Supporting Information

Why the Reactive Oxygen Species of the Fenton Reaction Switches from Oxoiron(IV) Species to Hydroxyl Radical in Phosphate Buffer Solutions? A Computational Rationale

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Table S1. Gas-phase electronic energy change (kcal/mol) of $[Fe^{II}H_2O]^{2+} + H_2PO_4^- \rightarrow [Fe^{II}H_2PO_4]^+ + H_2O$.

method	ΔE
B3LYP-D3/6-31+G(d)	–301.7
PBE0-D3/6-31+G(d)	–301.9
M06-D3/6-31+G(d)	–303.5
PW6B95-D3/6-31+G(d)	–296.9
PW6B95-D3/Def2-TZVP	–300.3
PW6B95-D3/Def2-QZVP	–300.0
BD(T)/Def2-TZVPP	–293.4

Table S2. Hydration energies (kcal/mol) of H_2O and $H_2PO_4^-$. Signed errors are given in parentheses.[a]

method	H_2O	$H_2PO_4^-$
SMD/PW6B95-D3/6-31+G(d)[d]	–9.3 (–3.0)	–76.9 (–8.9)
IEF-PCM/PW6B95-D3/6-31+G(d)[d]	–5.4 (0.9)	–67.1 (0.9)
CPCM/PW6B95-D3/6-31+G(d)[d]	–5.5 (0.8)	–67.2 (0.8)
Expt.	–6.3	–68

[a] Theoretical hydration energies were evaluated by the difference between solution-phase electronic energy and gas-phase electronic energy at solution-phase optimized geometry.

Table S3. Free energy change (kcal/mol) of successive H_2O exchange by $H_2PO_4^-$ for $[Fe^{II}(H_2O)_6]^{2+}$.[a]

n	CPCM/PBE0/6-31+G(d)	SMD/PBE0/6-31+G(d)	CPCM/M06/6-31+G(d)	CPCM/PW6B95/6-31+G(d)	CPCM/PBE0/Def2-TZVP[b]	CPCM/PBE0/Def2-QZVP[b]
1	–16.5	–13.7	–15.5	–17.4	–18.1	–16.9
2	–14.8	–12.9	–14.6	–15.2	–16.3	–15.4
3	–13.1	–13.4	–11.5	–10.8	–16.4	–14.2
4	–11.8	–13.3	–11.0	–13.6	–9.4	–7.5
5	–8.4	–14.7	–7.8	–7.4	–9.2	–8.8
6	–6.0	–8.0	–5.4	–4.1	–5.9	–5.3

[a] Grimme's D3 dispersion correction was included and experimental hydration energies of H_2O and $H_2PO_4^-$ were employed in all calculations.

[b] CPCM/PBE0/6-31+G(d) optimized geometries are used.

Table S4. Average bond distances and standard deviations (Å)

bond label[a]	bond distance	standard deviation
FeL_1	2.339	0.144
FeL_2	2.228	0.109
FeL_3	2.131	0.097
FeL_4	2.212	0.130
FeL_5	2.031	0.069
FeL_6	2.071	0.087
HB_1	2.166	0.518
HB_2	1.883	0.168
HB_3	3.101	0.396
HB_4	1.783	0.184
HB_5	1.830	0.199
HB_6	1.799	0.142
HB_7	1.701	0.085
HB_8	1.735	0.145
HB_9	1.982	0.183

[a] See Figure 1 for bond label

Table S5. Calculated $\langle S^2 \rangle$ values.

