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SUPPORTING INFORMATION

Interplay of Proton Transfer and Electron Transfer to Determine Concerted Behavior in the Oxidation of Glutathione by Oxidant-Base Pairs of Variable Redox Potential and pK_a

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Table S1. Values of ΔG°' (eV) versus GSH with Oxidant-Base Pairs

Buffer pKa	*ΔG°'PT*	*ΔG°'ET*		
		$Mo(CN)_8^{3-}$	$IrCl_6^{2-}$	$Fe(phen)_3^{3+}$
5.1	0.212871	0.209410	0.062408	-0.034594
5.6	0.183306	0.179924	0.032921	-0.064081
6.2	0.147827	0.144583	-0.002419	-0.099421
6.5	0.130088	0.126963	-0.020039	-0.117041
7.2	0.088696	0.086299	-0.060703	-0.157705

Detailed procedure for the calculation of $\Delta G^{\circ\prime}_{PT}$ and $\Delta G^{\circ\prime}_{ET}$:

The redox potentials for mediators were determined from half-wave redox potentials of experimental cyclic voltammograms with various scan rates. The apparent redox potentials for mediators were: $E^0_{app}(Mo(CN)_8^{3-}/Mo(CN)_8^{4-})$ = 0.583 V vs. Ag/AgCl; $E^0_{app}(IrCl_6^{2-}/IrCl_6^{3-})$ = 0.730 V vs. Ag/AgCl; $E^0_{app}(Fe(phen)_3^{3+}/Fe(phen)_3^{2+})$ = 0.827 V vs. Ag/AgCl. Eq. S1reported by Madej was used to calculate the E^0_{app} values of GSH in buffered solutions.[1] Here, pK_a value for thiol group of GSH is 8.7 (pK_{aSH}); $E^0(GS^\bullet/GS^-)$ = 0.58 V vs. Ag/AgCl, pH = pK_a.

$$E^{\circ}_{app}(GS^{\bullet}, H^{+}/GS^{-}) = E^{\circ}(GS^{\bullet}/GS^{-}) + 0.059\log\left(1 + \frac{H^{+}}{K_{aSH}}\right) \qquad \text{Eq. S1}$$

When pH = 5.1, $E^0_{app}(GS^\bullet, H^+/GS^-) = 0.58 + 0.059\log\left(1 + \frac{10^{-5.1}}{10^{-8.7}}\right) = 0.792406$ V;

pH = 5.6, $E^0_{app}(GS^\bullet, H^+/GS^-) = 0.58 + 0.059\log\left(1 + \frac{10^{-5.6}}{10^{-8.7}}\right) = 0.762920$ V;

pH = 6.2, $E^0_{app}(GS^\bullet, H^+/GS^-) = 0.58 + 0.059\log\left(1 + \frac{10^{-6.2}}{10^{-8.7}}\right) = 0.727581$ V;

pH = 6.5, $E^0_{app}(GS^\bullet, H^+/GS^-) = 0.58 + 0.059\log\left(1 + \frac{10^{-6.5}}{10^{-8.7}}\right) = 0.709961$ V;

pH = 7.2, $E^0_{app}(GS^\bullet, H^+/GS^-) = 0.58 + 0.059\log\left(1 + \frac{10^{-7.2}}{10^{-8.7}}\right) = 0.669298$ V.

Concerted mechanism was obtained for the mediated oxidation of GSH in the range of pH below pK_{aSH} (8.7). Eq. S2 and Eq. S3 show the concerted rate-determining step followed by the fast dimerization of the thiyl radical.

$$GSH + M^{+} + B \rightleftharpoons GS^{\bullet} + M + BH^{+} \quad \text{Eq. S2} \qquad GS^{\bullet} + GS^{\bullet} \rightleftharpoons GSSG \quad \text{Eq. S3}$$

According to the relationship between Gibbs free energy change, ΔG°', and equilibrium constants, the driving force for proton transfer (PT) was calculated by Eq. S4, where, R = 8.314462 J $\mathrm{mol^{-1}\ K^{-1}}$, T = 298 K, 1 eV = 1.60218 x 10^{-19} J, Avogadro constant N_A = 6.022 x 10^{23} $\mathrm{mol^{-1}}$, pH = pK_a.

$$\Delta G°'_{PT} = -RTln(\frac{K_{aSH}}{K_{a(base)}}) \qquad \text{Eq. S4}$$

When pH = 5.1, $\Delta G°'_{PT} = -8.314462\ \mathrm{J\ mol^{-1}K^{-1}}\ 298\ K\ ln(\frac{10^{-8.7}}{10^{-5.1}})$ = 20.53849 KJ $\mathrm{mol^{-1}}$ = $\frac{20.53849\ X\ 1000}{(1.60218\ X\ 10^{-19}\ )\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.212871 eV;

pH = 5.6, $\Delta G°'_{PT} = -8.314462\ \mathrm{J\ mol^{-1}K^{-1}}\ 298\ K\ ln(\frac{10^{-8.7}}{10^{-5.6}})$ = 17.68593 KJ $\mathrm{mol^{-1}}$ = $\frac{17.68593\ X\ 1000}{(1.60218\ X\ 10^{-19}\ )\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.183306 eV;

pH = 6.2, $\Delta G°'_{PT} = -8.314462\ \mathrm{J\ mol^{-1}K^{-1}}\ 298\ K\ ln(\frac{10^{-8.7}}{10^{-6.2}})$ = 14.26284 KJ $\mathrm{mol^{-1}}$ = $\frac{14.26284\ X\ 1000}{(1.60218\ X\ 10^{-19}\ )\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.147827 eV;

pH = 6.5, $\Delta G°'_{PT} = -8.314462\ \mathrm{J\ mol^{-1}K^{-1}}\ 298\ K\ ln(\frac{10^{-8.7}}{10^{-6.5}})$ = 12.55130 KJ $\mathrm{mol^{-1}}$ = $\frac{12.55130\ X\ 1000}{(1.60218\ X\ 10^{-19}\ )\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.130088 eV;

pH = 7.2, $\Delta G°'_{PT} = -8.314462\ \mathrm{J\ mol^{-1}K^{-1}}\ 298\ K\ ln(\frac{10^{-8.7}}{10^{-7.2}})$ = 8.557706 KJ $\mathrm{mol^{-1}}$ = $\frac{8.557706\ X\ 1000}{(1.60218\ X\ 10^{-19}\ )\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.088696 eV.

