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A comprehensive kinetic study on interaction of Ni(II) with γ-aminobenzoic acid

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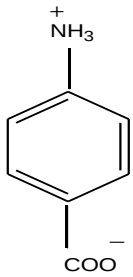
Abstract
The comprehensive kinetic study on interaction of Ni(II) with γ-aminobenzoic acid has been investigated at 25, 30, 35 and 40± 0.05 °C in the pH range 3.04-4.15, using Aminco Morrow Stopped Flow Spectrophotometer. The ionic strength was maintained at 0.1 M KNO_3. The deprotonated form of γ-aminobenzoic 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, Ni(II) ions, γ-aminobenzoic acid, Rate constant, activation parameters, energy of the molecule, heat of formation

Introduction

γ-aminobenzoic acid occurs in food stuffs in the free state and in compounds other than folic acid e. g. in yeast 20 to 30 % of the γ-aminobenzoic acid is present in combination with a polypeptide of glutamic acid. It 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 excreted in human urine in conjugated form with metal ions and in human faeces. It is also synthesised by the intestinal flora of humans. The average concentration of aminobenzoic acid in human sweat is 0.2 micrograms per 100 mL. γ-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 γ-aminobenzoic would no doubt give important information regarding type of interaction of polypeptide of glutamic acid to metal ions.

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



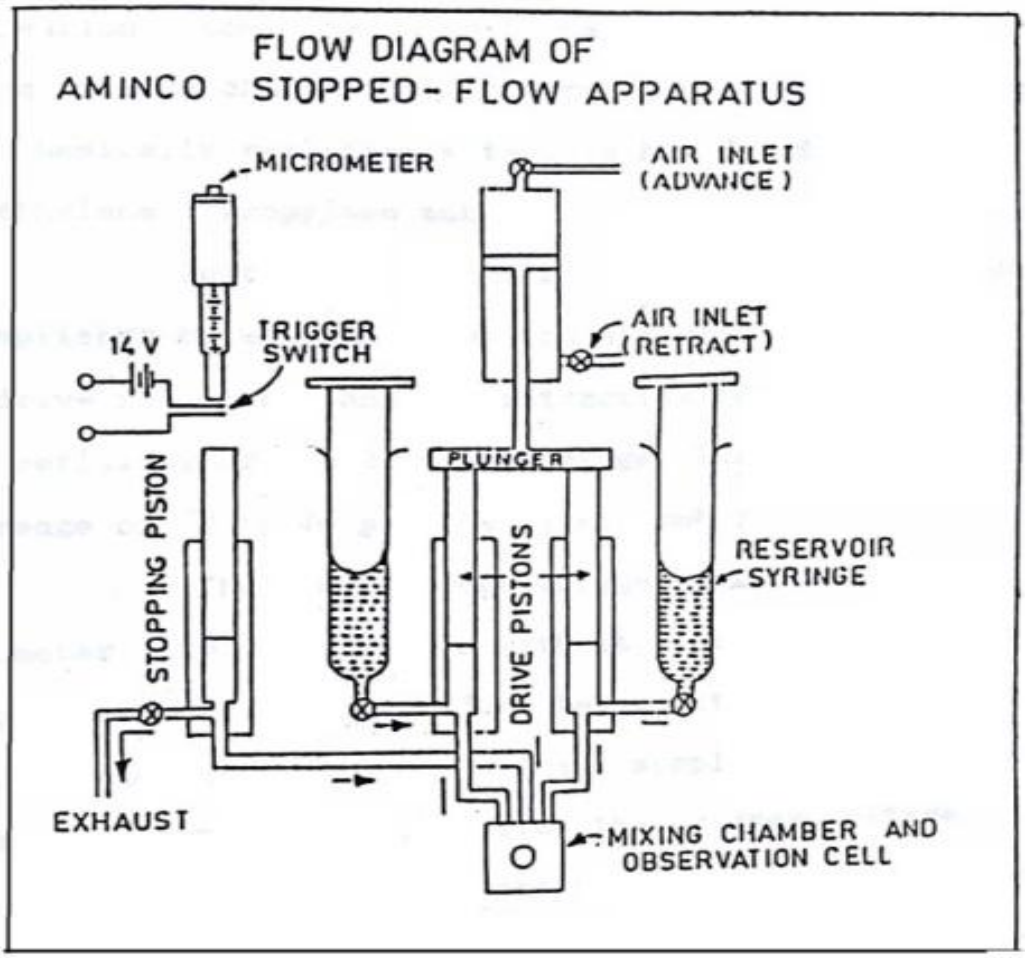
(γ-aminobenzoic acid) Zwitterion

According to Weber and Simeon eight membered rings are unstable due to large steric strain and this is in conformity with observations reported in literature [6]. Thus it is obvious that reaction of Ni (II) with γ-aminobenzoic acid would proceed without *any* ring formation. In order to check the reactivity of zwitterion and to know the different binding steps, their corresponding rate constants and activation parameters, kinetics of Ni(II) with γ-aminobenzoic acid was initiated. The kinetics of complexation of metal ions Ni(II) by γ-aminobenzoic acid would no doubt give important information regarding the types of interaction of these ions.

with γ-aminobenzoic acid and the clearance of γ-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 Ni(II) with γ-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 γ-aminobenzoic acid.