	spin state	calculated $\langle S^2 \rangle$	exact $\langle S^2 \rangle$
$[Fe^{II}(H_2O)_6]^{2+}$	quintet	6.0046	6.0000
$[Fe^{II}(H_2PO_4)(H_2O)_5]^{+}$	quintet	6.0048	6.0000
$[Fe^{II}(H_2PO_4)_2(H_2O)_4]$	quintet	6.0051	6.0000
$[Fe^{II}(H_2PO_4)_3(H_2O)_3]^{-}$	quintet	6.0050	6.0000
$[Fe^{II}(H_2PO_4)_4(H_2O)_2]^{2-}$	quintet	6.0050	6.0000
$[Fe^{II}(H_2PO_4)_5(H_2O)]^{3-}$	quintet	6.0051	6.0000
$[Fe^{II}(H_2PO_4)_6]^{4-}$	quintet	6.0051	6.0000
RC	quintet	6.0059	6.0000
$\mathbf{INT1_{OH/\bullet OH}}$	quintet	6.9681	6.0000
$\mathbf{INT2_{OH/\bullet OH}}$	quintet	7.0081	6.0000
$\mathbf{INT_{FeIII+\bullet OH}}$	quintet	7.0080	6.0000
$\mathbf{INT_{oxo}}$	quintet	6.1180	6.0000
$[Fe^{III}(H_2O)_6]^{3+}$	sextet	8.7546	8.7500
$[Fe^{III}(H_2PO_4)(H_2O)_5]^{2+}$	sextet	8.7554	8.7500
$[Fe^{III}(H_2PO_4)_2(H_2O)_4]^{+}$	sextet	8.7556	8.7500
$[Fe^{III}(H_2PO_4)_3(H_2O)_3]$	sextet	8.7556	8.7500
$[Fe^{III}(H_2PO_4)_4(H_2O)_2]^{-}$	sextet	8.7560	8.7500
$[Fe^{III}(H_2PO_4)_5(H_2O)]^{2-}$	sextet	8.7559	8.7500
$[Fe^{III}(H_2PO_4)(OH)(H_2O)_4]^{+}$	sextet	8.7568	8.7500
$[Fe^{III}(H_2PO_4)_2(OH)(H_2O)_3]$	sextet	8.7562	8.7500
$[Fe^{III}(H_2PO_4)_3(OH)(H_2O)_2]^{-}$	sextet	8.7557	8.7500
$[Fe^{III}(H_2PO_4)_4(OH)(H_2O)]^{2-}$	sextet	8.7560	8.7500
$[Fe^{III}(H_2PO_4)_5(OH)]^{3-}$	sextet	8.7558	8.7500
$[Fe^{III}(HPO_4)(H_2O)_5]^{+}$	sextet	8.7571	8.7500
$[Fe^{III}(H_2PO_4)(HPO_4)(H_2O)_4]$	sextet	8.7561	8.7500
$[Fe^{III}(H_2PO_4)_2(HPO_4)(H_2O)_3]^{-}$	sextet	8.7558	8.7500
$[Fe^{III}(H_2PO_4)_3(HPO_4)(H_2O)_2]^{2-}$	sextet	8.7560	8.7500
$[Fe^{III}(H_2PO_4)_4(HPO_4)(H_2O)]^{3-}$	sextet	8.7556	8.7500

Spin contamination for every intermediate was examined. It was found that for most intermediates spin contamination problem is negligible, except for $\mathbf{INT1_{OH/\bullet OH}}$, $\mathbf{INT2_{OH/\bullet OH}}$, and $\mathbf{INT_{FeIII+\bullet OH}}$, which exhibit a moderate spin contamination. For the three cases, the •OH is distant from the Fe(III) center and, thus, the spin coupling between •OH and five spins on Fe(III) is very weak. As a consequence, the anti-ferromagnetic coupling (quintet state) and ferromagnetic coupling (septet state) of these intermediates are very close in energy, resulting in spin-state mixing.[53]