The driving force of electron transfer (ET) reaction step was calculated by Eq. S5, where, M/M^+ represents mediator, n is the number of electron transfer, Faraday constant F = 96485 C $\mathrm{mol^{-1}}$, 1 J (joules) = 1 V(volts) X 1 C (coulombs).

$$\Delta G°'_{ET} = -nF(E^0_{app}(M/M^+) - E^0_{app}(GS^\bullet, H^+\ /GS^-)) \qquad \text{Eq. S5}$$

For the redox mediator $Mo(CN)_8^{3-}$/$Mo(CN)_8^{4-}$, when

pH = pK_a = 5.1,

$\Delta G°'_{ET} = -1\ X\ 96485\ \mathrm{C\ mol^{-1}}(0.583\ V - 0.792406\ \mathrm{V})$ = 20.20457 KJ $\mathrm{mol^{-1}}$ = $\frac{20.20457\ X\ 1000}{(1.60218\ X\ 10^{-19}\ )\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.209410 eV;

pH = pK_a = 5.6,

$\Delta G°'_{ET} = -1\ X\ 96485\ \mathrm{C\ mol^{-1}}(0.583\ V - 0.762920\ \mathrm{V})$ = 17.3596 KJ $\mathrm{mol^{-1}}$ = $\frac{17.3596\ X\ 1000}{(1.60218\ X\ 10^{-19})\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.179924 eV;

pH = pK_a = 6.2,

$\Delta G°'_{ET} = -1\ X\ 96485\ \mathrm{C\ mol^{-1}}(0.583\ V - 0.727581\ \mathrm{V})$ = 13.94988 KJ $\mathrm{mol^{-1}}$ = $\frac{13.94988\ X\ 1000}{(1.60218\ X\ 10^{-19})\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.144583 eV;

pH = pK_a = 6.5,

$\Delta G°'_{ET} = -1\ X\ 96485\ \mathrm{C\ mol^{-1}}(0.583\ V - 0.709961\ \mathrm{V})$ = 12.24984 KJ $\mathrm{mol^{-1}}$ = $\frac{12.24984\ X\ 1000}{(1.60218\ X\ 10^{-19})\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.126963 eV;

pH = pK_a = 7.2,

$\Delta G°'_{ET} = -1\ X\ 96485\ \mathrm{C\ mol^{-1}}(0.583\ V - 0.669298\ \mathrm{V})$ = 8.326436 KJ $\mathrm{mol^{-1}}$ = $\frac{8.326436\ X\ 1000}{(1.60218\ X\ 10^{-19})\ X\ (6.022\ \mathrm{X}\ 10^{23})}$ = 0.086299 eV;

The $\Delta G°'_{ET}$ values for $\mathrm{IrCl_6}^{2-}$/$\mathrm{IrCl_6}^{3-}$ and $\mathrm{Fe(phen)_3}^{3+}$/$\mathrm{Fe(phen)_3}^{2+}$ were calculated using the same procedures for $\mathrm{Mo(CN)_8}^{3-}$/$\mathrm{Mo(CN)_8}^{4-}$ and correlated values were listed in Table S1.

Diffusion coefficients of GSH, mediators and buffers components

Species	**Diffusion Coefficient/ 10^6 cm^2 s^{-1}**
GSH	$(5.13 \pm 0.05)^a$
$IrCl_6^{2-}/IrCl_6^{3-}$	$(7.0 \pm 1.0)^b$
$Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$	$(3.1 \pm 0.1)^b$
$Fe(bpy)_3^{3+}/Fe(bpy)_3^{2+}$	$(2.9 \pm 0.1)^b$
$Mo(CN)_8^{3-}/Mo(CN)_8^{4-}$	$(2.82 \pm 0.04)^b$
$H_2PO_4^-$	9.59^c
HPO_4^{2-}	7.59^c
malate^{1-}/ malate^{2-}	7.83^c
succinate^{1-}/ succinate^{2-}	7.83^c
citrate^{2-} / citrate^{3-}	6.23^c
maleate^{1-}/ maleate^{2-}	8.24^c

Table S2. Diffusion coefficient of all species used to simulate the cyclic voltammetry of GSH in the presence of different metal complexes and Brönsted bases B.

[a] Determined by Pulsed Gradient Echo (PGE) ^1H NMR as described in the experimental section; the diffusion coefficient of all the glutathione derived species (i.e. G$^•$, GG and G”) was assumed to be the same as that of glutathione (G). [b] Estimated though digital simulation of cyclic voltammograms of aqueous solutions of 1.0 mM of metal complex alone. [c] Obtained from the CRC Handbook of Chemistry and Physics; the same diffusion coefficient was assumed for all deprotonation states of malic, succinic, citric and maleic species.

Simulation of experimental CV response of GSH and $Fe(phen)_3SO_4$ with dilute buffer concentrations

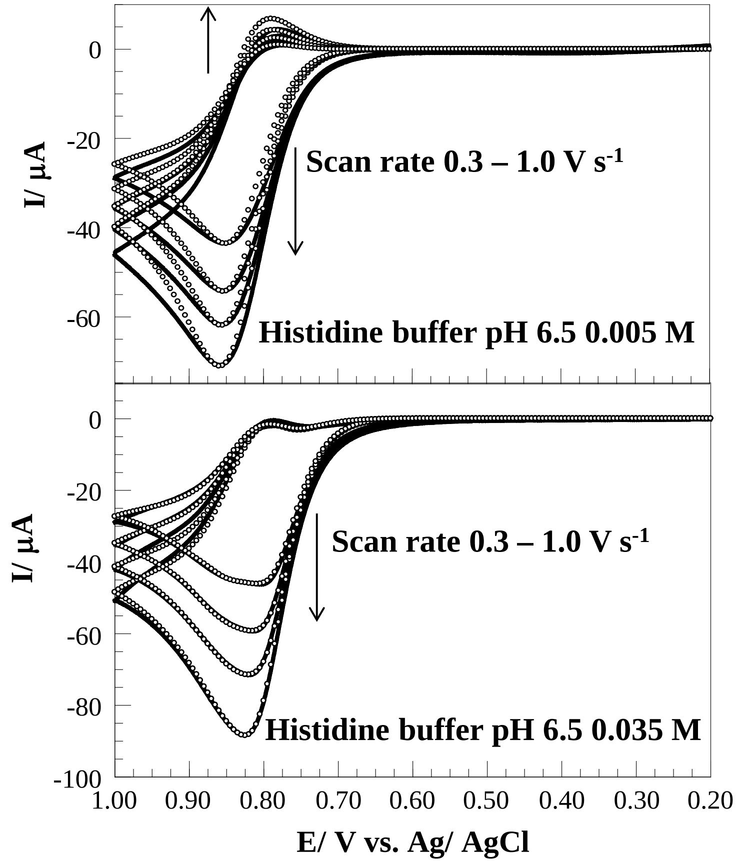

Figure S1. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $Fe(phen)_3SO_4$, in histidine buffer pH = pK_a = 6.5. Scan rates were 0.3, 0.5, 0.7 and 1.0 V s^{-1}.

