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Kinetics and mechanism of complexation of Co(II) with 4-aminobenzoic acid

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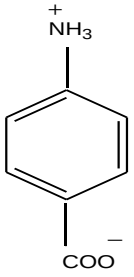
Abstract
Kinetic and mechanism of complexation of Co(II) with 4-aminobenzoic acid has been carried out under first order conditions as a function of pH and temperature. A reaction scheme consistent with the kinetic data has been proposed. The ionic strength was maintained at 0.1 M KNO_3. Kinetic results 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 overall rate constant has been resolved into stepwise rate constants. The suggested mechanism is confirmed by the calculation of activation parameters and water exchange rate constant. Deprotonated form of 4-aminobenzoic acid is more reactive and the protonated form interacts only to a small extent.

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

Introduction

4-aminobenzoic acid protects the skin against sunburn caused by ultraviolet radiation (UV, i. e. 290 - 320 nm). These rays inhibit DNA, RNA, protein synthesis and mitosis and cause release of prostaglandins, i.e. inflammation. It is also an intermediate in the synthesis of folate by bacteria, plants, and fungi. Many bacteria in the human intestinal tract such as *E. coli*, generate 4-aminobenzoic acid by the combined action of the enzymes 4-amino-4-deoxychorismate synthase and 4-amino-4-deoxychorismate lyase. It is also excreted in human urine in conjugated form with metal ions and in human faeces. The average concentration of aminobenzoic acid in human sweat is 0.2 micrograms per 100 mL. 4-aminobenzoic acid cures hypoprothrombinaemia produced in young rats by feeding sulphasuxidine. It stimulates the growth of the bacteria in the intestinal tract of humans and these then synthesise vitamin K necessary to restore the blood clotting mechanism to normal .Therefore, the kinetic study of metal ions by 4-aminobenzoic would no doubt give important information regarding type of interaction of polypeptide of glutamic acid to metal ions.

The structure of 4-aminobenzoic acid can be represented as:



(4-aminobenzoic acid) Zwitterion

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 4-aminobenzoic acid was initiated. The kinetics of complexation of metal ions Co(II) by 4-aminobenzoic acid would no doubt give important information regarding the types of interaction of these ions with 4-aminobenzoic acid and the clearance of 4-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 4-aminobenzoic acid . Such investigations are further desired for determining some important parameters, e.g. binding steps, rate constants corresponding to the binding steps K_{os} (outer sphere complex formation constant), k_o (Rate constant of water exchange) and activation parameters corresponding to the interaction of various reactive forms of the 4-aminobenzoic acid .

Materials and Methods

4-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., [Co(II)] >>[4-aminobenzoic acid] at 620nm by pH indicator method. The total transmittance change was kept small using linear log photometer so that relative voltage change could be observed on the oscilloscope. Cobalt nitrate, 10^{-3}M, buffer 10^{-2}M Lutidine and, μ= 0.l 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

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

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

Results and Discussion

Co(II)- 4-aminobenzoic acid Complexation

The kinetics of complexation of Co(II)–4-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[8-10]. As protonated form of the ligand predominates in the pH range 2-5 (pKa_1 = 2.50, pKa_2 = 4.87)[11], the kinetic study of interaction has been made in the pH range 3.04 - 4.15 at ionic strength 0.1M KNO_3 and at temperatures 25, 30, 35 and 40± 0.05°C, under the condition [Co(II)] >> [4-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 4-aminobenzoic acid at different pH's and temperatures
I = 0.10 M KNO_3 [Co(II)] = 5.94 x 10^{-2} M [4-aminobenzoic acid] = 4.86 x 10^{-3} M

