Kinetics and Mechanism of Formation of Trisgallatoiron(III) Complex from Monogallatotetraaquo Iron (III) and Bisgallato Diaquo Iron (III) Complexes

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Summary: Kinetics of formation of 1:3 complexes from 1:1 and 1:2 complexes between Fe(III) and gallic acid (3,4,5-trihydroxybenzoic acid) has been studied. The rates were measured spectrophotometrically by monitoring the rise of absorbance at 500 nm (the wave length of maximum absorbance for the tris complex). The reaction was driven by providing a sudden pH jump to 8.0 along with an excess of ligand. Under these conditions, 1:3 complex would completely predominate. The observed pseudo first order rate constant increased with increasing ligand concentration initially, but leveled off at higher ligand concentration. The rate of formation of 1:3 complex from 1:2 complex was slower than it's formation from 1:1 complex by about an order of magnitude. The mechanistic implications of these rate measurements are discussed.

Introduction

Complex formation between Iron(III) and gallic acid (3,4,5-trihydroxybenzoic acid) is strongly pH dependent [1]. Different complexes formed between a certain range of pH exist in equilibrium as M^{3+} and ML^{+}, ML^{+} and ML_2^{-}, ML_2^{-} and ML_3^{3-} [2] (where L = a bidentate ligand with a catecholate co-ordinating function. It is also known that monogallato Iron (III) i.e. ML^{+} dominates at pH 4.0, bisgallato iron(III) i.e. ML_2^{-} dominates at pH 5.4 and trisgallato Iron (III) i.e. ML_3^{3-} dominates at pH 8.0.

Rates of conversion of a complex formed at a particular pH to another complex of different stoichiometry at some other pH has been studied. Kazmi and McArdle [3] have reported the formation of bis and tris acetohydroxamoto complexes from the corresponding mono and bis compounds.

In the system under study these compounds are converted into one another by changing pH of their solution provided appropriate amounts of gallic acid is present in the solution. We have studied the rates of conversion of monogallatotetraaquoiron (III) and bisgallatodiaquoiron (III) complexes to trisgallato iron(III) complex by changing the pH of

monogallato and bisgallato complexes to 8.0. The rate dependence on concentration of ligand was also investigated.

Results and Discussion

The absorbance versus time data was fitted to an equation by a computer program "abc6" for the calculation of rate constants. This program is based on a linear regression analysis of the plots of ln of absolute values of A_t-A_α vs time which were linear up to at least 70% of the reaction (Figure 1). A summary of the rate constants for the formation of the tris complex from the mono and the bis complex as a function of ligand concentration is given in Table 1.

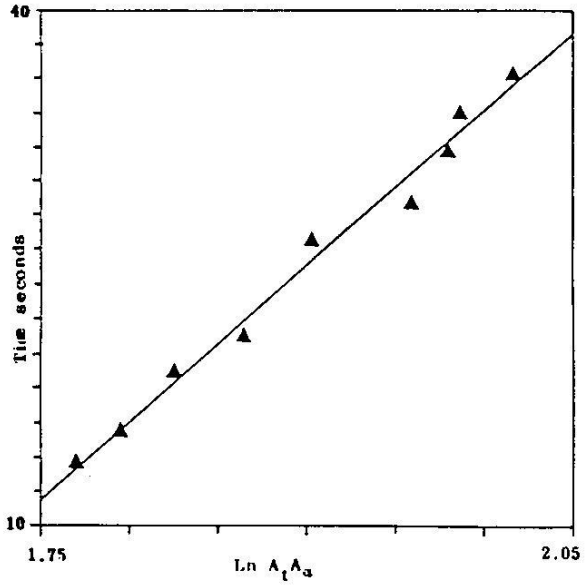


Fig.1 : pf Ln [A_t - Aα I v/s Time for the formation of trisgallatoiron(III) from monogallatoiron(III) complex.

The observed rate constants (K_{obs}) of formation of trisgallatoiron(III) complex from monogallatoiron(III) complex are higher than the K_{obs} of it's formation from bisgallato iron(III) complex for identical concentrations of the ligand K_{obs} for both these reactions increases with increasing concentration of gallic acid but level off at higher concentrations of gallic acid (Figure 2 and 3).