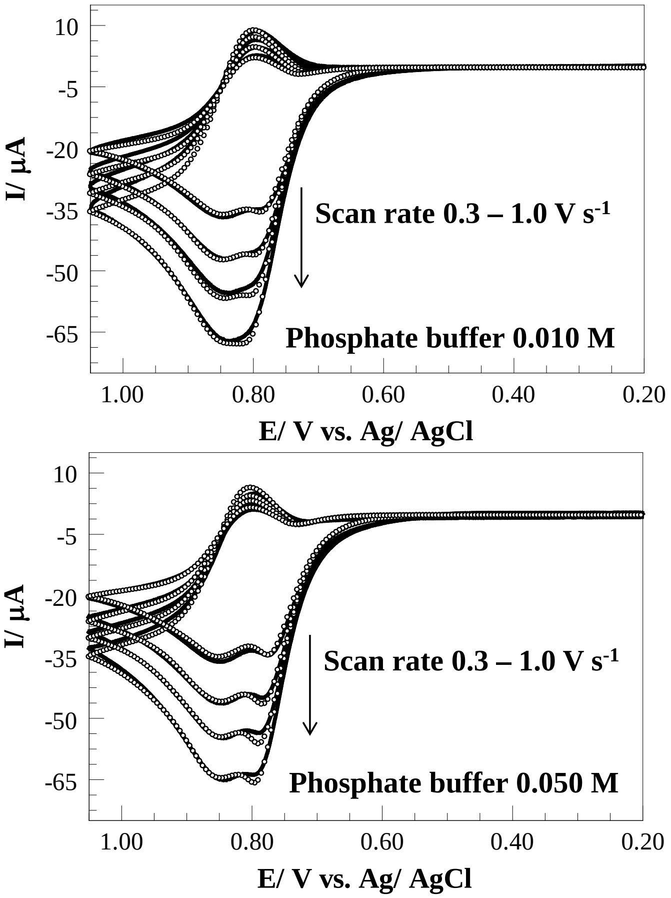

Figure S2. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM Fe(phen)$_3$SO$_4$, at pH 7.0. Scan rates were 0.3, 0.5, 0.7 and 1.0 V s^{-1}.

Simulation of experimental CV response of GSH and $Fe(phen)_3SO_4$ at various scan rates

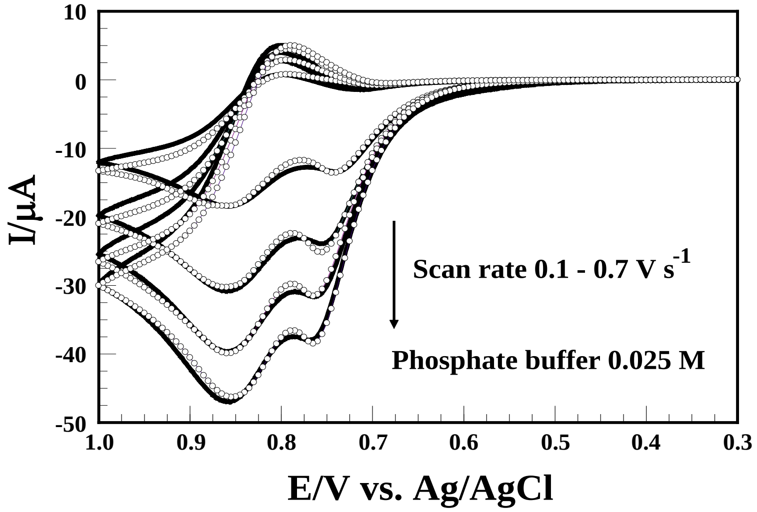

Figure S3. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $Fe(phen)_3SO_4$, at pH 10.00. Scan rates were 0.1, 0.3, 0.5 and 0.7 V s^{-1}.

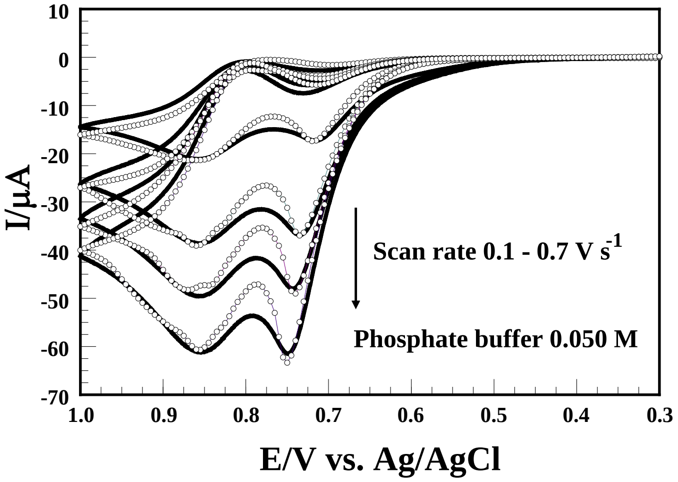

Figure S4. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $Fe(phen)_3SO_4$, at pH 10.00. Scan rates were 0.1, 0.3, 0.5 and 0.7 V s^{-1}.

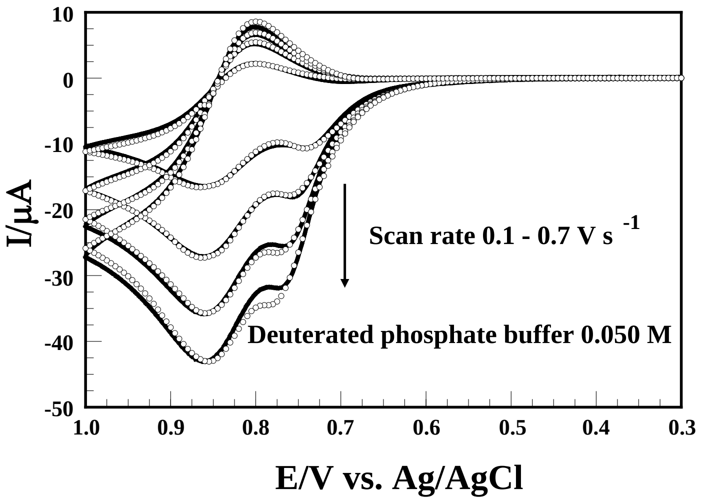

Figure S5. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $Fe(phen)_3SO_4$, at pD 10.00. Scan rates were 0.1, 0.3, 0.5 and 0.7 V s^{-1}.

