



## A kinetic study on the complexation of Cu(II) with $\alpha$ -Aminobenzoic acid

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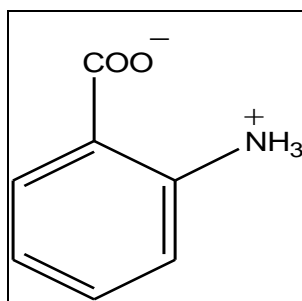
### Abstract

The kinetics of complexation of Cu(II) with  $\alpha$ -Aminobenzoic acid has been investigated at 25, 30, 35 and  $40 \pm 0.05^\circ\text{C}$  in the pH range 2.12-4.65 using Aminco Morrow Stopped Flow Spectrophotometer. The anionic form of  $\alpha$ -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. The values of activation parameters corresponding to stepwise rate constants have also been evaluated. 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, stepwise rate constants activation parameters, energy of the molecule, heat of formation

### Introduction

$\alpha$ -Aminobenzoic acid (2-aminobenzoic acid or anthranilic acid) is used in the production of azo dyes and saccharin. 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. It is also used in preparing perfumes to imitate jasmine and orange smell, in pharmaceuticals as diuretics e.g. furosemide) and UV-absorber as well as mold inhibitors in soy sauce.  $\alpha$ -Aminobenzoic acid is an important B - complex factor. 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.



( $\alpha$ -Aminobenzoic acid) Zwitterion

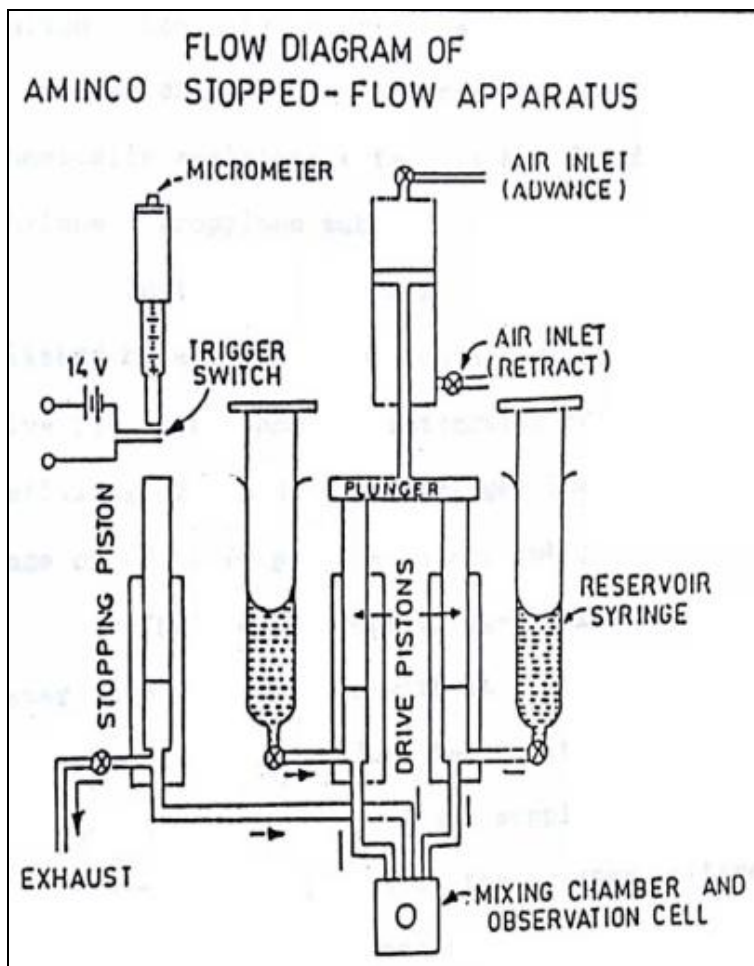
It can also be assumed that due to intramolecular hydrogen bonding between the protonated amino group and carboxylate group of the zwitterion, the zwitterion species should be unreactive towards Co (II). In order to check the reactivity of zwitterion and to know the different binding steps, their corresponding rate constants and activation parameters, kinetics of Co(II) with 2 aminobenzoic acid was initiated. The kinetics of complexation of metal ions Cu(II) by  $\alpha$ -Aminobenzoic acid would no doubt give important information regarding the types of interaction of these ions with  $\alpha$ -Aminobenzoic acid and the clearance of  $\alpha$ -Aminobenzoic acid or metal ions in the form of metal – ligand complex through the animal body<sup>1-7</sup>. 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 Cu(II) with  $\alpha$ -Aminobenzoic acid. Such investigations are further desired for determining some important parameters, e.g. activation parameters corresponding to the interaction of various reactive forms of the  $\alpha$ -Aminobenzoic acid, energy of the molecule and heat of formation of the molecule.