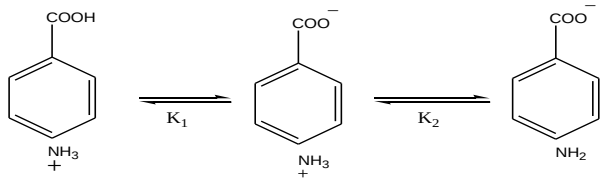
Temp. (±0.05°C)	pH	k'obs (s-1)	kobs x 10-1 (M-1 s-1)	Temp. (±0.05°C)	pH	k'obs (s-1)	kobs10-1 (M-1 s-1)
25	3.04	4.73	7.96	35	3.04	14.5	24.4
25	3.21	5.6	9.43	35	3.28	20	33.7
25	3.48	12.1	20.3	35	3.5	28.9	48.6
25	3.71	22.9	38.5	35	3.71	47.1	79.3
25	3.92	35.1	59.1	35	3.92	76	128
25	4.03	50.1	84.3	35	4.04	105	176
25	4.14	58	97.6	35	4.15	124	208
30	3.06	9.56	16.1	40	3.04	21	35.2
30	3.24	14	23.6	40	3.21	26.3	44.3
30	3.5	20.5	34.5	40	3.5	37.9	63.8
30	3.73	34.4	57.9	40	3.71	58.6	98.7
30	3.92	50	84.2	40	3.92	88.5	149
30	4.04	70.7	119	40	4.03	127	214
30	4.15	86.7	148				

The rate equation for Co(II)- 4-aminobenzoic acid interaction can be written as

$$\text{Rate} = -d/dt[Co(II)]$$
$$= -d/dt[\text{4-aminobenzoic acid }]$$
$$= k_{obs}[\text{4-aminobenzoic acid }][Co(II)] \quad \text{----------(2)}$$
$$= k'_{obs}[\text{4-aminobenzoic acid }] \quad \text{---------- (3)}$$

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

The dissociation equilibria of 4-aminobenzoic acid can be represented as



$$H_2L^{+} \underset{K_1}{\rightleftharpoons} HL \underset{K_2}{\rightleftharpoons} L^{-} \qquad \text{-------- (4)}$$

$$K_1 = [H^+][HL] / [H_2L^+]$$

$$K_2 = [H^+][L^-] / [HL] \qquad \text{--------- (5)}$$

These three forms of ligand can react with Co(II) ions as follows

$$H_2L^+ + Co(II) \xrightarrow{k_1} CoL^+ + 2H^+ \qquad \text{-------- (6)}$$

$$HL + Co(II) \xrightarrow{k_2} CoL^+ + H^+ \qquad \text{------- (7)}$$

$$L^- + Co(II) \xrightarrow{k_3} CoL^+ \qquad \text{------- (8)}$$

Rate from equation 6, 7 and 8, can be written as

$$\text{Rate} = d/dt[CoL^+]$$

$$= \{ k_1 [H_2L^+] + k_2 [HL] + k_3[L^-]\}[Co(II)] \qquad \text{------- (9)}$$

From equation 5, it can be shown that

$$[L^-] = K_1 K_2 [H_2L^+] / [H^+]^2 \qquad \text{-------(10)}$$

$$[HL] = K_1 [H_2L^+] / [H^+] \qquad \text{------- (11)}$$

Substituting the values of [HL] and $[L^-]$ from equation (10) and (11) into equation (9) and on rearranging, we get:

$$\text{Rate} = \{ k_1 [H^+]^2 + k_1 K_1 [H^+] + k_3 K_1 K_2\} [Co(II)] [H_2L^+] / [H^+]^2 \qquad \text{------- (12)}$$

Substituting the values of [HL] and $[L^-]$ from equation (10) and (11) into equation (2), and on simplification, we get:

$$\text{Rate} = k_{obs} \{ k_1 [H^+]^2 + K_1 [H^+] + K_1 K_2\} [Co(II)][H_2L^+] / [H^+]^2 \qquad \text{------- (13)}$$

Comparing equation (12) and (13) and assuming that diprotonated form $[H_2 L^+]$ is unreactive, i.e. $k_1 \sim 0$, it can be shown that

$$k_{obs} \{ [H^+]^2 + K_1 [H^+] + K_1 K_2\} / K_1[H^+] = k_2 + k_3K_2 / K_1[H^+] \qquad \text{------- (14)}$$

Linear plots of $k_{obs} \{ [H^+]^2 + K_1 [H^+] + K_1 K_2\} / K_1[H^+]$ versus $[H^+]^{-1}$ at temperatures 25, 30, 35 and 40 ° C are shown in Fig.1. The values of K_1 and K_2 are obtained from the intercept and slope respectively. The values of K_1 and K_2 at 25°C were taken from literature and these values were corrected for different temperature using the equation (15)