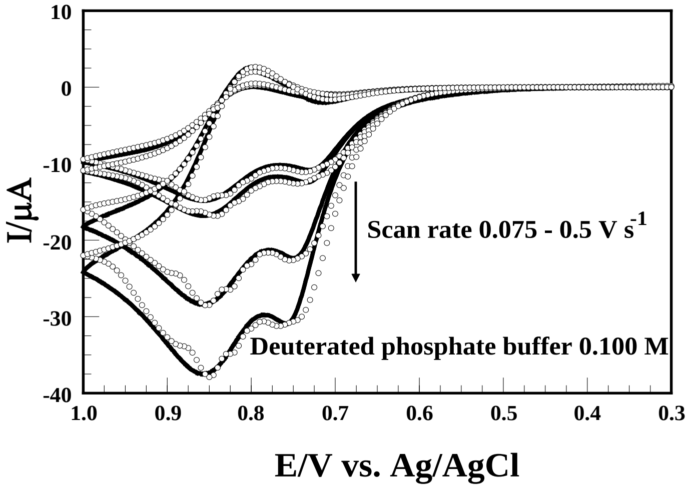

Figure S6. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $Fe(phen)_3SO_4$, at pD 10.00. Scan rates were 0.075, 0.1, 0.3 and 0.5 V s^{-1}.

Simulation of experimental CV response of GSH and $K_4Mo(CN)_8$ at various scan rates

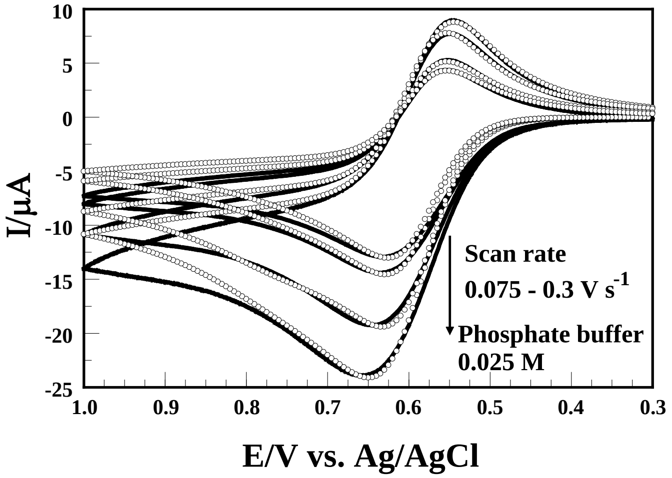

Figure S7. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $K_4Mo(CN)_8$, at pH 10.00. Scan rates were 0.075, 0.1, 0.2 and 0.3 V s^{-1}.

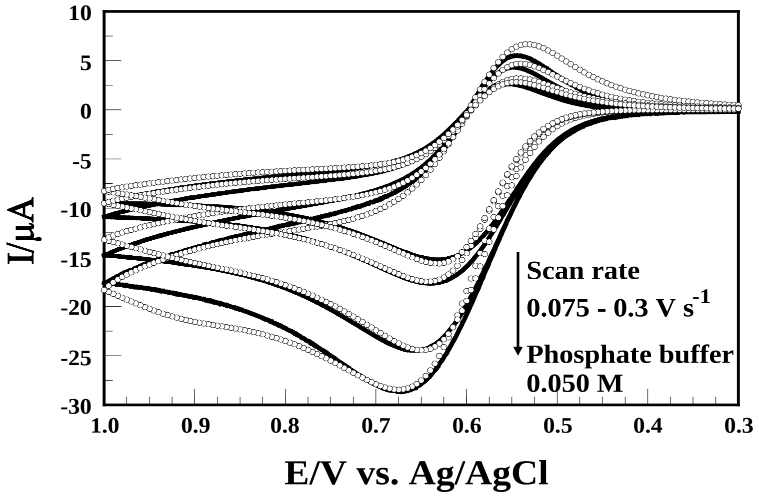

Figure S8. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $K_4Mo(CN)_8$, at pH 10.00. Scan rates were 0.075, 0.1, 0.2 and 0.3 V s^{-1}.

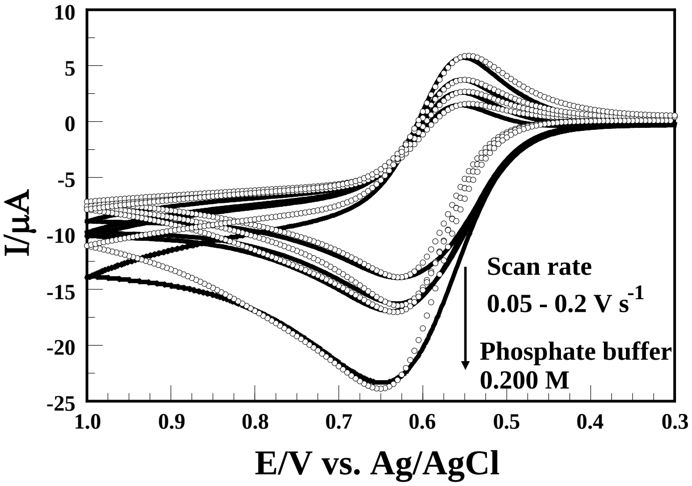

Figure S9. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $K_4Mo(CN)_8$, at pH 10.00. Scan rates were 0.05, 0.075, 0.1 and 0.2 V s^{-1}.

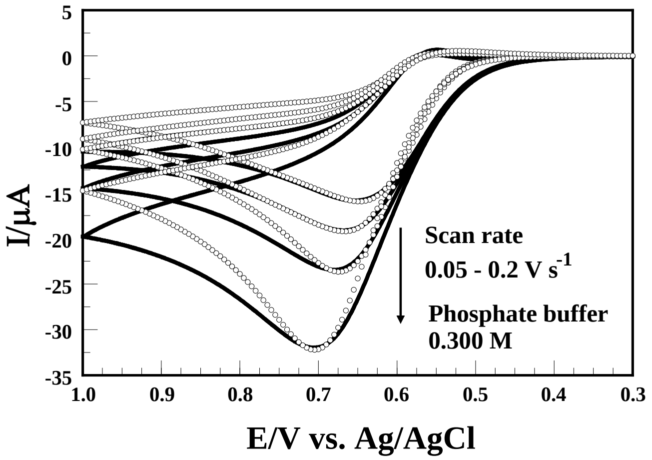

Figure S10. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $K_4Mo(CN)_8$, at pH 10.00. Scan rates were 0.05, 0.075, 0.1 and 0.2 V s^{-1}.