### Materials and Methods

$\alpha$ -Aminobenzoic acid(B.D.H.),  $\text{KNO}_3$  (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 ( $\sim 0.05$  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.,  $[M(II)] \gg [\alpha\text{-Aminobenzoic acid}]$  ( $M = \text{Cu}$ ) at 620nm by pH indicator method<sup>2</sup>. The driving syringes and reaction chamber of the stopped flow assembly were thermostated at 25, 30, 35 and  $40 \pm 0.05^\circ\text{C}$  by German(NBE) thermostat. Metal ions and ligand were stored in driving syringes. These two solutions were pushed into the observation cell by pneumatic action of the plunger. The observation cell is an integrated part of Aminco Morrow spectrophotometer and the changes brought about by the reacting solutions are monitored directly through a photo cell and recorded on storage oscilloscope.



Cobalt nitrate,  $10^{-2}\text{M}$ , buffer  $10^{-2}\text{M}$  Lutidine and,  $\mu = 0.1 \text{ M KNO}_3$  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

$$k_{obs} = k'_{obs}[\text{Cu(II)}] \quad (1)$$

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

## Results and Discussion

### Cu(II)- $\alpha$ -Aminobenzoic acid Complexation

The kinetics of complexation of Cu(II) –  $\alpha$ -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<sup>[8-9]</sup>. As protonated form of the ligand predominates in the pH range 2-4 ( $\text{pK}_{a1} = 2.14$ ,  $\text{pK}_{a2} = 4.95$ )<sup>[19]</sup>, the kinetic study of interaction has been made in the pH range 2.12-4.65 at ionic strength  $0.1\text{M KNO}_3$  and at temperatures 25, 30, 35 and  $40 \pm 0.05^\circ\text{C}$ , under the condition  $[\text{Cu(II)}] \gg [\alpha\text{-Aminobenzoic acid}]$ . 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 Cu(II) with  $\alpha$ -Aminobenzoic acid at different pH's and temperatures, I = 0.10 M KNO<sub>3</sub>, [Cu(II)] = 1.73 x 10<sup>-2</sup> M, [ $\alpha$ -Aminobenzoic acid] = 1.66 x 10<sup>-3</sup> M

Temp. ( $\pm 0.05^\circ\text{C}$ )	pH	$k'_{\text{obs}} \times 10^2 (\text{s}^{-1})$	$k_{\text{obs}} \times 10^{-1} (\text{M}^{-1} \text{s}^{-1})$	Temp. ( $\pm 0.05^\circ\text{C}$ )	pH	$k'_{\text{obs}} 10^2 (\text{s}^{-1})$	$k_{\text{obs}} 10^{-1} (\text{M}^{-1} \text{s}^{-1})$
25	2.12	1.45	8.361	35	2.18	9.92	57.34
25	2.59	1.58	9.143	35	2.74	12.4	71.82
25	3.36	1.67	9.628	35	3.27	15.9	92.16
25	3.68	8.38	48.42	35	3.69	40.3	232.8
25	4.02	13.8	79.74	35	4.08	65.5	378.3
25	4.27	23.6	136.7	35	4.37	84.0	485.6
25	4.58	32.8	189.6	35	4.62	99.2	573.2
30	2.13	4.12	23.80	40	2.20	20.5	118.2
30	2.58	5.11	29.56	40	2.68	22.4	129.3
30	3.37	6.13	35.43	40	3.21	25.7	148.5
30	3.69	17.0	98.49	40	3.65	57.5	332.4
30	3.99	25.1	145.3	40	3.98	95.4	551.6
30	4.28	41.3	238.8	40	4.10	106	610.9
30	4.62	52.3	302.5	40	4.65	152	878.3