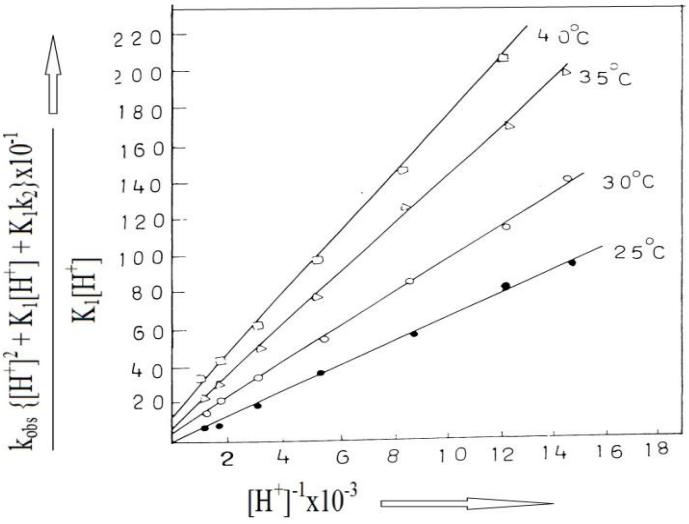


Fig 1: Variation of k_{obs} $\{[H^+]^2 + K_1[H^+] + K_1k_2\}x10^{-1}$ /$K_1[H^+]$

versus $[H^+]^{-1}$ for Co(II)-4-aminobenzoic acid interaction at different temperatures

At the temperature of our investigation, the corrected values of K_3^T were evaluated using the thermodynamic relation:

$$pK_a^T = \{\triangle H\ (T_2 - T_1) / 4.576T_2.T_1\} + pK_a^{25\ ^oC} \quad \text{----------(15)}$$

The values of k_2 and k_3 are reported in Table 2. Values of energies of activation corresponding to specific rate constants k_2 and k_3 were calculated from linear plot of log k versus 1/T and those of entropies and enthalpies of activation corresponding to k_2 and k_3 were calculated from linear plot of log k/T versus 1/T

Calculation of Water Exchange Rate Constant (k_o)

The rate of substitution on metal ion is controlled by the rate of water exchange and rate determining step is the loss of water molecule from the inner coordination sphere, i.e.

$$M(H_2O)_6^{2+} + L^{n-} \underset{\text{Fast}}{\overset{K_{os}}{\rightleftharpoons}} (H_2O)_5M^{2+}(H_2O)L^{n-}$$

$$(H_2O)_5M^{2+}(H_2O)L^{n-} \xrightarrow[-H_2O]{k_o\ \text{Slow}} (H_2O)_5ML^{(2-n)+} \quad \text{---------- (16)}$$

The rate law in terms of outer sphere complex formation (K_{os}) and the rate constant of water loss (k_o) from equation (19) be written as

$$d/dt\ (H_2O)_5ML^{(2-n)+} = k_o\left[(H_2O)_5M^{2+}(H_2O)L^{n-}\right]$$

$$= k_oK_{os}\left[\ M(H_2O)_6^{2+}\right]\left[\ L^{n-}\right] \quad \text{---------- (17)}$$

So the rate law in terms of outer sphere complex formation (K_{os}) for Co(II)- 4-aminobenzoic acid can be written as

$$\text{Rate} = d/dt\ [Co(II)L] = K_{os}\ k_o\ [Co(II)\ ]\ [L] \quad \text{----------(18)}$$

Rate from equation 6,7 and 8 can be written as

$$\text{Rate} = d/dt[Co(II)L^{+}]$$

$$= \{ k_1 [H_2L^{+}] + k_2 [HL] + k_3[L^{-}]\}[Co(II)] \quad \text{---------- (19)}$$

Assuming that the diprotonated form $[H_2L^{+}]$ is unreactive $k_1 \sim 0$, and $k_3 > > k_2$ (Table 2), therefore equation (19) reduces to

$$\text{Rate} = \{k_3[L^{-}]\}[Co(II)] \quad \text{---------- (20)}$$

Comparing equation 18 and 20, we get

$$k_3 = K_{os}\, k_o \quad \text{---------- (21)}$$

In order to calculate the value of k_o, we must know the value of K_{os}. The value of K_{os} was calculated using the equation which was given by Fuoss on statistical grounds,