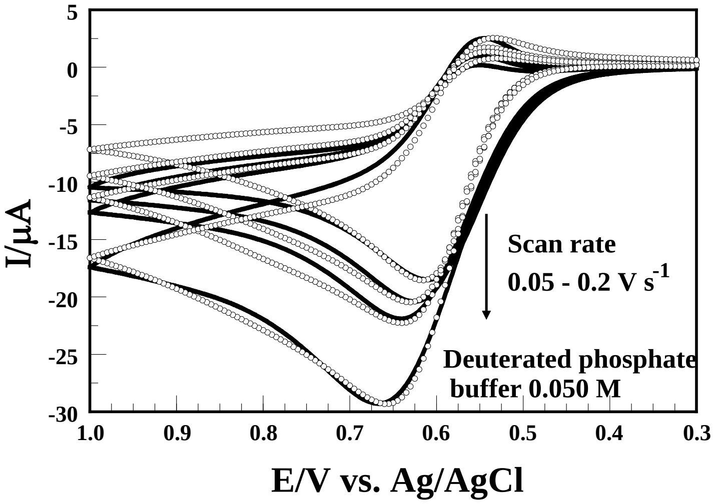

Figure S11. Experimental (solid line) and simulated (open circles) CV response of 1.0 mM GSH + 1.0 mM $K_4Mo(CN)_8$, at pD 10.00. Scan rates were 0.05, 0.075, 0.1 and 0.2 V s^{-1}.

Parameters used in digital simulations of cyclic voltammograms

The following are the electrochemical and kinetic parameters that best fitted the experimental voltammetry. The CV data for the oxidation of GSH by electrogenerated mediators recorded in DI water with various concentrations of phosphate buffer and 1.0 M NaCl as the supporting electrolyte at a 3 mm diameter glassy carbon electrode at room temperature. The values in the tables obtained from the average of the simulated electrochemical and kinetic parameters at various scan rates between 0.05 – 1 V s^{-1}. The numbers on the left side of the parameter tables in the supporting information mean the same number of the reaction steps of Table 1 and Table 2 in the paper.

Units for fitted parameters: redox potential (E) : V ; diffusion coefficient (D) : cm^2 s^{-1} ; heterogeneous rate constant (k_s) : cm s^{-1}; transfer coefficient (α) : unitless ; homogeneous rate constants for the forward (k_f) and back (k_b) reactions: s^{-1} (first-order reactions), L mol^{-1} s^{-1} (second-order reactions) ; equilibrium constants (K_{eq}) : $K_{eq} = k_f/k_b$.

i. Simulations of CV experiments done to obtain Brönsted plots:

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 50 mM malic buffer pH 5.1 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{4-} + e^- = Mo(CN)_8^{3-}$	0.5831	0.1	0.5
3	$G^\bullet$ + e- = G	NA	NA	NA
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$Mo(CN)_8^{4-} + G = Mo(CN)_8^{3-} + G^\bullet$	(3.13±0.01) x 10^{-3}	(1.1±0.1) x 10^{3}	(3.5±0.5) x 10^{5}
5	$Mo(CN)_8^{4-} + G^\bullet = Mo(CN)_8^{3-}$ + G”	NA	NA	NA
4	$G^\bullet + G^\bullet$ = GG	1.0 x 10^{10}	1.0 x 10^{9}	0.10
6	$Mo(CN)_8^{4-}$ = P	1.00 x 10^{4}	1.00 x 10^{-2}	1.00 x 10^{-6}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 50 mM succinic buffer pH 5.6 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{4-} + e^- = Mo(CN)_8^{3-}$	0.5880	0.05	0.5
3	$G^\bullet$ + e- = G	NA	NA	NA
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$Mo(CN)_8^{4-} + G = Mo(CN)_8^{3-} + G^\bullet$	(1.287±0.01) x 10^{-3}	(1.6±0.2) x 10^{3}	(1.2±0.2) x 10^{6}
5	$Mo(CN)_8^{4-} + G^\bullet = Mo(CN)_8^{3-}$ + G”	NA	NA	NA
4	$G^\bullet + G^\bullet$ = GG	1.0 x 10^{10}	1.0 x 10^{9}	0.10
6	$Mo(CN)_8^{4-}$ = P	1.00 x 10^{4}	1.00 x 10^{-2}	1.00 x 10^{-6}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 50 mM maleic buffer pH 6.2 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{4-} + e^- = Mo(CN)_8^{3-}$	0.5837	0.05	0.5
3	$G^\bullet$ + e- = G	NA	NA	NA
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$Mo(CN)_8^{4-} + G = Mo(CN)_8^{3-} + G^\bullet$	(4.03±0.07) x 10^{-3}	(3.2±0.5) x 10^{3}	(8±1) x 10^{5}
5	$Mo(CN)_8^{4-} + G^\bullet = Mo(CN)_8^{3-}$ + G”	1 x 10^{5}	(8±2) x 10^{5}	8±2
4	$G^\bullet + G^\bullet$ = GG	1.0 x 10^{10}	1.0 x 10^{9}	0.10
6	$Mo(CN)_8^{4-}$ = P	1.00 x 10^{4}	1.00 x 10^{-2}	1.00 x 10^{-6}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 50 mM histidine buffer pH 6.5 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{4-} + e^- = Mo(CN)_8^{3-}$	0.5821	0.05	0.5
3	$G^\bullet$ + e- = G	NA	NA	NA
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$Mo(CN)_8^{4-} + G = Mo(CN)_8^{3-} + G^\bullet$	(7.38±0.03) x 10^{-3}	(4.6±0.2) x 10^{3}	(6.3±0.2) x 10^{5}
5	$Mo(CN)_8^{4-} + G^\bullet = Mo(CN)_8^{3-}$ + G”	1.0 x 10^{5}	1.0 x 10^{6}	1.0 x 10^{1}
4	$G^\bullet + G^\bullet$ = GG	1.0 x 10^{10}	1.0 x 10^{9}	0.10
6	$Mo(CN)_8^{4-}$ = P	1.00 x 10^{4}	1.00 x 10^{-2}	1.00 x 10^{-6}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 50 mM phosphate buffer pH 7.0 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{4-} + e^- = Mo(CN)_8^{3-}$	0.5796	0.04	0.5
3	$G^\bullet$ + e- = G	0.6791	1.0×10^{-5}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$Mo(CN)_8^{4-} + G = Mo(CN)_8^{3-} + G^\bullet$	$(2.08 \pm 0.06) \times 10^{-2}$	$(7.7 \pm 0.4) \times 10^{3}$	$(3.7 \pm 0.3) \times 10^{5}$
5	$Mo(CN)_8^{4-} + G^\bullet = Mo(CN)_8^{3-} + G''$	1×10^{5}	$(9 \pm 2) \times 10^{5}$	9 ± 2
4	$G^\bullet + G^\bullet = GG$	1.0×10^{10}	1.0×10^{9}	0.10
6	$Mo(CN)_8^{4-} = P$	1.00×10^{4}	1.00×10^{-2}	$1.0 \quad 10^{-6}$