The rate equation for Cu(II) –  $\alpha$ -Aminobenzoic acid interaction can be written as

$$\text{Rate} = -d/dt[\text{Cu(II)}]$$

$$= -d/dt[\alpha\text{-Aminobenzoic acid}]$$

$$= k_{\text{obs}} [\alpha\text{-Aminobenzoic acid}] [\text{Cu(II)}]$$

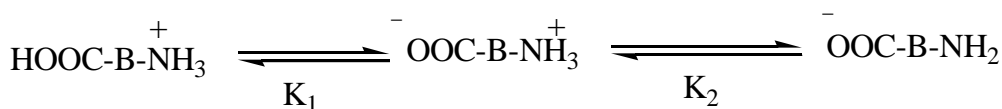
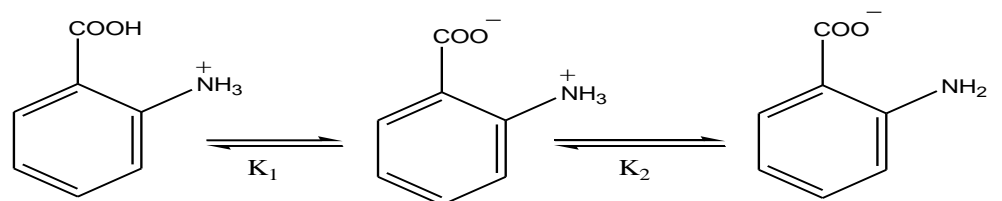
$$= k'_{\text{obs}} [\alpha\text{-Aminobenzoic acid}]$$

$$\text{Where } k'_{\text{obs}} = k_{\text{obs}} [\text{Cu(II)}]$$

(2)

(3)

The dissociation equilibria of  $\alpha$ -Aminobenzoic acid can be represented as



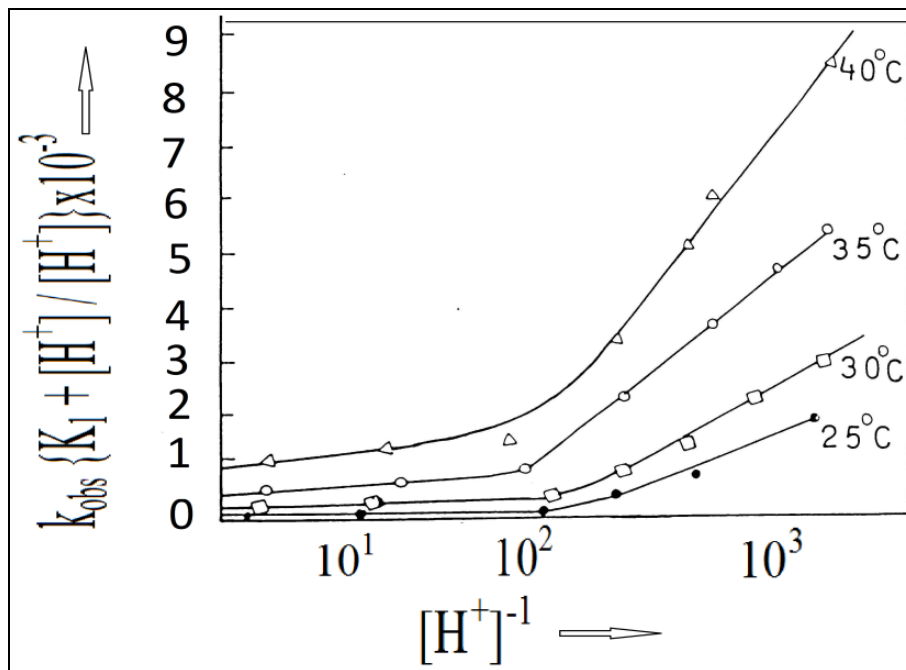
(4)

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

$$\text{Rate} = k'_{\text{obs}} \left\{ \left[ \text{HOOC-B-NH}_3^+ \right] + \left[ \text{OOC-B-NH}_3^+ \right] \left[ \text{OOC-B-NH}_2^- \right] \right\}$$

(5)

Where  $\text{HOOC-B-NH}_3^+$ ,  $\text{OOC-B-NH}_3^+$  and  $\text{OOC-B-NH}_2^-$  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<sup>10-13</sup>, then the plots of  $k_{\text{obs}} \{1 + K_3 / [\text{H}^+]\}$  versus  $[\text{H}^+]^{-1}$  should be linear. However, these plots at 25, 30, 35 and 40 $\pm$ 0.05  $^\circ\text{C}$  were found to be nonlinear (Fig 1).



