left[\overset{+}{Co}\text{-}OOC\text{-}B\text{-}NH_2 \right]\left[H^+ \right]}{\left[\overset{+}{Co}\text{-}OOC\text{-}B\text{-}\overset{+}{N}H_3 \right]} \qquad \text{-------------- (24)}$$

Therefore, C can be written as

C = $k_{21}\,/\,k_{23}k_{35}$ -------------- (25)

but it is known from the literature and also clear from Scheme 2, that

$$k_{43}/k_{34} = k_{12}\,K_{23}\,/\,k_{21}\,K_2 \qquad \text{-------------- (26)}$$

From equations (25) and (26), C can be written as,

C = $k_{12}\,k_{34}\,/\,K_2\,k_{43}\,k_{35}$ ------------ (27)
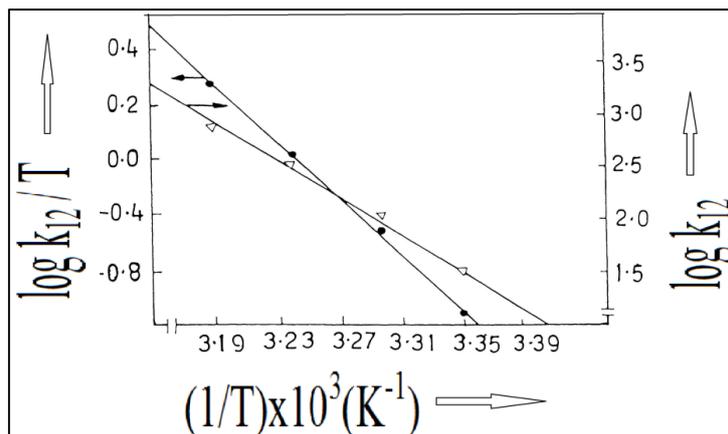
Using values of A, B and C from Table 2, the values of k_{12} and $(k_{43} + k_{46})$ and $k_{43}k_{35}\,/\,k_{34}$ were obtained. These values are given in Table 3. From Table 3, it is difficult to infer which of the two rate constants, k_{43} or k_{46} is larger. But from Scheme 2, it can be predicted that k_{43} is larger than k_{46} due to strong electrostatic attraction between negatively charged oxygen and positively charged Co (II) ion. Values of energies of activation corresponding to specific rate constants k_{12} and $(k_{43} + k_{46})$ were calculated from linear plot of log k versus 1 / T and those of entropies and enthalpies of activation corresponding to k_{12} and $(k_43 + k_{46})$ were calculated from linear plot of log k/T versus l/T (Fig.2 and 3). These values are given in Table 3

**Table 2:** Values of A, B and C for the complexation of Co (II) with 2-aminobenzoic acid

Temp.($\pm$ 0.05 °C)	A (s^{-1})	B ($M^{-1}s^{-1}$)	C (M^{-1})
25	$3.90X10^{-2} \pm 0.04$	31.6 ± 0.9	65.4 ± 1.4
30	$6.08X10^{-2} \pm 0.05$	169 ± 1.5	23.1 ± 0.6
35	$1.39X10^{-1} \pm 0.07$	322 ± 3.7	48.2 ± 0.8
40	$2.10X10^{-1} \pm 0.2$	596 ± 5.7	55.9 ± 1.8

Table 3: Values of $(k_{43} + k_{46})$, k_{12} and $k_{43}k_{35} / k_{34}$ for the complexation of Co (II) with 2-aminobenzoic acid

Temp.($\pm$ 0.05 °C)	$(k_{43} + k_{46})x10^{-2}$ ($M^{-1}s^{-1}$)	$k_{12} x10^{-1}$ ($M^{-1}s^{-1}$)	$k_{43}k_{35} / k_{34} x10^{-5}$ ($M^{-1}s^{-1}$)
25	24.0	3.18	0.300
30	37.5	16.9	4.12
35	85.8	32.2	4.51
40	130	59.6	6.57

Fig 2: Variation of log k_{12} and log k_{12} / T versus (1/T) for the interaction of Co (II)- 2-aminobenzoic acid
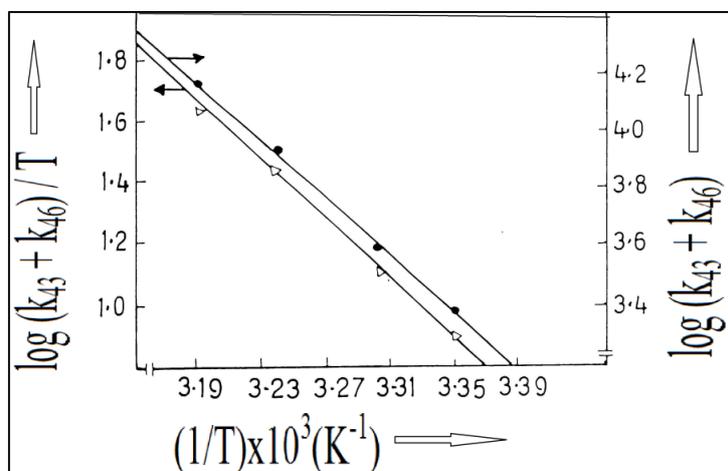
Fig 3: Variation of log $(k_{43}+ k_{46})$ and log $(k_{43}+ k_{46)}$ / T versus (1/T) for the interaction of Co (II)- 2-aminobenzoic acid

The high values of $\Delta H^{\#}$ corresponding to k_{12} step confirm that the monoprotonated form of 2-aminobenzoic acid is less reactive whereas low value of $\Delta H^{\#}$ corresponding to k_{43} and k_{46} supports the high reactivity of deprotonated form of 2-aminobenzoic acid. The low value of entropy corresponding to k_{43} and k_{46} can be attributed to the fact that the transition state for this complex is highly charged and clearly shows that the reaction is between two oppositely charged ions (Table 4).