Materials and Methods

γ-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., [Ni(II)] >>[γ-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. Nickel 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

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

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

Results and Discussion

Ni(II)- γ-aminobenzoic acid Complexation

The kinetics of complexation of Ni(II)–γ-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 2-5 (pKa_1 = 2.50, pKa_2 = 4.87) [18], 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 [Ni(II)] >> [γ-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 Ni(II) with γ-aminobenzoic acid at different pH's and temperatures
I = 0.10 M KNO_3
[Ni(II)] = 6.1 x 10^{-2} M
[γ-aminobenzoic acid] = 4.86 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	3.04	1.21	19.9	35	3.07	5.2	85.3
25	3.2	1.69	27.8	35	3.29	7.26	119
25	3.49	3.73	61.2	35	3.51	10.5	172
25	3.72	7.38	121	35	3.76	17.1	281
25	3.94	9.94	163	35	3.9	23.1	379
25	4.03	15	246	35	4.04	31.3	514
25	4.13	17.8	292	35	4.15	38.1	625
30	3.07	3	49.2	40	3.09	6.86	113
30	3.25	4.4	72.1	40	3.25	9.15	150
30	3.5	6.4	105	40	3.5	13	214
30	3.74	10.5	173	40	3.74	19.8	325
30	3.92	16.1	264	40	3.91	28.6	469
30	4.06	21.6	355	40	4.04	37	608
30	4.15	25.9	425	40	4.14	46.5	762

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

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

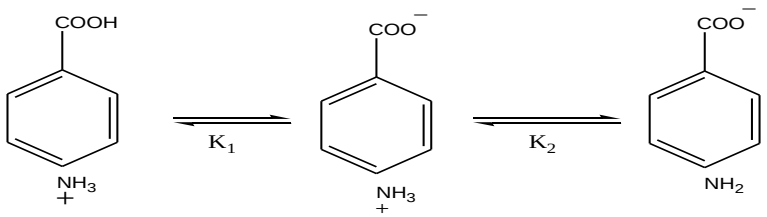
= -d/dt[γ-aminobenzoic acid]

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

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

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

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



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

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

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

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

$$H_2L^+ + Ni(II) \xrightarrow{k_1} NiL^+ + 2H^+ \quad \text{---- (6)}$$

$$HL + Ni(II) \xrightarrow{k_2} NiL^+ + H^+ \quad \text{---- (7)}$$

$$L^- + Ni(II) \xrightarrow{k_3} NiL^+ \quad \text{----- (8)}$$

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

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

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

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:

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

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

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

Comparing equation (12) and (13) and assuming that diprotonated form $[H_2 L^+]$ is unreactive, i.e. k_1 ~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)

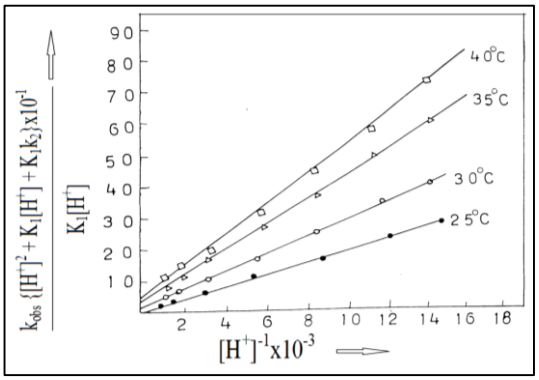


Fig 1: Variation of $k_{obs} \{[H^+]^2 + K_1[H^+] + K_1k_2\}x10^{-1} / K_1[H^+]$ versus $[H^+]^{-1}$ for Ni(II) -γ-aminobenzoic acid interaction at different temperatures.

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

$$pK_a^T = \{\Delta H \; (T_2 - T_1) / 4.576T_2.T_1\} + pK_a^{25\,^oC} \qquad \text{--(15)}$$

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.