Table 1: Ligand concentration dependence of K_{obs} of formation of trisgallate iron(III) complexes from mono and bisgallate iron (III) complexes
Mono and bisgallate iron(III) complexes = 7.5 x 10^{-4}M. Gallic acid = 7.500 x 10^{-4}M to 4.5 x 10^{-3}M
λ= 500 n.m. T = 25°C μ=0.2 in NaCl

Gallic acid Moles/Litre	K_{obs} S^{-1} From mono complex	From bis complex
7.500 x 10^{-4}	3.984 x 10^{-3}	1.068 x 10^{-3}
1.499 x 10^{-3}	1.044 x 10^{-2}	1.329 x 10^{-3}
2.249 x 10^{-3}	1.240 x 10^{-2}	1.500 x 10^{-3}
2.988 x 10^{-3}	1.370 x 10^{-2}	1.620 x 10^{-3}
3.749 x 10^{-3}	1.422 x 10^{-2}	1.728 x 10^{-3}
4.500 x 10^{-3}	1.449 x 10^{-2}	1.804 x 10^{-4}

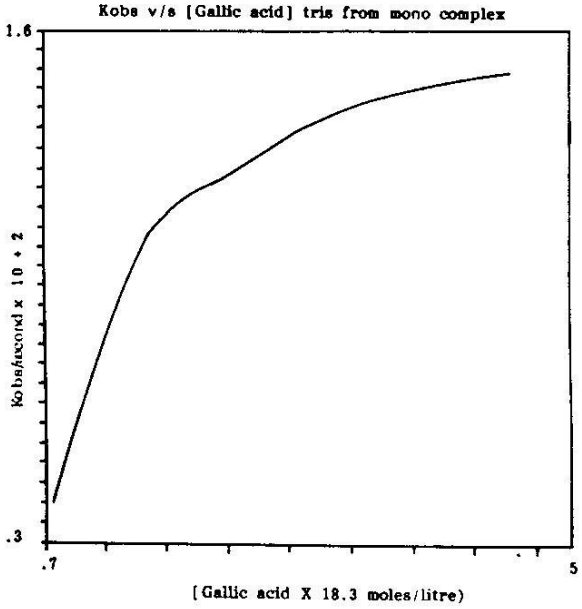


Fig. 2: K_{obs} v/s [Gallic acid] for the formation of trisgallatoiron(III) complex from monogallatotetraaquoiron(III) complex.

A possible mechanism and rate law consistent with the observations can be derived for these observations.

(A) The first proposed mechanism:

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

$$Fe(H_2L)(H_2O)_4^+ + H_2L^{2-} \xrightarrow{k_2} Fe(H_2L)_2(H_2O)_2^- \quad (b)$$

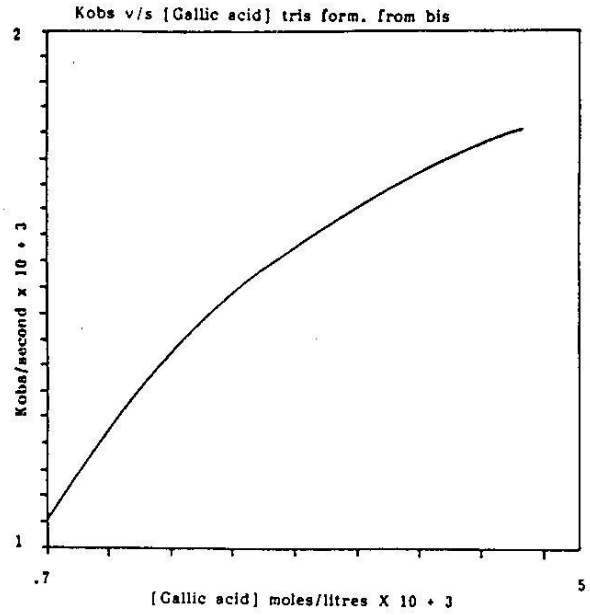


Fig. 3. K_{obs} v/s [Gallic acid] for the formation of trisgallateiron(III) complex from bisgallatatetraagquoiron(III) complex.