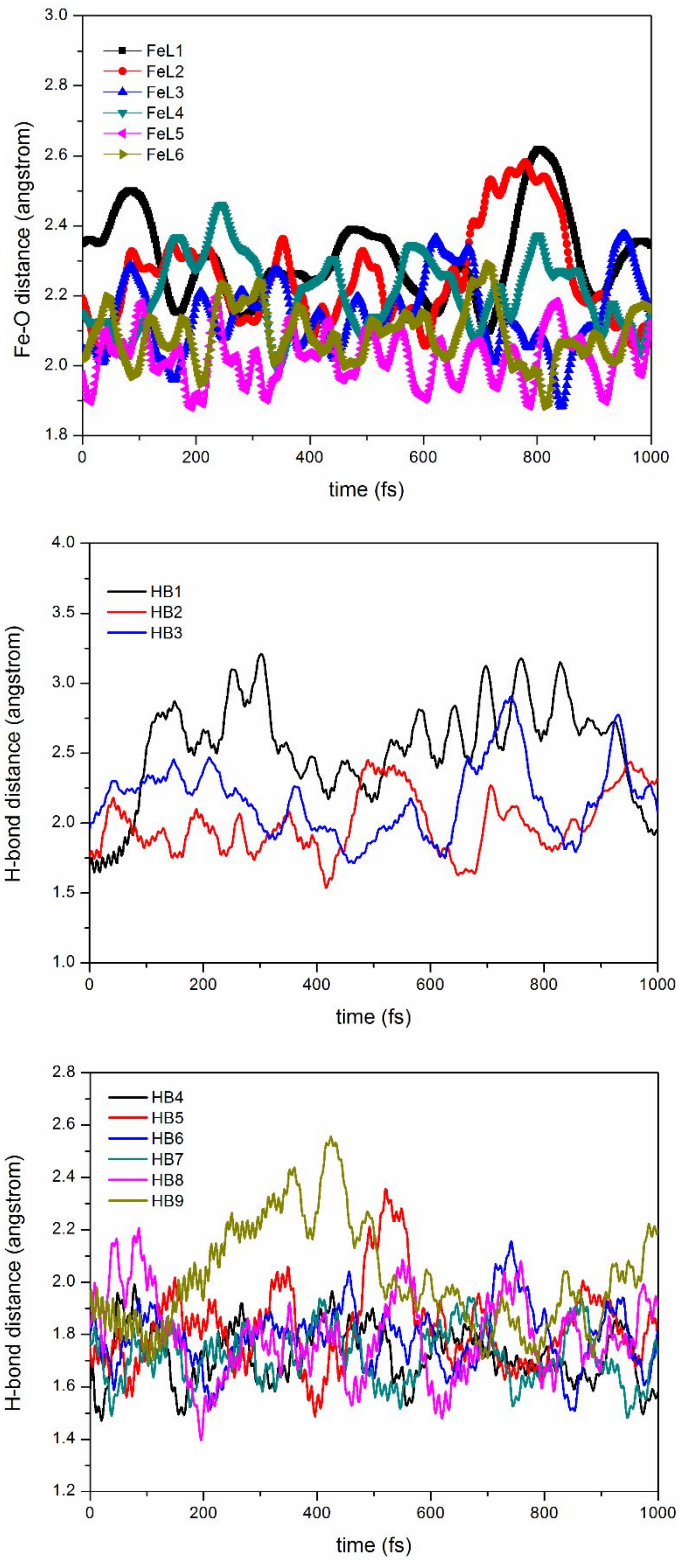

Figure S1. Time evolution of Fe-ligand and H-bond distances for trajectory 2. See Figure 1 for bond label.

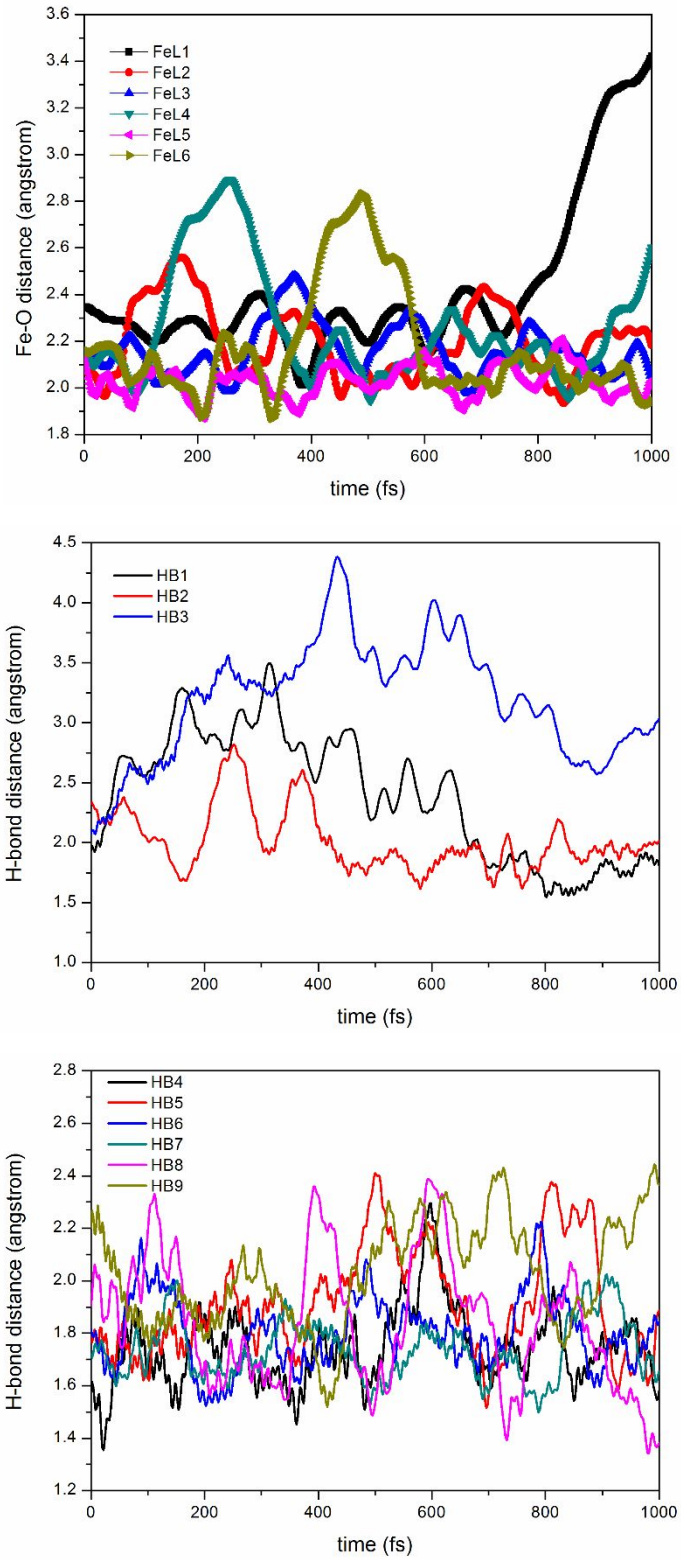

Figure S2. Time evolution of Fe-ligand and H-bond distances for trajectory 3. See Figure 1 for bond label.