$$K_{os} = 4\pi N a^3 .e^{-u/KT} / 3000 \quad \text{--------- (22)}$$

Where $u = Z_1Z_2 e_o^2 / aD - Z_1Z_2 e_o^2 x / D(1 + xa)$

And $x^2 = 8\pi N e_o^2 u/1000DKT$

Where
N = Avogadro's number
a=Distance of closest approach of two ions
K = Boltzmann's constant
e_o=Charge of an electron in esu units
D = Bulk dielectric constant
u = Ionic strength
Z_1Z_2 =Charge of reactants
Distance of closest approach of two ions often taken 5Å for reactions of two aqua cations with ordinary ligands. After substituting the values of all the terms in equation (22), the value of K_{os} can be approximated to 1.98 mol dm^{-3} at all temperatures .The values of k_o are reported in Table 2. The high values of $\Delta H^{\#}$ corresponding to k_2 step confirm that the mono-protonated form 4-aminobenzoic acid is less reactive whereas low value of $\Delta H^{\#}$ corresponding to k_3 supports the high reactivity of deprotonated form of 4-aminobenzoic acid. The negative value of entropy corresponding to k_3 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 3).

Table 2: Values of k_2 and k_3 and k_o for the complexation of Co(II) with 4-aminobenzoic acid

Temp.(± 0.05°C	k_2 x10^{-1}($M^{-1}s^{-1}$)	k_3 x10^{-3}($M^{-1}s^{-1}$)	k_o x10^{-3}(s^{-1})
25	-	4.28	0.22
30	5.0	5.33	0.27
35	8.0	6.92	0.35
40	12.5	7.43	0.38

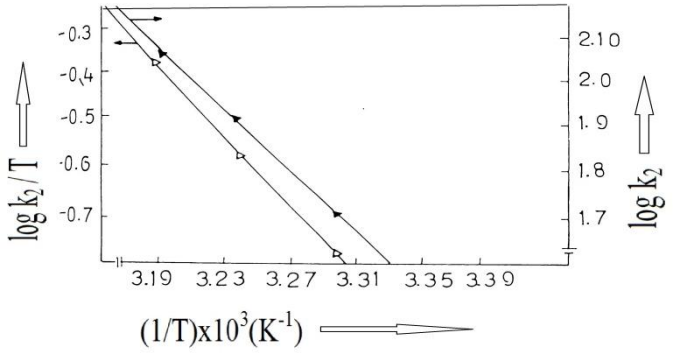


Fig 2: Variation of log k_2 and log k_2 / T versus (1/T) for the interaction of Co(II)-4-aminobenzoic acid

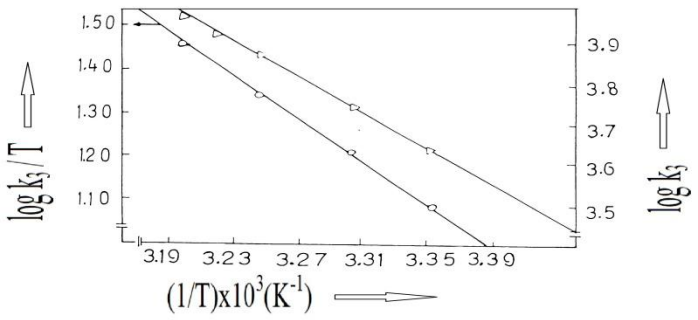


Fig 3: Variation of log k_3 and log k_3 / T versus (1/T) for the interaction of Co(II)-4-aminobenzoic acid

Table 3: Values of activation parameters corresponding to k_2 and k_3 steps for the complexation of Co(II) with 4-aminobenzoic acid

	k_2	**k_3**
$\Delta H^{\#}$(kJmol^{-1})	49.3±2.3	44.1±2.2
$\Delta E^{\#}$(kJmol^{-1})	57.4±2.2	30.4±1.9
$\Delta S^{\#}$(JK^{-1}mol^{-1})	-80.2±3.4	-58.0±1.6

Mechanism

The high values of $\Delta H^{\#}$ corresponding to k_2 step confirm that the monoprotonated form of 4-aminobenzoic acid is less reactive whereas low value of $\Delta H^{\#}$ corresponding to k_3 supports the high reactivity of deprotonated form of 4-aminobenzoic acid. (Table 3). Due to strong electrostatic interaction between the positive charge of Co(II) and negative charge on the oxygen, it is inferred that k_2 is greater than k_3. The value of activation parameters corresponding to k_3 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. It has been found that the deprotonated form is more reactive than the protonated form.

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