1.0 mM K_3IrCl_6 + 3.0 mM GSH + 35 mM malic buffer pH 5.1 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$IrCl_6^{2-} + e^- = IrCl_6^{3-}$	0.7245	0.1	0.5
3	$G^\bullet$ + e- = G	0.7904	1.0×10^{-6}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$IrCl_6^{2-} + G = IrCl_6^{3-} + G^\bullet$	$(7.2 \pm 0.2) \times 10^{-2}$	$(5.0 \pm 0.2) \times 10^{3}$	$(6.5 \pm 0.1) \times 10^{4}$
5	$IrCl_6^{2-} + G^\bullet = IrCl_6^{3-} + G''$	1.0×10^{11}	$(4.2 \pm 0.5) \times 10^{6}$	$(4.2 \pm 0.5) \times 10^{-5}$
4	$G^\bullet + G^\bullet = GG$	1×10^{9}	5×10^{8}	0.5
6	$IrCl_6^{2-} = P$	NA	NA	NA

1.0 mM K_3IrCl_6 + 3.0 mM GSH + 35 mM succinic buffer pH 5.6 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$IrCl_6^{2-} + e^- = IrCl_6^{3-}$	0.7319	0.1	0.5
3	$G^\bullet$ + e- = G	0.7590	8.0×10^{-7}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$IrCl_6^{2-} + G = IrCl_6^{3-} + G^\bullet$	$(3.46 \pm 0.05) \times 10^{-1}$	$(1.3 \pm 0.1) \times 10^{4}$	$(3.8 \pm 0.5) \times 10^{4}$
5	$IrCl_6^{2-} + G^\bullet = IrCl_6^{3-} + G''$	1.0×10^{11}	$(6.5 \pm 0.8) \times 10^{6}$	$(6.5 \pm 0.8) \times 10^{-5}$
4	$G^\bullet + G^\bullet = GG$	1×10^{10}	5×10^{8}	0.05
6	$IrCl_6^{2-} = P$	NA	NA	NA

1.0 mM K_3IrCl_6 + 3.0 mM GSH + 35 mM maleic buffer pH 6.2 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$IrCl_6^{2-} + e^- = IrCl_6^{3-}$	0.7361	0.1	0.5
3	$G^\bullet$ + e- = G	0.7259	1.0×10^{-6}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$IrCl_6^{2-} + G = IrCl_6^{3-} + G^\bullet$	1.45 ± 0.05	$(4.1 \pm 0.5) \times 10^{4}$	$(2.8 \pm 0.4) \times 10^{4}$
5	$IrCl_6^{2-} + G^\bullet = IrCl_6^{3-} + G''$	1.0×10^{11}	$(5.2 \pm 0.6) \times 10^{6}$	$(5.2 \pm 0.6) \times 10^{-5}$
4	$G^\bullet + G^\bullet = GG$	1×10^{9}	5×10^{8}	0.5
6	$IrCl_6^{2-} = P$	NA	NA	NA

1.0 mM K_3IrCl_6 + 3.0 mM GSH + 35 mM citrate buffer pH 6.4 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$IrCl_6^{2-} + e^- = IrCl_6^{3-}$	0.7354	0.1	0.5
3	$G^{\bullet}$ + e- = G	0.7142	8.0×10^{-7}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$IrCl_6^{2-} + G = IrCl_6^{3-} + G^{\bullet}$	2.3±0.2	$(3.7\pm0.5) \times 10^4$	$(1.6\pm0.3) \times 10^4$
5	$IrCl_6^{2-} + G^{\bullet} = IrCl_6^{3-} + G”$	1.0×10^{11}	$(5.4\pm0.5) \times 10^6$	$(5.4\pm0.5) \times 10^{-5}$
4	$G^{\bullet} + G^{\bullet}$ = GG	8×10^8	5×10^8	0.6
6	$IrCl_6^{2-}$ = P	NA	NA	NA

1.0 mM K_3IrCl_6 + 3.0 mM GSH + 35 mM phosphate buffer pH 7.2 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$IrCl_6^{2-} + e^- = IrCl_6^{3-}$	0.7226	0.1	0.5
3	$G^{\bullet}$ + e- = G	0.6675	1.0×10^{-5}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$IrCl_6^{2-} + G = IrCl_6^{3-} + G^{\bullet}$	8.5±0.1	$(1.5\pm0.2) \times 10^5$	$(1.7\pm0.2) \times 10^4$
5	$IrCl_6^{2-} + G^{\bullet} = IrCl_6^{3-} + G”$	1.0×10^{11}	$(9.7\pm1.0) \times 10^6$	$(9.7\pm1.0) \times 10^{-5}$
4	$G^{\bullet} + G^{\bullet}$ = GG	1×10^9	5×10^8	0.5
6	$IrCl_6^{2-}$ = P	1.00×10^1	1.53×10^{-2}	1.53×10^{-3}

1.0 mM $Fe(phen)_3SO_4$ + 1.0 mM GSH + 50 mM malic buffer pH 5.1 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Fe(phen)_3^{3+} + e^- = Fe(phen)_3^{2+}$	0.8259	0.1	0.5
3	$G^{\bullet}$ + e- = G	NA	NA	NA
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$Fe(phen)_3^{3+} + G = Fe(phen)_3^{2+} + G^{\bullet}$	3.98±0.02	$(1.10\pm0.01) \times 10^5$	$(2.76\pm0.01) \times 10^4$
5	$Fe(phen)_3^{3+} + G^{\bullet} = Fe(phen)_3^{2+} + G”$	1.00×10^{11}	$(4.25\pm0.07) \times 10^7$	$(4.25\pm0.07) \times 10^{-4}$
4	$G^{\bullet} + G^{\bullet}$ = GG	7.0×10^8	1.0×10^9	1.4
6	$Fe(phen)_3^{3+}$ = P	1.00×10^7	2.21×10^{-2}	2.21×10^{-9}