**Fig 1:** Variation of  $k_{obs} \{ 1 + K_3 / [H^+] \}$  versus  $[H^+]^{-1}$  for Cu(II)  $\alpha$ -Aminobenzoic acid interaction at different temperatures

The rate equation for Cu(II) –  $\alpha$ -Aminobenzoic acid interaction can be written as

$$\text{Rate} = -d/dt[\text{Cu(II)}]$$

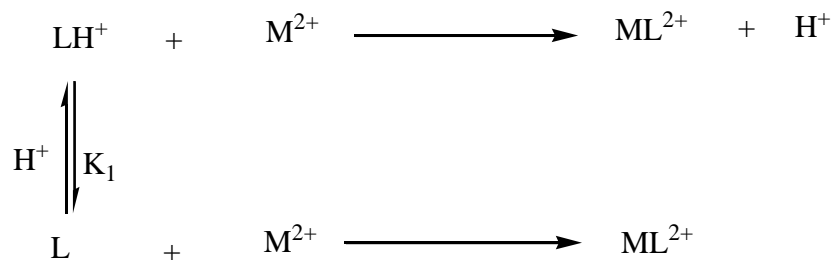
$$= -d/dt[\alpha\text{-Aminobenzoic acid}]$$

$$= k_{obs} [\text{Cu(II)}] [\alpha\text{-Aminobenzoic acid}] \tag{2}$$

$$= k'_{obs} [\alpha\text{-Aminobenzoic acid}] \tag{3}$$

Where  $k'_{obs} = k_{obs} [\text{Cu(II)}]$

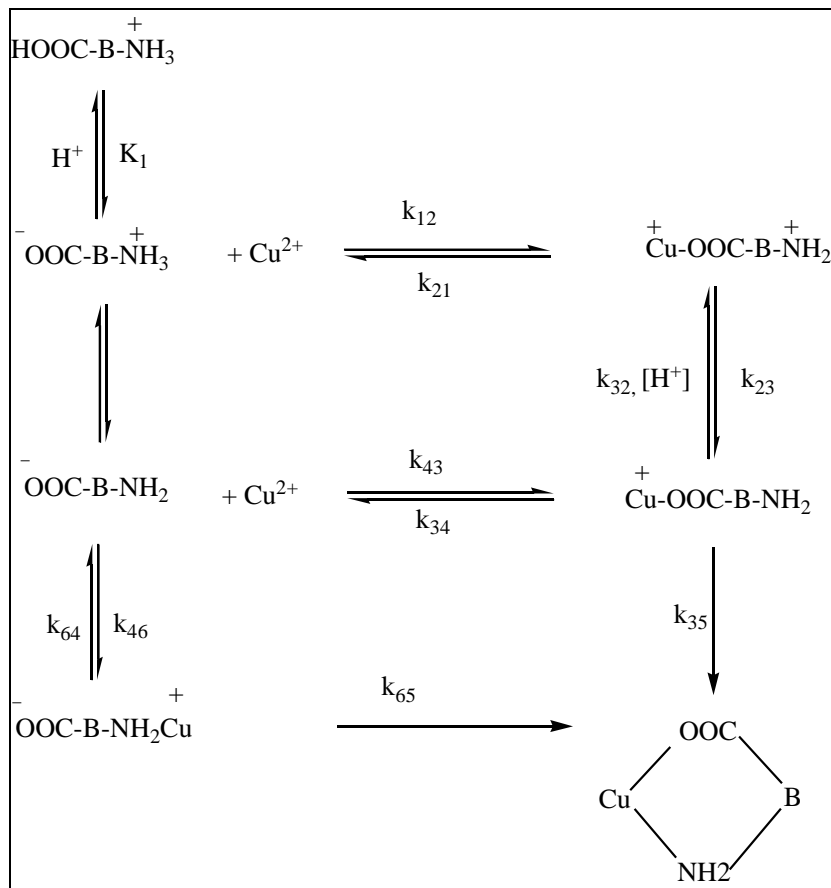
The interaction of monoprotonated and deprotonated forms of the ligand was visualised by earlier workers<sup>7-9</sup> through



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 Cu(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 Cu(II) with  $\alpha$ -Aminobenzoic acid, which could explain non linearity of the curves was suggested:



The rate from scheme 2 can be given as

$$\text{Rate} = k_{35} \left[ \text{Cu-OOC-B-NH}_2^+ \right] + k_{65} \left[ \text{OOC-B-NH}_2\text{Cu}^+ \right] \quad (5)$$

