ESI (ELECTRONIC SUPPLEMENTARY INFORMATION)

# Mechanistic studies on oxidation of Hydrogen Peroxide by an oxo-bridged diiron complex in aqueous acidic media

**Suranjana Das, Jhimli Bhattacharyya, and Subrata Mukhopadhyay***

**Department of Chemistry, Jadavpur University, Kolkata 700 032, India**

**E-mail: smukhopadhyay@chemistry.jdvu.ac.in**

1. **Calculations for the expected absorption (measured at 510 nm) and comparison with the observed value (see Fig. 2(ii) of the main text)**

$[Fe(III,III)]_t = [Fe(III,III)]_0 \exp(-k_0 t)$  (first-order decay of the diiron(III,III) complex)

whence, we can write,

$2.303\log_{10}[Fe(III,III)]_t = 2.303\log_{10}[Fe(III,III)]_0 - kt$

Thus, at t = 60 seconds (1 minute, see Fig. 2(ii) of the main text), $[Fe(III,III)]_t = 4.86 \times 10^{-5}$ (M) ($k_0 = 47.9 \times 10^{-5}$ s$^{-1}$, see Table 1 of the manuscript), [Fe(III,III)] consumed = $[Fe(III,III)]_0$ - $[Fe(III,III)]_{60\ seconds}$ = $(5.0 \times 10^{-5} - 4.86 \times 10^{-5})$ (M) = $1.40 \times 10^{-6}$ (M).

[Ferroin] produced at 60 seconds (1 minute) = $2 \times$ [Fe(III,III)] consumed = $2.80 \times 10^{-6}$ (M).

Absorbance of the solution at 60 seconds (1 minute) at 510 nm = $(4.86 \times 10^{-5} \times 790)$ + $(2.80 \times 10^{-6} \times 1.1 \times 10^4)$ = 0.069.

The observed absorbance at 510 nm (Figure 2 of the manuscript, spectrum (ii)) = 0.073, which is very near to the calculated value (0.069).

In spectrum (ii) to (ix) (Fig. 2 of the main text) progressive generation of more and more $[Fe(phen)_3]^{2+}$ is reflected and the diiron(III,III) complex decayed continually. This, along with the fact that at 1 minute (spectrum (ii) of Fig. 2, which is the nearest spectrum after the spectrum of immediate mixing of the reagents) the spectral data nicely matched with the calculated value (at 510 nm described above), clearly establishes that isosbestic point must not be due to any induction period of the reaction, rather isosbestic may be due to a post-kinetic phenomenon like

$$[Fe(phen)_2(H_2O)_2]^{2+} + phen \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Fe(phen)_3]^{2+} \ldots \qquad \ldots \qquad \ldots \qquad (1)$$
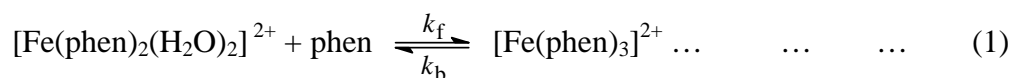
The equilibrium constant of this reaction is high ($10^{10}$ $M^{-1}$) and the formation rate constant ($k_f$) of $[Fe(phen)_3]^{2+}$ is also high ($7.5 \times 10^5$ $M^{-1}s^{-1}$, see main text), much quicker than the observed kinetics and so this equilibrium could not affect the observed kinetics. We have already clarified that there is no induction period. The loss of diiron(III,III) complex is equal to twice that of formation of $[Fe(phen)_3]^{2+}$ at any time. Moreover, we already have discussed in the manuscript that after one-electron rate step the subsequent steps are fast leading to $[Fe(phen)_2(H_2O)_2]^{2+}$ which then forms $[Fe(phen)_3]^{2+}$ in presence of excess 1,10-phenanthroline.

The 390 nm isosbestic should appear due to a particular (single) equilibrium where one of the species must be $[Fe(phen)_3]^{2+}$. Another species which is in equilibrium with it ($[Fe(phen)_3]^{2+}$) is expected to be $[Fe(phen)_2(H_2O)_2]^{2+}$ (and possibly not $[Fe(phen)(H_2O)_4]^{2+}$ as the initial diiron(III,III) complex contains two 1,10-phenanthroline per iron(III)).

2. **Estimation of the maximum possible value of the pre-equilibrium constant ($K_e$) for the adduct formation between 1 and $H_2O_2$**

From *Scheme 1* (see text)

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

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

$[Int] = K_e[1][H_2O_2]$ (S3)

$[Int_1] = K_1K_e[1][H_2O_2]/[H^+]$ (S4)

$[Int_2] = K_1K_2K_e[1][H_2O_2]/[H^+]^2$ (S5)

Total iron concentration, $T_c = [1] + [2] + [3] + [Int] + [Int_1] + [Int_2]$ (S6)

or, $T_c = [1] + K_{a1}[1]/[H^+] + K_{a1}K_{a2}[1]/[H^+]^2 + K_e[1][H_2O_2]$

$\quad\quad K_1K_e[1][H_2O_2]/[H^+] + K_1K_2K_e[1][H_2O_2]/[H^+]^2$ (S7)

Rearranging,

$T_c/[1] = 1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2 + K_e[H_2O_2] +$

$\quad\quad K_1K_e[H_2O_2]/[H^+] + K_1K_2K_e[H_2O_2]/[H^+]^2$ (S8)

To derive the rate law (see eqn. 9, main text), the summation of the last three terms of eqn. (S8) must be much smaller than the summation of the first three terms. The minimum value of $(1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2)$ would be achieved at lowest pH studied, *viz.* at pH 3.5 which renders $(1 + K_{a1}/[H^+] + K_{a1}K_{a2}/[H^+]^2)_{min} \sim 1$. Thus, $(K_e[H_2O_2] + K_1K_e[H_2O_2]/[H^+] + K_1K_2K_e[H_2O_2]/[H^+]^2)$ must be much smaller than 1, say, $10^{-1}$. In other words, $K_e[H_2O_2]$ should also be much smaller than 1.

For the inequality, $K_e[H_2O_2] \ll 1$, say $K_e[H_2O_2] = 0.01$, it results $(K_e)_{max} \sim 10$ as the minimum concentration of $H_2O_2$ used is $1.0 \times 10^{-3}$ M.

Thus, the estimated upper limit of $K_e$ is at the level of 10.