1.0 mM $Fe(phen)_3SO_4$ + 1.0 mM GSH + 50 mM succinic buffer pH 5.6 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Fe(phen)_3^{3+} + e^- = Fe(phen)_3^{2+}$	0.8251	0.1	0.5
3	$G^{\bullet}$ + e- = G	NA	NA	NA
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$Fe(phen)_3^{3+} + G = Fe(phen)_3^{2+} + G^{\bullet}$	$(1.31\pm0.01) \times 10^1$	$(4.6\pm0.1) \times 10^5$	$(3.52\pm0.08) \times 10^4$
5	$Fe(phen)_3^{3+} + G^{\bullet} = Fe(phen)_3^{2+} + G”$	1.0×10^{11}	$(1.2\pm0.2) \times 10^7$	$(1.2\pm0.2) \times 10^{-4}$
4	$G^{\bullet} + G^{\bullet}$ = GG	7.0×10^8	1.0×10^9	1.4
6	$Fe(phen)_3^{3+}$ = P	1.00×10^7	2.21×10^{-2}	2.21×10^{-9}

1.0 mM $\mathrm{Fe(phen)_3SO_4}$ + 1.0 mM GSH + 50 mM maleic buffer pH 6.2 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$\mathrm{Fe(phen)_3^{3+}} + e^- = \mathrm{Fe(phen)_3^{2+}}$	0.8268	0.1	0.5
3	$G^{\bullet}$ + e- = G	NA	NA	NA
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$\mathrm{Fe(phen)_3^{3+}} + G = \mathrm{Fe(phen)_3^{2+}} + G^{\bullet}$	$(5.1\pm0.3) \times 10^1$	$(1.3\pm0.1) \times 10^6$	$(2.50\pm0.06) \times 10^4$
5	$\mathrm{Fe(phen)_3^{3+}} + G^{\bullet} = \mathrm{Fe(phen)_3^{2+}} + G''$	1.0×10^{11}	$(4\pm1) \times 10^7$	$(4\pm1) \times 10^{-4}$
4	$G^{\bullet} + G^{\bullet} = GG$	7.0×10^8	1.0×10^9	1.4
6	$\mathrm{Fe(phen)_3^{3+}} = P$	1.00×10^7	2.21×10^{-2}	2.21×10^{-9}

1.0 mM $\mathrm{Fe(phen)_3SO_4}$ + 1.0 mM GSH + 50 mM histidine buffer pH 6.5 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$\mathrm{Fe(phen)_3^{3+}} + e^- = \mathrm{Fe(phen)_3^{2+}}$	0.8275	0.1	0.5
3	$G^{\bullet}$ + e- = G	NA	NA	NA
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$\mathrm{Fe(phen)_3^{3+}} + G = \mathrm{Fe(phen)_3^{2+}} + G^{\bullet}$	1.0×10^2	$(3.0\pm0.2) \times 10^6$	$2.8\pm0.2 \times 10^4$
5	$\mathrm{Fe(phen)_3^{3+}} + G^{\bullet} = \mathrm{Fe(phen)_3^{2+}} + G''$	1.0×10^{11}	$(5.3\pm0.6) \times 10^7$	$(5.3\pm0.6) \times 10^{-4}$
4	$G^{\bullet} + G^{\bullet} = GG$	3.0×10^8	1.0×10^9	3.3
6	$\mathrm{Fe(phen)_3^{3+}} = P$	1.00×10^7	2.21×10^{-2}	2.21×10^{-9}

1.0 mM $\mathrm{Fe(phen)_3SO_4}$ + 1.0 mM GSH + 50 mM phosphate buffer pH 7.0 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$\mathrm{Fe(phen)_3^{3+}} + e^- = \mathrm{Fe(phen)_3^{2+}}$	0.8303	0.1	0.5
3	$G^{\bullet}$ + e- = G	0.6791	2.0×10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2	$\mathrm{Fe(phen)_3^{3+}} + G = \mathrm{Fe(phen)_3^{2+}} + G^{\bullet}$	$(3.7\pm0.1) \times 10^2$	$(9.8\pm0.6) \times 10^6$	$(2.69\pm0.08) \times 10^4$
5	$\mathrm{Fe(phen)_3^{3+}} + G^{\bullet} = \mathrm{Fe(phen)_3^{2+}} + G''$	1.0×10^{11}	$(1.9\pm0.5) \times 10^7$	$(1.9\pm0.5) \times 10^{-4}$
4	$G^{\bullet} + G^{\bullet} = GG$	$(8\pm1) \times 10^8$	1.0×10^9	(1.3 ± 0.2)
6	$\mathrm{Fe(phen)_3^{3+}} = P$	1.00×10^7	2.21×10^{-2}	2.21×10^{-9}

Simulations of CV experiments done at pH 10.00 and pD 10.00.

1.0 mM $\mathrm{Fe(phen)_3SO_4}$ + 1.0 mM GSH + 25 mM phosphate buffer pH 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$\mathrm{Fe(phen)_3^{3+}} + e^- = \mathrm{Fe(phen)_3^{2+}}$	0.8285	0.1	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0×10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2×10^4	2×10^9	1

2b	$Fe(phen)_3^{3+} + GS^- = Fe(phen)_3^{2+} + GS^\bullet$	1.33 x 10^{4}	(1.4±0.3) x 10^{7}	(1.1±0.2) x 10^{3}
5	$Fe(phen)_3^{3+} + GS^\bullet = Fe(phen)_3^{2+} +$ GS”	4.0 x 10^{11}	(6.6±0.4) x 10^{6}	(1.6±0.1) x 10^{-5}
4	$GS^\bullet + GS^\bullet = GSSG$	(1.3±0.4) x 10^{9}	(2.7±0.4) x 10^{9}	2.3±0.8
6	$Fe(phen)_3^{3+} = P$	1.0 x 10^{7}	2.21 x 10^{-2}	2.21 x 10^{-9}

1.0 mM $Fe(phen)_3SO_4$ + 1.0 mM GSH + 50 mM phosphate buffer pH 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Fe(phen)_3^{3+} + e^- = Fe(phen)_3^{2+}$	0.8225	0.1	0.5
3	$GS^\bullet$ + e- = GS^-	0.5845	1.0 x 10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2 x 10^{4}	2 x 10^{9}	1
2b	$Fe(phen)_3^{3+} + GS^- = Fe(phen)_3^{2+} + GS^\bullet$	(1.2±0.2) x 10^{4}	(7.3±0.2) x 10^{7}	(6.5±0.3) x 10^{3}
5	$Fe(phen)_3^{3+} + GS^\bullet = Fe(phen)_3^{2+} +$ GS”	4.0 x 10^{11}	5.0 x 10^{6}	1.25 x 10^{-5}
4	$GS^\bullet + GS^\bullet = GSSG$	(3±1) x 10^{8}	2.0 x 10^{9}	8.5±0.4
6	$Fe(phen)_3^{3+} = P$	(3.7±0.2) x 10^{7}	2.21 x 10^{-2}	(1.0±0.1) x 10^{-9}