Steady state approximations for non-chelated species

$$\left[ \text{Cu-OOC-B-NH}_3^+ \right], \left[ \text{Cu-OOC-B-NH}_3^+ \right] \text{ and } \left[ \text{OOC-B-NH}_2\text{Cu}^+ \right] \text{ can be given as}$$

$$\begin{aligned} \frac{d}{dt} \left[ \text{Cu-OOC-B-NH}_3^+ \right] &= k_{12} \left[ \text{OOC-B-NH}_3^+ \right] \left[ \text{Cu}^{2+} \right] + k_{32} \left[ \text{Cu-OOC-B-NH}_2^+ \right] \left[ \text{H}^+ \right] \\ &\quad - k_{21} \left[ \text{Cu-OOC-B-NH}_3^+ \right] - k_{23} \left[ \text{Cu-OOC-B-NH}_2^+ \right] = 0 \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{d}{dt} \left[ \text{OOC-B-NH}_2\text{Cu}^+ \right] &= k_{46} \left[ \text{OOC-B-NH}_2^- \right] \left[ \text{Cu}^{2+} \right] - k_{64} \left[ \text{OOC-B-NH}_2\text{Cu}^+ \right] \\ &\quad - k_{65} \left[ \text{OOC-B-NH}_2\text{Cu}^+ \right] = 0 \end{aligned} \quad (7)$$

$$\begin{aligned}
 \frac{d}{dt} \left[ \overset{+}{\text{Cu-OOC-B-NH}_2} \right] &= k_{43} \left[ \overset{-}{\text{OOC-B-NH}_2} \right] \left[ \text{Cu}^{2+} \right] + k_{23} \left[ \overset{+}{\text{Cu-OOC-B-NH}_3} \right] \\
 &\quad - k_{32} \left[ \overset{+}{\text{Cu-OOC-B-NH}_2} \right] \left[ \text{H}^+ \right] - k_{35} \left[ \overset{+}{\text{Cu-OOC-B-NH}_2} \right] \\
 &\quad - k_{34} \left[ \overset{+}{\text{Cu-OOC-B-NH}_2} \right] = 0
 \end{aligned} \tag{8}$$

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

$$\left[ \overset{-}{\text{OOC-B-NH}_2\text{Cu}} \overset{+}{} \right] = k_{46} \left[ \overset{-}{\text{OOC-B-NH}_2} \right] \left[ \text{Cu}^{2+} \right] / (k_{64} + k_{65}) \tag{9}$$

$$\left[ \overset{+}{\text{Cu-OOC-B-NH}_2} \right] = \frac{(k_{21} + k_{23}) k_{43} \left[ \overset{-}{\text{OOC-B-NH}_2} \right] \left[ \text{Cu}^{2+} \right] + k_{23} k_{12} \left[ \overset{-}{\text{OOC-B-NH}_3} \right]}{(k_{34} + k_{35})(k_{21} + k_{23}) + k_{21} k_{32} [\text{H}^+]} \tag{10}$$

Substituting the value of  $\left[ \overset{-}{\text{OOC-B-NH}_2} \right]$  and  $\left[ \overset{-}{\text{OOC-B-NH}_3} \right]$  from equation 4,

$$\left[ \overset{-}{\text{OOC-B-NH}_3} \right] = K_1 \left[ \text{HOOC-B-NH}_3 \right] / [\text{H}^+] \tag{11}$$

$$\left[ \overset{-}{\text{OOC-B-NH}_2} \right] = K_1 K_2 \left[ \text{HOOC-B-NH}_3 \right] / [\text{H}^+]^2 \tag{12}$$

We get equation 13

$$\begin{aligned}
 \left[ \overset{-}{\text{OOC-B-NH}_2\text{Cu}} \overset{+}{} \right] &= k_{46} K_1 K_2 \left[ \text{HOOC-B-NH}_3 \right] \left[ \text{Cu}^{2+} \right] / (k_{64} + k_{65}) [\text{H}^+] \\
 \left[ \overset{+}{\text{Cu-OOC-B-NH}_2} \right] &= \frac{(k_{21} + k_{23}) k_{43} K_1 K_2 + k_{23} k_{12} K_1 [\text{H}^+]}{(k_{34} + k_{35}) (k_{21} + k_{23}) + k_{21} k_{32} [\text{H}^+]} \times \frac{\left[ \text{HOOC-B-NH}_3 \right] \left[ \text{Cu}^{2+} \right]}{[\text{H}^+]^2}
 \end{aligned} \tag{13}$$