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

$$\downarrow k_o \text{ Slow } -H_2O$$

$$(H_2O)_5ML^{(2-n)+} \qquad \text{---- (16)}$$

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

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

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

So the rate law in terms of outer sphere complex formation (Kos) for Ni(II γ-aminobenzoic acid can be written as

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

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

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

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

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

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

Comparing equation 18 and 20, we get

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

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,

$$Kos = 4\pi N \, a^3 . \, e^{-u / K T} / 3000 \qquad \text{--- (22)}$$

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

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

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 γ-aminobenzoic acid is less reactive whereas low value of $\Delta H^{\#}$ corresponding to k_3 supports the high reactivity of deprotonated form of γ-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 Ni(II) with γ-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	---	1.26	0.63
30	1.50	1.61	0.81
35	3.20	2.17	1.09
40	4.65	2.49	1.25

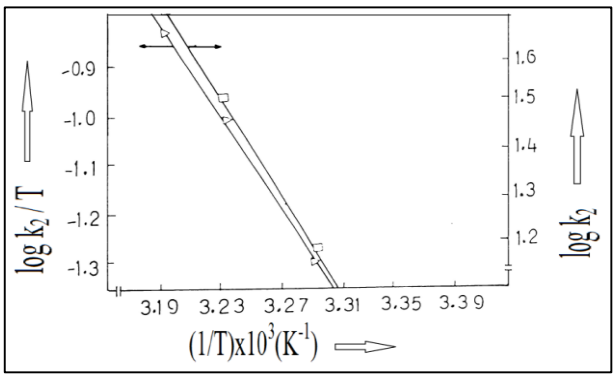


Fig 2: Variation of log k_2 and log k_2 / T versus (1/T) for the interaction of Ni(II) -γ-aminobenzoic acid.

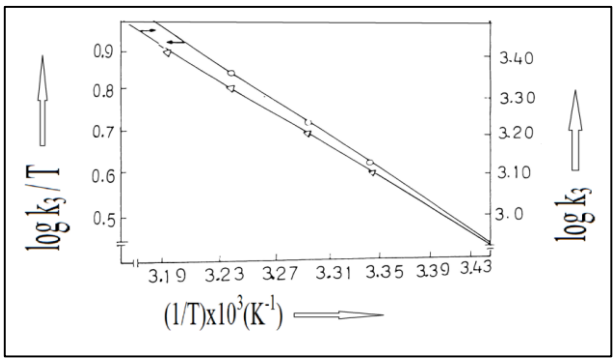


Fig 3: Variation of log k_3 and log k_3 / T versus (1/T) on the interaction of Ni(II)-γ-aminobenzoic acid.

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

	k_2	k_3
$\Delta H^{\#}$(kJmol^{-1})	61.6±2.2	38.3±0.9
$\Delta E^{\#}$(kJmol^{-1})	84.9±1.6	34.8±1.7
$\Delta S^{\#}$(JK^{-1}mol^{-1})	17.5 ± 0.7	-87.9±1.4

Mechanism

The high values of $\Delta H^{\#}$ corresponding to k_2 step confirm that the monoprotonated form of γ-aminobenzoic acid is less reactive whereas low value of $\Delta H^{\#}$ corresponding to k_3 supports the high reactivity of deprotonated form of γ-aminobenzoic acid. (Table 3). Due to strong electrostatic interaction between the positive charge of Ni(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.

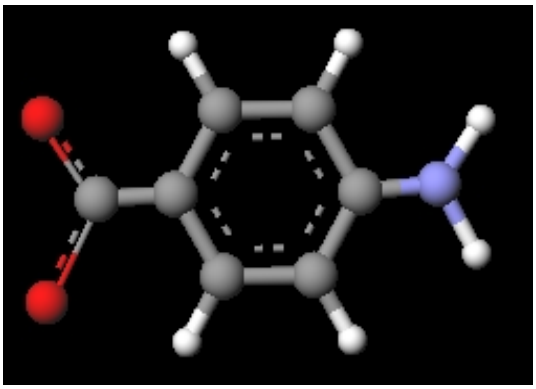


Fig 4: Deprotonated form of Ni(II)-γ-aminobenzoic acid
Final Geom Energy = -18005.2533 kcal/mol
Heat of Formation = 34745.2703 kcal/mol

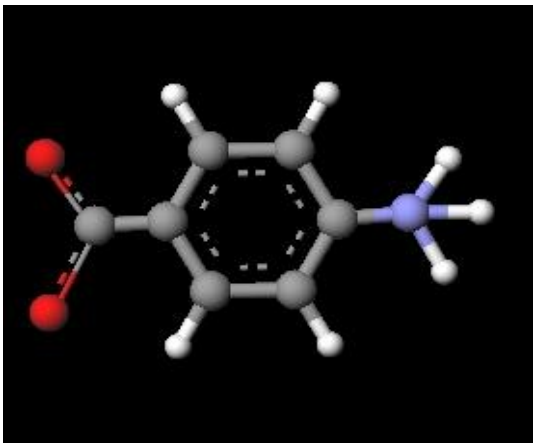


Fig 5: Protonated form of Ni(II)-γ-aminobenzoic acid
Final Geom Energy = - 42524.18 kcal/mol
Heat of Formation = - 26.7593 kcal/mol

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 protonated form has been calculated. Values of the energies as well as heat of formation were calculated after optimizing the geometry of the molecules[14-17]. 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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