Supporting Information

to

pH Effects on Iron-Catalyzed Oxidation using Fenton's Reagent

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Mathematical Justification of Use of Scavenging Factor, Θ

Key reactions relating to Fenton-mediated hydroxyl radical production and consumption by both target formic acid (HCOOH) and a scavenger (Scav) that competes with formic acid for hydroxyl radicals can be written:

Fenton $\rightarrow$ $HO^{\bullet}$ Production rate = k $M.s^{-1}$

where production rate can be assumed constant for any given pH, $[Fe]_T$, $[HCOOH]_T$ and $[H_2O_2]_T$

$HCOOH + HO^{\bullet} \rightarrow$ products Rate constant k_{HCOOH}

$Scav + HO^{\bullet} \rightarrow$ products Rate constant k_{Scav}

Rate expressions for these reactions can be written as:

$$\frac{d[HCOOH]}{dt} = -k_{HCOOH}[HCOOH][HO^{\bullet}]$$

$$\frac{d[Scav]}{dt} = -k_{Scav}[Scav][HO^{\bullet}]$$

$$\frac{d[HO^{\bullet}]}{dt} = k - k_{HCOOH}[HCOOH][HO^{\bullet}] - k_{Scav}[Scav][HO^{\bullet}]$$

Since $HO^{\bullet}$ is both produced and consumed in these reactions, it will reach a steady state concentration, $[HO^{\bullet}]_{ss}$ thus

$$\frac{d[HO^{\bullet}]_{ss}}{dt} = 0 = k - k_{HCOOH}[HCOOH][HO^{\bullet}]_{ss} - k_{Scav}[Scav][HO^{\bullet}]_{ss}$$

where $[HO^{\bullet}]_{ss} = \dfrac{k}{k_{HCOOH}[HCOOH] + k_{Scav}[Scav]}$

Obviously, if no scavenger had been present,

$$[HO^{\bullet}]_{SS}^{\text{No Scav}} = \frac{k}{k_{HCOOH}[HCOOH]}$$

Thus, a rate expression for the degradation of HCOOH that accounts for the presence of a scavenger but is expressed in scavenger free terms can be written as:

$$\frac{d[\mathrm{HCOOH}]}{dt} = -\left(\frac{[\mathrm{HO}^{\bullet}]_{ss}}{[\mathrm{HO}^{\bullet}]_{ss}^{\text{No Scav}}}\right) k_{\mathrm{HCOOH}}[\mathrm{HCOOH}][\mathrm{HO}^{\bullet}]_{ss}^{\text{No Scav}}$$

$$= -\left(\frac{k_{\mathrm{HCOOH}}[\mathrm{HCOOH}]}{k_{\mathrm{HCOOH}}[\mathrm{HCOOH}] + k_{\mathrm{Scav}}[\mathrm{Scav}]}\right) k_{\mathrm{HCOOH}}[\mathrm{HCOOH}][\mathrm{HO}^{\bullet}]_{ss}^{\text{No Scav}}$$

$$= -\,\Theta\; k_{\mathrm{HCOOH}}[\mathrm{HCOOH}][\mathrm{HO}^{\bullet}]_{ss}^{\text{No Scav}}$$

where $\Theta = \dfrac{k_{\mathrm{HCOOH}}[\mathrm{HCOOH}]}{k_{\mathrm{HCOOH}}[\mathrm{HCOOH}] + k_{\mathrm{Scav}}[\mathrm{Scav}]}$