Substituting for  $\left[ \overset{-}{\text{OOC-B-NH}_2\text{Cu}} \overset{+}{} \right]$  and  $\left[ \overset{+}{\text{Cu-OOC-B-NH}_2} \right]$  in equation (5), the rate law becomes:

$$\text{Rate} = \left\{ \frac{k_{35}(k_{21} + k_{23}) k_{43} K_1 K_2 + k_{23} k_{12} K_1 [\text{H}^+]}{(k_{34} + k_{35}) (k_{21} + k_{23}) + k_{21} k_{32} [\text{H}^+]} + \frac{k_{46} k_{65} K_1 K_2}{k_{64} + k_{65}} \right\} \times \frac{\left[ \text{HOOC-B-NH}_3 \right] \left[ \text{Cu}^{2+} \right]}{[\text{H}^+]^2} \tag{14}$$

The expected behaviour of the reaction of Cu(II) and  $\alpha$ -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:

$$\text{Rate} = \left\{ \frac{k_{43} K_1 K_2 + k_{12} K_1 [H^+] + k_{46} K_1 K_2 + k_{46} K_1 K_2 k_{21} k_{32} [H^+] / k_{23} k_{35}}{1 + k_{21} k_{32} [H^+] / k_{23} k_{35}} \right\} \times \frac{[HOOC-B-NH_3^+][Cu^{2+}]}{[H^+]^2} \quad (15)$$

Since the product  $K_1 K_2$  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,

$$\text{Rate} = \left\{ \frac{(k_{43} + k_{46}) K_1 K_2 + k_{12} K_1 [H^+]}{1 + k_{21} k_{32} [H^+] / k_{23} k_{35}} \right\} \times \frac{[HOOC-B-NH_3^+][Cu^{2+}]}{[H^+]^2} \quad (16)$$

For Cu(II) -  $\alpha$ -aminobenzoic acid complexation reaction equation 2 can be written as

$$\text{Rate} = k_{\text{obs}} \{ [H^+]^2 + K_1 [H^+] + K_1 K_2 \} \frac{[HOOC-B-NH_3^+][Cu^{2+}]}{[H^+]^2} \quad (17)$$

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

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

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

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

$$k_{\text{obs}} = \frac{A + B[H^+]}{C[H^+] + 1} \times \frac{K_1}{\{ [H^+]^2 + K_1 [H^+] + K_1 K_2 \}} \quad (20)$$

Where

$$A = (k_{43} + k_{46}) K_2 \quad (21)$$

$$B = k_{12} \quad (22)$$

$$C = k_{21} k_{32} / k_{23} k_{35} \quad (23)$$

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

$$K_{23} = k_{23} / k_{32} = \frac{[Cu-OOC-B-NH_2^+][H^+]}{[Cu-OOC-B-NH_3^+]} \quad (24)$$

Therefore, C can be written as

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

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

$$k_{43} / k_{34} = k_{12} K_{23} / k_{21} K_2 \quad (26)$$

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

$$C = k_{12} k_{34} / K_2 k_{43} k_{35} \quad (27)$$

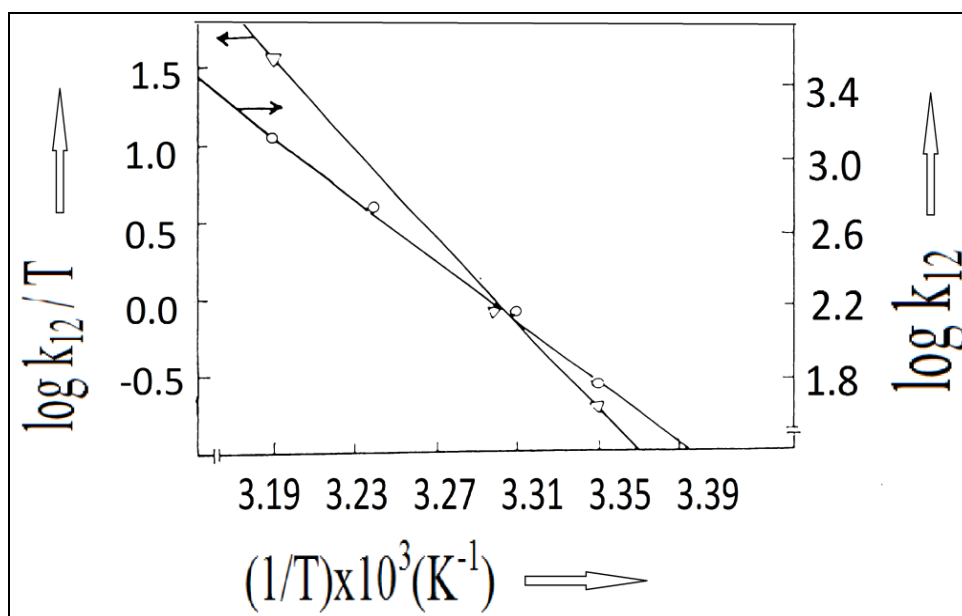
Using values of A, B and C from Table 2, the values of  $k_{12}$  and  $(k_{43} + k_{46})$  and  $k_{43}k_{35} / k_{34}$  were obtained. These values are given in Table 3. From Table 3, it is difficult to infer which of the two rate constants,  $k_{43}$  or  $k_{46}$  is larger. But from Scheme 2, it can be predicted that  $k_{43}$  is larger than  $k_{46}$  due to strong electrostatic attraction between negatively charged oxygen and positively charged Cu(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  $1/T$  ( Fig.2 and 3). These values are given in Table 3