Applying steady state approximation for the H_2L^{2-}, considering the rate of formation and disappearance of H_2L^{2-} at equilibrium, on deriving these equations and substituting values obtained, we get a final rate equation in which

$$\text{Rate} = \frac{k_2 k_1 [H_3L^-]\,[Fe(H_2L)(H_2O)_4]^+}{k_{-1} + k_2\,[Fe(H_2L)(H_2O)^+_4]} = K_{obs}$$

(B) The second proposed mechanism:

$$[Fe(H_2L)(H_2O)_4^+] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(H_2L)(H_2O)_3(OH)]+[H^+] \quad (1)$$

$$[Fe(H_2L)(H_2O)_3(OH)]+H_2L^{2-} \xrightarrow{k_2} [Fe(H_2L)_2(H_2O)_2]^- \quad (2)$$

Rate of formation of $[Fe(H_2L)_2(H_2O)_2]^-$

$$\frac{d[Fe(H_2L)_2H_2O)_2]^-}{dt} = K_2[Fe(H_2L)(H_2O)_3(OH)]\,[H_2L^{2-}] \quad (3)$$

Considering the rate of formation and the rate of disappearance of intermediate $[Fe(H_2L)(H_2O)_3(OH)]$, substituting the values and on deriving these equations we get a final equation where K_{obs}

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

Now at lower $[H_2L^{2-}]$ concentration, $k_2\,[H_2L^{2-}]$ is negligible as compared to $k_{-1}\,[H^+]$ therefore,

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

So in this condition the 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 negligible as compared to $k_2[H_2L^2]$, therefore.

$$K_{obs} = k_1$$

which means that K_{obs} will not increase with the increasing concentration of $[H_2L^{2-}]$ Table (1) and figure (2) exhibits the leveling off of K_{obs} at higher $[H_2L^{2-}]$ concentrations.

The above observations are in accordance with the proposed (B) mechanism and follow the rate low.

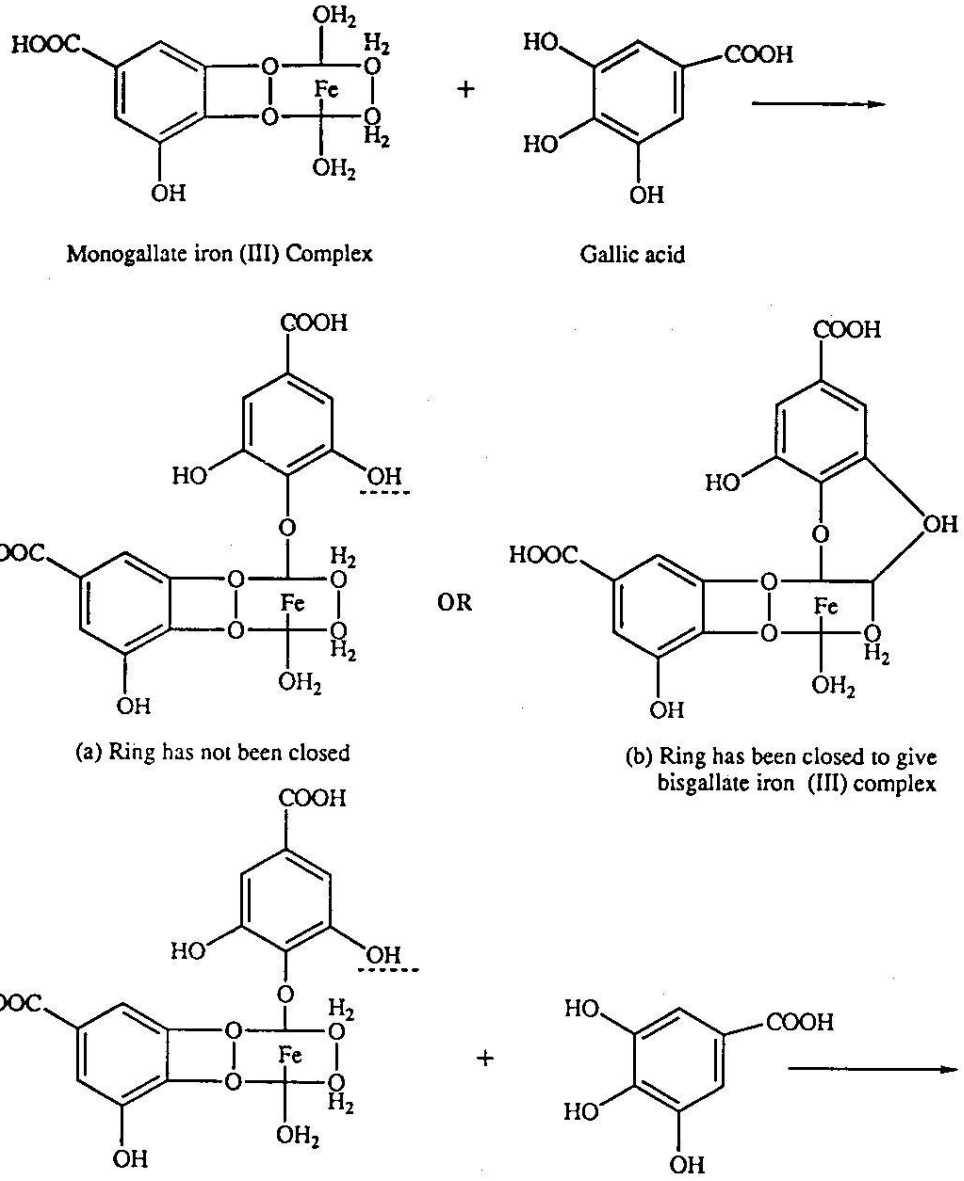
The K_{obs} of formation of trisgallatoiron(III) are larger in case where the starting specie is monogallato iron (III) as compared to the K_{obs} values when the starting specie is bisgallato iron(III) (Table 1). It could be due to the following reasons.