Table 4: Values of activation parameters corresponding to k_{43} and k_{46} for the complexation of Co (II) with 2-aminobenzoic acid
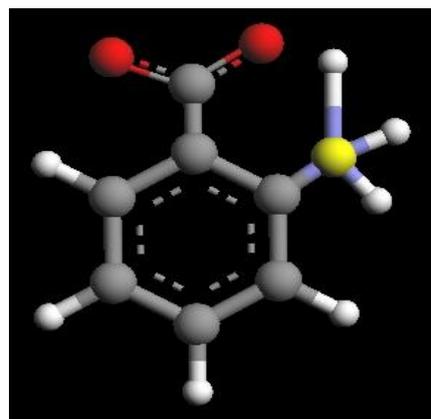
	$(k_{43} + k_{46})$	k_{12}
$\Delta H^{\#}$($kJmol^{-1}$)	161 ± 2.4	202 ± 3.3
$\Delta E^{\#}$($kJmol^{-1}$)	87.3 ± 2.3	160 ± 3.6
$\Delta S^{\#}$($JK^{-1}mol^{-1}$)	329 ± 4.5	476 ± 6.5

Mechanism
Based on Scheme 2, following mechanism for the complexation of Co (II) with 2-aminobenzoic acidhas been suggested
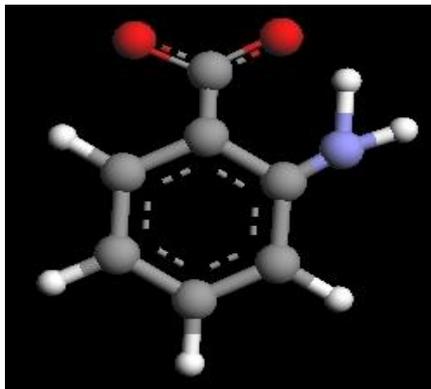
Fig 4: Deprotonated form of 2-aminobenzoic acid
Final Geom Energy = -21196.13 kcal/mol
Heat of Formation = 30679.94 kcal/mol

Fig 5: Monorotonated form of 2-aminobenzoic acid
Final Geom Energy = -38891.63 kcal/mol
Heat of Formation = -54.43 kcal/mol

The deprotonated form react with Co (II) in two ways (i) Ring formation via nitrogen and (ii) Ring formation via oxygen. It is evident from Table 3 that deprotonated form will react more rapidly with Co (II) as compared to the monoprotonated form. Due to strong electrostatic interaction between the positive charge of Co (II) and negative charge on the oxygen of 2-aminobenzoic acid, it is inferred that k_{46} and k_{43} is greater than k_{12}. The value of activation parameters corresponding to k_{46} and k_{43} further confirm that the deprotonated form is more reactive than the zwitterionic form of the ligand. This mechanism is further confirmed by the values of energy of activation and entropy of activation. This mechanism is further confirmed from the molecular modelling method in which the energy as well as the heat of formation of the zwitterionic form and deprotonated form has been calculated [14-18]. Values of the energies as well as heat of formation were calculated after optimizing the geometry of the molecules. These values are given in Fig 4 and 5. It has been found that the deprotonated form is more reactive than the protonated form.

References
1. Eigen M, Wilkins RG. Adv. Chern. Ser. No. 1965; 49(55).
2. Wilkins RG. Acc. Chem. Res. 1970; 3:408.
3. Siegel H, McCornik DB, J Am. Chem. Soc. 1971; 43:2041.
4. Molinaro FS, Little RG, Jbers JA. J Am. Chem. Soc. 1977; 99:5628.
5. Eklund H, *et al*., J Mol. Bio. 1979; 1027:27.
6. Fast Reaction in Solution, EF. Caldin, John Wiley and Sons, Inc. New York, 1964.
7. Mechanisms of Inorganic Reactions, F. Basolo and RG. Pearson IInd Ed. John Wiley and Sons. New York, 1967.
8. Voss RH, Jordan RB. J Am. Chem. Soc. 1976; 98:2173.
9. Letter JE, Jordan RB. J Am. Chem. Soc. 1975; 97:2381.
10. Malhotra HC, Sharma GC. Gazz. Chim. Ital. 1988; 118:323.
11. Malhotra HC. Jai Prakash, Sharma GC. J Ind. Chern. Soc. 1986; LX(III):1045.
12. Malhotra HC, Yogeshwar Sharma, Jain AK. J Ind. Chem. Soc. 1990; 67:192.
13. Malhotra HC, Jain AK. J Ind. Chem. Soc. 1990; 67:365.
14. Thompson MA, Zerner MC. J Am. Chem. Soc. 1991; 113:8210.
15. Mark A, Thompson, Eric D. Glendening, and David Feller. J Phys. Chem. 1994; 98:10465-10476.
16. Mark A, Thompson, Gregory K. Schenter J Phys. Chem. 1995; 99:6374-6386.
17. Mark A, Thompson J Phys. Chem. 1996; 100:14492-14507.
18. http/www.arguslab.com/arguslab.com/ArgusLab.html
19. http://www.sas.upenn.edu/~marisa/documents/pkatables.pdf