**Table 2:** Values of A, B and C for the complexation of Cu(II) with  $\alpha$ -Aminobenzoic acid

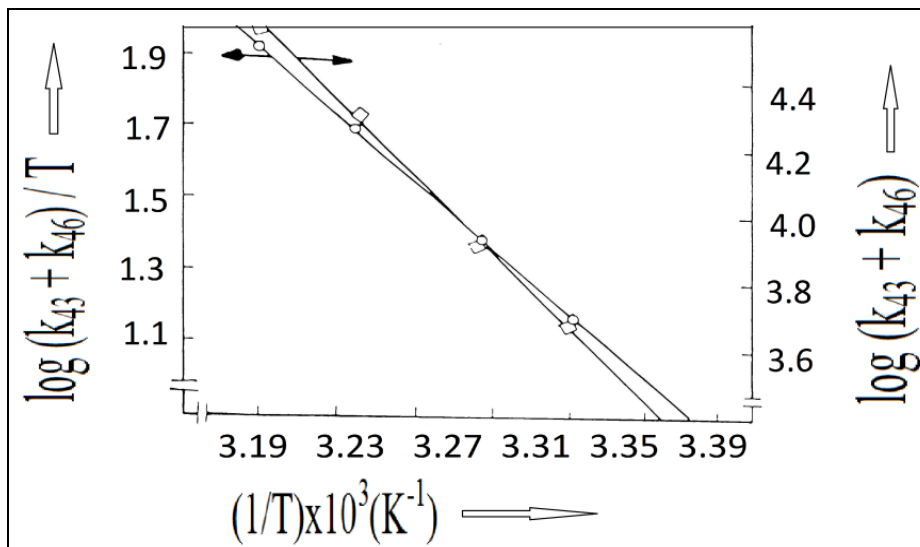
Temp.( $\pm 0.05^\circ\text{C}$ )	A $\times 10^2$ ( $\text{s}^{-1}$ )	B ( $\text{M}^{-1}\text{s}^{-1}$ )	C ( $\text{M}^{-1}$ )
25	$7.58 \pm 0.5$	$58.5 \pm 1.7$	$77.6 \pm 1.5$
30	$12.3 \pm 0.2$	$287 \pm 4.5$	$36.2 \pm 0.8$
35	$27.8 \pm 0.4$	$621 \pm 6.4$	$46.0 \pm 1.3$
40	$42.4 \pm 0.3$	$1158 \pm 12.4$	$57.9 \pm 1.7$

**Table 3:** Values of  $(k_{43} + k_{46})$ ,  $k_{12}$  and  $k_{43}k_{35} / k_{34}$  for the complexation of Cu(II) with  $\alpha$ -Aminobenzoic acid

Temp.( $\pm 0.05^\circ\text{C}$ )	$(k_{43} + k_{46}) \times 10^{-2}$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_{12} \times 10^{-1}$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_{43}k_{35} / k_{34} \times 10^{-5}$ ( $\text{M}^{-1}\text{s}^{-1}$ )
25	46.7	5.85	0.465
30	76.2	28.7	4.89
35	172	62.1	8.31
40	262	116	12.3



**Fig 2:** Variation of  $\log k_{12}$  and  $\log k_{12} / T$  versus  $(1/T)$  for the interaction of Cu(II)-  $\alpha$ -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 Cu(II)-  $\alpha$ -Aminobenzoic acid

