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Title of the manuscript: **Mechanistic studies on oxidation of L-Ascorbic acid by an oxo-bridged diiron complex in aqueous acidic media**

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Estimation of $(K_1)_{\max}$, the maximum possible value of the pre-equilibrium constant for the inner-sphere adduct formation between 1 and HA$^-$

From *Scheme 1* (see text)

$[\mathbf{2}] = K_{a1}[\mathbf{1}]/[H^+]$ (S1)

$[\mathbf{3}] = K_{a1}K_{a2}[\mathbf{1}]/[H^+]^2$ (S2)

$[\mathbf{I}_1] = K_1[\mathbf{1}][HA^-]$ (S3)

$[\mathbf{I}_2] = K_2K_{a1}[\mathbf{1}][HA^-]/[H^+]$ (S4)

Total iron concentration, $T_c = [\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] + [\mathbf{I}_1] + [\mathbf{I}_2]$ (S5)

or, $T_c = [\mathbf{1}] + K_{a1}[\mathbf{1}]/[H^+] + K_{a1}K_{a2}[\mathbf{1}]/[H^+]^2) + K_1[\mathbf{1}][HA^-] + K_2K_{a1}[\mathbf{1}][HA^-]/[H^+]$ (S6)

Rearranging,

$[\mathbf{1}] = T_c[H^+]^2/\{([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) + (K_1[HA^-][H^+]^2 + K_2K_{a1}[HA^-][H^+])\}$ (S7)

The minimum value of $([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$ will be at highest experimental pH *viz.* 5.5, is of the order of 10^{-9}.

Assuming $(K_1[HA^-][H^+]^2 + K_2K_{a1}[HA^-][H^+]) << ([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$ as both K_1 and K_2 are expected to be small, it results,

$\{(K_1[HA^-][H^+]^2 + K_2K_{a1}[HA^-][H^+])\}_{\max} \leq 10^{-10}$ (S8)

The maximum value of ($K_1[\mathrm{HA}^-][\mathrm{H}^+]^2 + K_2K_{a1}[\mathrm{HA}^-][\mathrm{H}^+]$) will be arising from the lowest experimental pH (3.00) with highest experimental $[\mathrm{H_2A}]_\mathrm{T}$ (5×10^{-3} M) and can be expressively written as $5 \times 10^{-10}K_1 + 10 \times 10^{-10}K_2$ and thus the inequality (Equation S8) becomes,

$$5 \times 10^{-10}K_1 + 10 \times 10^{-10}K_2 \leq 10^{-10} \qquad \text{(S9)}$$

An estimated $(K_1)_\mathrm{max}$ will be thus be 10^{-1} and K_2 will be further less.

We are thus able to write Equation (S7) as,

$$[\mathbf{1}] = \mathrm{T_c}[\mathrm{H}^+]^2/([\mathrm{H}^+]^2 + K_{a1}[\mathrm{H}^+] + K_{a1}K_{a2}) \qquad \text{(S10)}$$

Rate of the reaction = $\mathrm{T_c} \times k_0$

Therefore, $\mathrm{T_c} \times k_0 = k_1[\mathbf{I}_1][\mathrm{HA}^-] + k_2[\mathbf{I}_2][\mathrm{HA}^-]$ (from *Scheme 1,* see text) (S11)

Hence, using Equations (S3), (S4), (S10) and Equation (4) of the text, Equation (S11) becomes,

$$k_0([\mathrm{H}^+]^2 + K_{a1}[\mathrm{H}^+] + K_{a1}K_{a2})(K_a + [\mathrm{H}^+])^2/([\mathrm{H}^+]^2[\mathrm{H_2A}]_\mathrm{T}^2K_a^2) = k_1K_1 + k_2K_2K_{a1}(1/[\mathrm{H}^+])$$

This is the Equation 9 of the text.

Evidence of precursor complex (adduct) formation between the diiron(III,III) complex and ascorbate

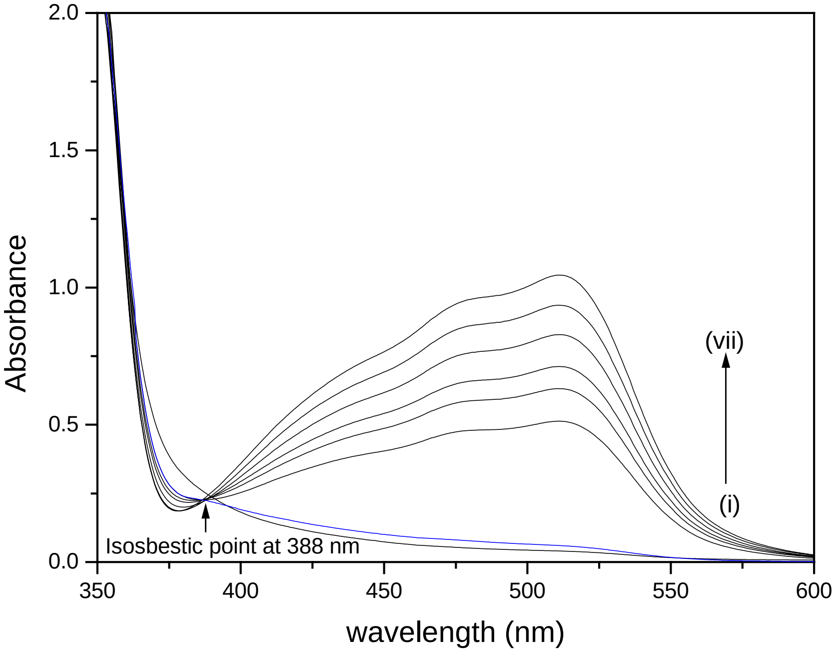

Figure S1. The spectrum of 5 × 10^{-5} M diiron(III,III) complex solution at [phen] = 3.0 × 10^{-3} M, *I* = 1.0 M ($NaNO_3$) is shown in (i). The spectrum of the diiron(III,III) complex is independent on the pH range 3.0 – 6.0. The curve shown in blue is constructed by plotting absorbances measured immediately after mixing the reagents with λ when 5 × 10^{-5} M diiron(III,III) complex is reacted with 2.5 × 10^{-4} M ascorbic acid at pH 3.00 in presence of 3 × 10^{-3} M phen (25.0 °C, *I* = 1.0 M ($NaNO_3$)). The plot of the absorbances thus found at very initial times with λ (dotted line) significantly differ from (i), the spectrum of the pure diiron(III,III) complex, indicating formation of precursor complex between the diiron(III,III) complex and ascorbate. The spectra (ii) – (vi) represent those of equilibrium mixtures of the complex with several stoichiometrically deficient amount of ascorbic acid concentration ($[H_2A]_T$ in mM = 0.025, 0.030, 0.035, 0.040 and 0.045

respectively) at pH 3.85, C_{phen} = 3.0 mM, I = 1.0 M ($NaNO_3$), T = 25.0 °C. (vii) is the spectrum of equilibrium mixture of stoichiometric amount of complex and ascorbic acid solutions (both at 0.05 mM) at C_{phen} = 3.0 mM, I = 1.0 M ($NaNO_3$) and T = 25.0 °C. The isosbestic point at 388 nm is shown in this figure (see text). The spectrum of the pure diiron(III,III) complex does not pass through the isosbestic at 388 nm.