Kinetics of Formation of Fe(III) Complexes of 3,4,5 Trihydroxybenzoic Acid

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Summary: 3,4,5, Trihydroxybenzoic acid (Gallic acid) is a strong chelating agent and forms complexes of high stability constants with Iron(III), Ligand concentration and pH dependence of kinetics of formation of monogallatotetraaquoiron(III) complex were studied in various acetate buffers of pH 3.84 to 5.0. Pseudo first order rate constants (with ligand in excess) were found to increase with pH as well as increasing concentration of the ligand but level off at higher concentration of ligand. A rate law was derived and the mechanism for the formation of monogallatotetraaquoiron(III) was proposed which complies with the rate law.

Introduction

Kinetics of formation of bidentate monocomplexes of iron(III) with salicylic acid, sulphosalicylic acid, 8-hydroxyquinoline and salicylaldehyde with possible mechanism [1] and bidentate ligands forming six membered chelate rings with malonic acid n-butylmalonic, benzylmalonic and cyclobutane have been reported [2]. Rates and mechanism of iron(III) monohydroxamato complexes have also been reported [3]. This work was carried out with the objective to study whether the rate of iron(III) chelate formation is controlled by the release of first coordinated water molecule or by chelate ring closure as was found [4-6] for some bivalent metal chelates containing a six membered ring. Kinetic properties of bidentate hydroxamic acids were compared with those of the bidentate as well as monodentate ligands studied before. Formation of iron(III) ferrioxamine B [7] has been studied with stopped flow technique and the kinetics of formation and the rate law were determined. Many other workers have also reported [8-10] the kinetics of formation of iron(III) complexes with similar ligands.

Gallic acid behaves as good iron chelator resulting in the formation of highly colored complexes with different metal to gallic acid ratio at different pH [11]. In view of the strong affinity of Gallic acid for iron(III) and rapid formation of complexes a systematic study of the rates of formation of the monogallatotetraquo iron(III) complex has been carried out. The effect of ligand concentration and pH on the rates of formation has been studied. From these results we have found the rate law and have proposed a mechanism for these formation.

Results and Discussion

Table-1 shows the dependence of k_{obs} on ligand concentration at pH 3.88 to 5.00. From this data the following observations may be noted.

i) k_{obs} (observed rate constant) of the reaction between gallic acid and iron(III) species increase with the increasing concentration of gallic acid (Table-1) and it levels off (Fig. 1) at high concentration of gallic acid at all pH.

Table-1: Ligand concentration dependence of rates of formation of Gallic acid and Iron (III) complexes at various pH is acetate buffer.

$[Fe^{3+}] = 1.5 \times 10^{-4}M$, $[G.A.]$ $3 \times 10^{-4}M$ to $9 \times 10^{-3}M$
Wave Length = 560 n.m., T = 25°C
U = 0.2 M in NaCl

[G.A.] moles/ litre 10³	k_{obs}/second pH						
	3.84	4.02	4.20	4.40	4.60	4.79	5.00
0.300	0.106	0.111	0.148	0.155	0.229	0.569	0.824
0.600	0.149	0.158	0.275	0.396	0.491	0.796	1.085
0.900	0.228	0.304	0.375	0.560	0.688	0.969	1.195
1.200	0.300	0.381	0.536	0.726	0.864	1.125	1.285
1.500	0.,348	0.453	0.668	0.792	0.949	1.290	1.435
2.250	0.552	0.707	0.899	1.023	1.202	1.467	1.665
3.750	0.838	1.015	1.167	1.260	1.435	1.726	1.989
4.500	0.960	1.179	1.307	1.424	1.595	1.780	2.056
6.000	1.191	1.375	1.484	1.549	1.750	1.910	2.146
7.500	1.225	1.413	1.574	1.679	1.835	2.090	2.286
9.000	1.307	1.522	1.627	1.795	1.855	2.189	2.346

Fig. I
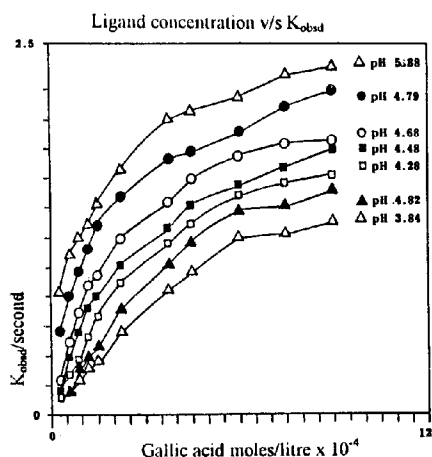
ii) k_{obs} increases with increasing pH at all concentrations of gallic acid (Table 1 and 2).

iii) The spread of k_{obs} is larger at lower pH and it decreases progressively as pH increase (Table-1). For a thirty fold increase in gallic acid concentration at pH approximately 4.0, a thirteen fold increase is observed in k_{obs} whereas for the same increase in gallic acid concentration at pH approximately 5.0 the increase in k_{obs} is only about