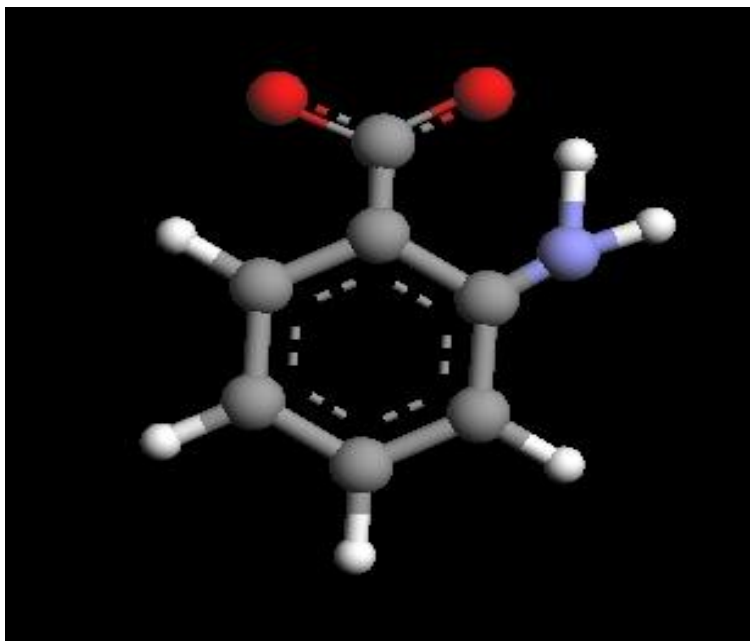
The high values of  $\Delta H^\ddagger$  corresponding to  $k_{12}$  step confirm that the monoprotonated form of  $\alpha$ -Aminobenzoic acid is less reactive whereas low value of  $\Delta H^\ddagger$  corresponding to  $k_{43}$  and  $k_{46}$  supports the high reactivity of deprotonated form of  $\alpha$ -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 Cu(II) with  $\alpha$ -Aminobenzoic acid

	$(k_{43} + k_{46})$	$k_{12}$
$\Delta H^\ddagger(\text{kJmol}^{-1})$	$86.1 \pm 2.3$	$269 \pm 2.5$
$\Delta E^\ddagger(\text{kJmol}^{-1})$	$95.7 \pm 1.8$	$154 \pm 2.3$
$\Delta S^\ddagger(\text{JK}^{-1}\text{mol}^{-1})$	$83.6 \pm 1.6$	$661 \pm 8.6$

### Mechanism

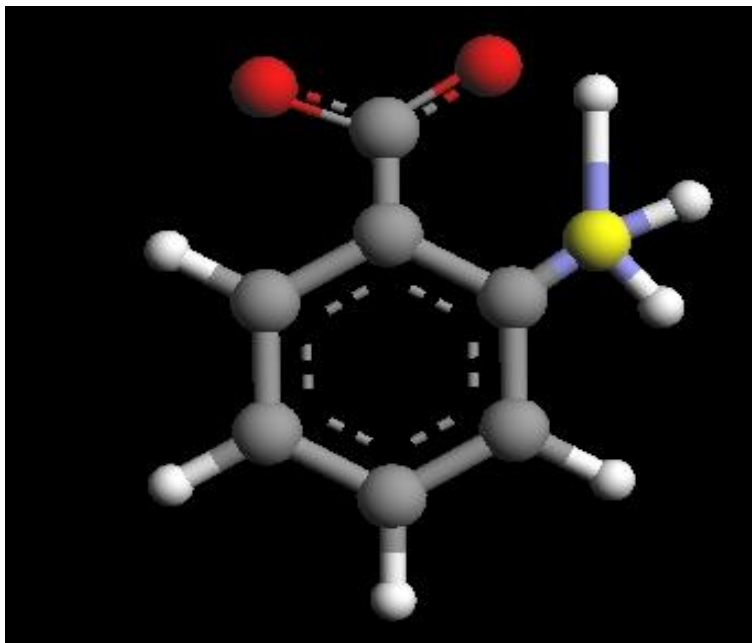
Based on Scheme 2, following mechanism for the complexation of Cu(II) with  $\alpha$ -Aminobenzoic acid has been suggested



**Fig 4:** Deprotonated form of  $\alpha$ -Aminobenzoic acid

Final Geometry Energy = -21196.13 kcal/mol

Heat of Formation = 30679.94 kcal/mol



**Fig 5:** Mono protonated form of  $\alpha$ -Aminobenzoic acid

Final Geometry Energy = -38891.63 kcal/mol

Heat of Formation = -54.43 kcal/mol

The deprotonated form react with Cu(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 Cu(II) as compared to the monoprotonated form. Due to strong electrostatic interaction between the positive charge of Cu(II) and negative charge on the oxygen of  $\alpha$ -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<sup>15-18</sup>. 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.

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