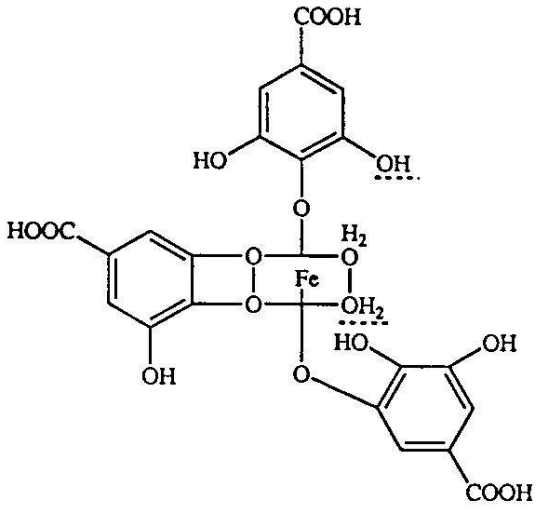
i) For the addition of ligands more sites are available in case of monogallato iron (III) complex as it is surrounded by four water molecules and only one bidentate gallate ion, this possibility decreases in case of bisgallato iron (III) complex where two bidentate gallate ions are already surrounding the metal ion with only two water molecules.

The higher values of K_{obs} for the formation of trisgallato iron (III) complex from monogallato iron (III) complex are likely to proceed through the formation of bisgallato by the addition of a gallic acid molecule first, followed by another molecule to produce a trisgallato complex. But through this process the K_{obs} of tris formation from mono would not be higher.

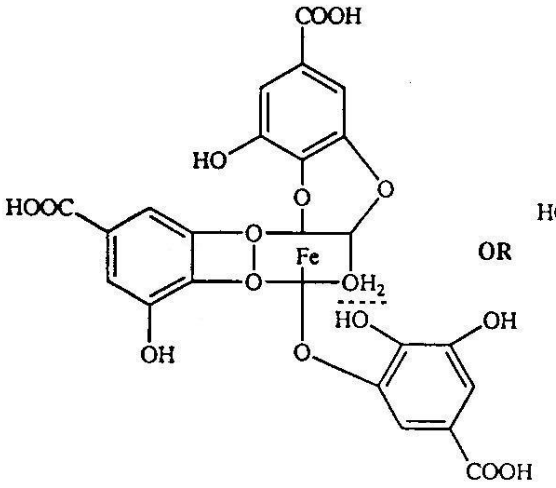
The higher K_{obs} values are possible only if we assume that when first molecule of gallic acid attacks the monogallatoiron (III) complex the ring closure of this attacking molecule as shown in Figure 4 is a slower process then the attack of another molecule of gallic acid. Similar observations has been reported elsewhere [4,5 and 6]. Through this mechanism formation of bisgallatoiron(III) species is not completed and so existence of an intermediate is ruled out. During slow process of ring closure of the first gallic acid molecule the second molecule attacks to complete the formation of trisgallato iron (III) complex, hence direct formation of trisgallatoiron(III) complex from the monogallatoiron (III) complex is faster than the formation of trisgallato iron (III) from the bisgallato iron (III) complex. This is in accordance with the observations.