Table-2: 1/Kobs v/s 1/G.A. concentration of the rates of formation of Gallic acid and Iron (III) complexes at various pH in acetate buffer
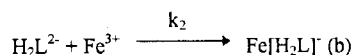
$[Fe^{3+}] = 1.5 \times 10^{-4}M$, $[G.A.]$ $3 \times 10^{-4}M$ to $9 \times 10^{-3}M$
Wave Length = 560 n.m., T = 25°C
U = 0.2 M in NaCl

[G.A.⁻¹] moles/ litre 10³	k_{obs}^{-1}/second pH						
	3.84	4.02	4.20	4.40	4.60	4.79	5.00
3333	9.433	9.001	6.756	6.455	3.344	1.757	1.213
1666	6.711	6.329	3.636	2.525	2.036	1.256	0.921
1111	4.386	3.289	2.666	1.785	1.453	1.032	0.836
833	3.333	2.624	1.865	1.377	1.157	0.888	0.778
666	2.873	2.207	1.497	1.263	1.054	0.775	0.696
444	1.811	1.414	1.112	0.977	0.832	9.681	0.600
266	1.193	0.985	0.856	0.788	0.697	0.579	0.502
222	1.041	0.848	0.765	0.702	0.627	0.562	0.486
166	0.839	0.727	0.674	0.645	0.571	0.523	0.466
133	0.797	0.707	0.635	0.595	0.454	0.487	0.437
111	0.765	0.657	0.614	0.557	0.539	0.457	0.425

two fold. This difference may have been more clear if we could obtain the data at pH lower than 3.84 with the acetate buffers used. With these observations a possible mechanism and rate law can be derived for the simple reaction.

$$Fe^{3+} + C_6H_2(OH)_3COO^- \longrightarrow FeC_6H_2O^-(OH)_2COO^-$$
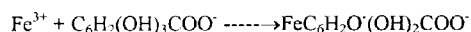
(A) The first possible mechanism is as follows,

$$H_3L^- \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} H_2L^{2-} + H^+ \quad (a)$$

$$H_2L^{2-} + Fe^{3+} \overset{k_2}{\longrightarrow} Fe[H_2L]^- \quad (b)$$

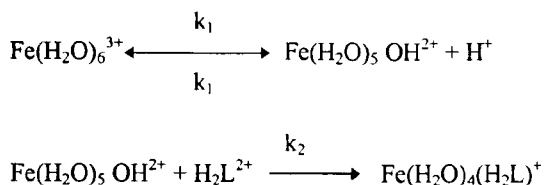Applying steady state approximation for the $[H_2L^{2-}]$ and considering its rate of formation and rate of disappearance at equilibrium the following rate equation is obtained.
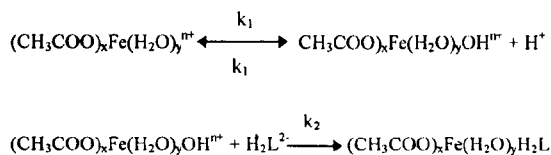
$$Rate = \frac{k_2k_1 \, [H_3L^-][Fe^{3+}]}{k_1 + k_2 \, [Fe^{3+}]} = k_{obs} \, [Fe^{3+}] \quad (1)$$

At a given pH k_1 $[H^+]$ is equal to k_1

(B) The second possible mechanism for this reaction is as follows

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$$Fe(H_2O)_6^{3+} \underset{k_1}{\overset{k_1}{\longleftrightarrow}} Fe(H_2O)_5 OH^{2+} + H^+$$

$$Fe(H_2O)_5 OH^{2+} + H_2L^{2+} \overset{k_2}{\longrightarrow} Fe(H_2O)_4(H_2L)^+$$

The above stated reaction may also be possibly starting with an iron acetate species having some acetate ions in it and may be written as,

$$(CH_3COO)_xFe(H_2O)_y^{n+} \underset{k_1}{\overset{k_1}{\longleftrightarrow}} CH_3COO)_xFe(H_2O)_yOH^{n+} + H^+$$

$$(CH_3COO)_xFe(H_2O)_yOH^{n+} + H_2L^{2-} \overset{k_2}{\longrightarrow} (CH_3COO)_xFe(H_2O)_yH_2L$$

(In above equations x may not be equal to y)

Table-3: Slope v/s H^+ in Gallic acid concentration dependence of k_{obs}
$[Fe^{3+}] = 1.5 \times 10^{-4}$M, [G.A.] $= 3 \times 10^{-4}$M to 9×10^{-3}M
Wave Length $= 560$ n.m., T $= 25°C$
U $= 0.2$ M in NaCl

Slope	H^+ moles/litre
0.00287	14.45×10^{-5}
0.00277	9.55×10^{-5}
0.00193	6.31×10^{-5}
0.00174	3.98×10^{-5}
0.00088	2.51×10^{-5}
0.00041	1.62×10^{-5}
0.00025	1.00×10^{-5}

$1/K_{obsd}$ v/s $1/$Ligand concentration

Fig. 2:

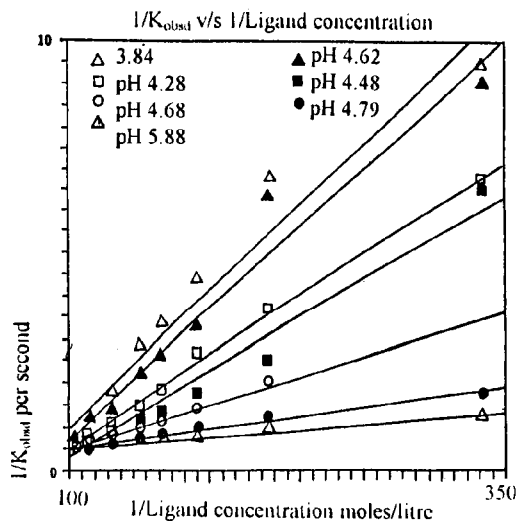Slope v/s $[H^+]$ of Fe (GA) formation
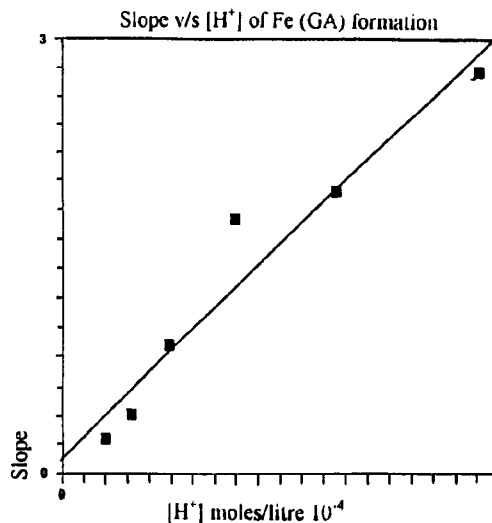
$[H^+]$ moles/litre 10^{-4}

Fig. 3

From the rate of formation of the product and intermediate, and the rate of disappearance of the intermediate in the above mentioned reaction and on transformation of various intermediate steps and substituting different values a final equation is obtained which gives the relation of k_{obs} as follows.

$$k_{obs} = \frac{k_1k_2 \, [H_2L^{2-}]}{k_1[H^+] + k_2 \, [H_2L^{2-}]} \quad (2)$$

Now at low $[H_2L^{2-}]$ concentration $k_2[H_2L^{2-}]$ is approximately equal to zero as compared to $k_1[H^+]$ therefore

$$k_{obs} = \frac{k_1k_2}{k_1[H]^+} [H_2L^{2-}]$$

$$Let \quad \frac{k_1k_2}{k_1[H^+]} = k'$$

so at lower pH values k_{obs} will increase with the increasing concentration of $[H_2L^{2-}]$ and at very high concentration of $[H_2L^{2-}]$ the term $k_{-1}[H^+]$ becomes approximately equal to zero as compared to $k_2[H_2L^{2-}]$ therefore

$$k_{obs} = k_1$$

which means the k_{obs} will not increase and in our data [Tab. 1 and Fig. 1] at higher concentration of the [H_2L^{2-}] leveling off has been very significant.

The above observations are in accordance with the proposed mechanism 'B' given in equation (2) above. From this equation we get $1/k_{obs}$ as

$$1/k_{obs} = \frac{k_1[H^+] + k_2[H_2L^{2-}]}{k_1\,k_2\,[H_2L^{2-}]}$$

$$= \frac{1}{k_1} + \frac{k_1\,k_1\,[H^+]}{k_2} \quad \frac{1}{[H_2L^{2-}]}$$

A plot of $1/k_{obs}$ v/s $1/[H_2L^{2-}]$ at various pH, a temperature of 25°C (Fig. 2, Tab. 2 and 3) shows high pH dependence. And the pH dependence of the slope is

$$Slope = \frac{k_1\,k_1}{k_2} \quad [H^+]$$

And the slope v/s [H^+] gives the value of k_1 k_1/k_2 and the value of k_1/k_1 i.e. the equilibrium constant for the hydrolysis reaction.

$$Fe(H_2O)_6^{3+} \xleftarrow[\quad k_1 \quad]{\quad k_1 \quad} Fe(H_2O)_5OH^{2+} + H^+$$
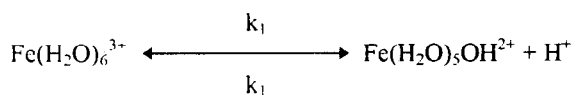
is known from the literature [12] k_1 is obtained from intercept obtained in figure 2 a plot of $1/K_{obs}$ v/s $1/[H_2L]^{2+}$ and hence the value of formation rate constant k_2 was calculated to be 1.56×10^2 at 25°C.

Experimental

Solutions of respective concentrations used in each experiment were freshly prepared in the acetate

buffers. All the experiments were carried out with the help of stopped flow apparatus in which the cuvet (placed in cell compartment of spectronic 21) and the capillaries were jacketed in a rubber tubing through which water from thermostatic controlled water bath was kept circulating. All other solutions of iron (III) and gallic acid were immersed in water bath at least 15-20 minutes before using. The rates were followed by monitoring the rise in absorbance data at appropriate λ_{max} (560 n.m. for Fe(III)L). The out put of the spectrophotometer was read through 12 bit analog to digital convertor (Sunset labs, California, USA) into a PC compatible computer.

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