Figure (4)

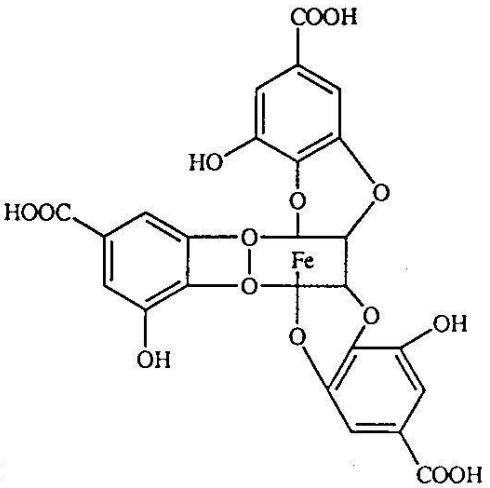




Attachment of second gallic acid molecule without ring closure



(c) No ring closure even after attachment of second molecules



(d) Both the rings have closed to produce trisgallate iron (III) complex

ii) Bisgallato iron (III) has *cis* and *trans* isomers. Formation of trisgallatoiron(III) complex from trans isomer will be slower due to difficulty in ring closure process.

The formation of trisgallatoiron(III) complex from monogallatoiron(III) complex ring closure may occur through successive attacks by the side atoms of the ligand which is quite easy. This argument would be valid if we assume that inter conversion rates of cis and trans isomers are comparable.

iii) The reacting species in formation of trisgallatoiron(III) from monogallatoiron(III) complex is neutral $[Fe(H_2L)(H_2O)_3(OH)]$ whereas the reacting specie in the formation from bisgallatoiron(III) complex $[Fe(H_2L)_2(H_2O)(OH)^{2-}]$ is an anion.

Therefore we conclude that the K_{obs} of formation from monogallato species is bound to be higher as compared to the K_{obs} of formation from bisgallatoiron(III) species. This is exactly in accordance to the observation.

Experimental

Solutions containing 7.5 x 10^{-3} mole/L of monogallatotetraquoiron(III) and bisgallatodiaquo iron(III) complexes were prepared separately in acetate buffers of pH 4.0 and 5.4 by dissolving appropriate amounts of ferric sulfate and gallic acid. These complex ion solutions were allowed to stabilize for about 15 minutes. Gallic acid solutions of 8.393 x 10^{-4}M, 1.666 x 10^{-3}M, 25000 x 10^{-3}M, 3.33 x 10^{-3}M, 4.166 x 10^{-3}M and 5.00 x 10^{-3}M were prepared in buffer of pH 8.0.

Conversion of mono to tris complex

Each gallic acid solution mentioned above was mixed separately with monogallatiron(III) complex solution in a volume ratio of 9:1 in a spectrophotometer cell which was placed in cell holder of spectronic 21 (fitted with a general purpose sample compartment (GPSC) through which water was circulating from a thermostatic water bath of Haake Germany immediately and the data was recorded with the real time graph version of MPLI (Multi purpose lab interface - an A/D conversion package; Vernier Software, Oregon, USA). The wavelength was set at 500 nm which is the λ_{max} of the tris complex [4]. This mixing was such that the effective concentration of the monogallato iron (III) complex became 7.5 x 10^{-4}M and the effective concentration of the gallic acid solutions became 7.490 x 10^{-4}M, 1.49 x 10^{-3}M, 2.25 x 10^{-3}M, 2.99 x 10^{-3}M, 3.440 x 10^{-3}M and 4.500 x 10^{-3}M respectively.

Conversion of bis to tris complex

The experiments were repeated as above by using bisgallatoiron(III) complex solution for onwards conversion to trisgallatoiron(III) complex.

References

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