1.0 mM $Fe(phen)_3SO_4$ + 1.0 mM GSH + 100 mM phosphate buffer pH 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Fe(phen)_3^{3+} + e^- = Fe(phen)_3^{2+}$	0.8225	0.1	0.5
3	$GS^\bullet$ + e- = GS^-	0.5845	1.0 x 10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2 x 10^{4}	2 x 10^{9}	1
2b	$Fe(phen)_3^{3+} + GS^- = Fe(phen)_3^{2+} + GS^\bullet$	1.053 x 10^{4}	(1.1±0.1) x 10^{8}	(1.04±0.09) x 10^{3}
5	$Fe(phen)_3^{3+} + GS^\bullet = Fe(phen)_3^{2+} +$ GS”	4.0 x 10^{11}	(8±2)x 10^{6}	(2.0±0.4) x 10^{-5}
4	$GS^\bullet + GS^\bullet = GSSG$	(1.9±0.9) x 10^{8}	(6.3±0.2) x 10^{8}	4.1±0.2
6	$Fe(phen)_3^{3+} = P$	4.0 x 10^{7}	2.21 x 10^{-2}	5.52 x 10^{-10}

1.0 mM $Fe(phen)_3SO_4$ + 1.0 mM GSH + 50 mM deuterated phosphate buffer pD 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Fe(phen)_3^{3+} + e^- = Fe(phen)_3^{2+}$	0.8325	0.1	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0 x 10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2 x 10^4	2 x 10^9	1
2b	$Fe(phen)_3^{3+} + GS^- = Fe(phen)_3^{2+} + GS^{\bullet}$	1.553x 10^4	7 x 10^6	450.61
5	$Fe(phen)_3^{3+} + GS^{\bullet} = Fe(phen)_3^{2+}$ + GS”	4.0 x 10^{11}	5.0 x 10^6	1.25 x 10^{-5}
4	$GS^{\bullet} + GS^{\bullet} = GSSG$	6 x 10^9	2.0 x 10^9	0.33
6	$Fe(phen)_3^{3+} = P$	1.0 x 10^7	2.21 x 10^{-2}	2.21 x 10^{-9}

1.0 mM $Fe(phen)_3SO_4$ + 1.0 mM GSH + 100 mM deuterated phosphate buffer pD 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Fe(phen)_3^{3+} + e^- = Fe(phen)_3^{2+}$	0.8325	0.1	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0 x 10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2 x 10^4	2 x 10^9	1
2b	$Fe(phen)_3^{3+} + GS^- = Fe(phen)_3^{2+} + GS^{\bullet}$	1.553x 10^4	(1.3±0.4) x 10^8	(8.5±0.3) x 10^3
5	$Fe(phen)_3^{3+} + GS^{\bullet} = Fe(phen)_3^{2+}$ + GS”	4.0 x 10^{11}	(1.7±0.8) x 10^8	(4.2±0.2) x 10^{-4}
4	$GS^{\bullet} + GS^{\bullet} = GSSG$	6 x 10^9	2.0 x 10^9	0.33
6	$Fe(phen)_3^{3+} = P$	1.0 x 10^7	2.21 x 10^{-2}	2.21 x 10^{-9}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 25 mM phosphate buffer pH 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{3-} + e^- = Mo(CN)_8^{4-}$	0.5916	0.03	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0 x 10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2 x 10^4	2 x 10^9	1
2b	$Mo(CN)_8^{4-} + GS^- = Mo(CN)_8^{3-} + GS^{\bullet}$	1.3182	(2.87±0.06) x 10^3	(2.17±0.04) x 10^3
5	$Mo(CN)_8^{4-} + GS^{\bullet} = Mo(CN)_8^{3-}$ + GS”	1 x 10^5	1 x 10^5	0.1
4	$GS^{\bullet} + GS^{\bullet} = GSSG$	(2.3±0.3) x 10^{10}	5.0 x 10^{10}	2.2±0.2
6	$Mo(CN)_8^{4-} = P$	2.00 x 10^3	1.00 x 10^{-4}	5.00 x 10^{-8}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 50 mM phosphate buffer pH 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{3-} + e^- = Mo(CN)_8^{4-}$	0.5916	0.03	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0 x 10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2 x 10^4	2 x 10^9	1
2b	$Mo(CN)_8^{4-} + GS^- = Mo(CN)_8^{3-} + GS^{\bullet}$	1.3182	(4.2±0.7) x 10^3	(3.2±0.4) x 10^3
5	$Mo(CN)_8^{4-} + GS^{\bullet} = Mo(CN)_8^{3-}$ + GS”	1 x 10^6	1 x 10^5	0.1
4	$GS^{\bullet} + GS^{\bullet} = GSSG$	(5.3±0.6) x 10^7	1.0 x 10^{10}	(1.9±0.2) x 10^2
6	$Mo(CN)_8^{4-} = P$	2.00 x 10^3	1.00 x 10^{-4}	5.00 x 10^{-8}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 100 mM phosphate buffer pH 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{3-} + e^- = Mo(CN)_8^{4-}$	0.5916	0.03	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0×10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2×10^4	2×10^9	1
2b	$Mo(CN)_8^{4-} + GS^- = Mo(CN)_8^{3-} + GS^{\bullet}$	1.2679	$(5.5\pm1.9) \times 10^3$	$(4.1\pm1.5) \times 10^3$
5	$Mo(CN)_8^{4-}$ + $GS^{\bullet}$ = $Mo(CN)_8^{3-}$ + GS”	1×10^6	1×10^5	0.1
4	$GS^{\bullet} + GS^{\bullet} = GSSG$	$(2.1\pm0.2) \times 10^8$	1.0×10^{10}	$(1.3\pm0.2) \times 10^2$
6	$Mo(CN)_8^{4-} = P$	2.00×10^3	1.00×10^{-4}	5.00×10^{-8}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 200 mM phosphate buffer pH 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{3-} + e^- = Mo(CN)_8^{4-}$	0.6096	0.0045±0.001	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0×10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2×10^4	2×10^9	1
2b	$Mo(CN)_8^{4-} + GS^- = Mo(CN)_8^{3-} + GS^{\bullet}$	2.6558	$(3.6\pm0.2) \times 10^4$	$(1.3\pm0.8) \times 10^4$
5	$Mo(CN)_8^{4-}$ + $GS^{\bullet}$ = $Mo(CN)_8^{3-}$ + GS”	1×10^6	2×10^5	0.2
4	$GS^{\bullet} + GS^{\bullet} = GSSG$	5.0×10^9	1.0×10^5	2.0×10^5
6	$Mo(CN)_8^{4-} = P$	2.00×10^3	1.00×10^{-4}	5.00×10^{-8}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 300 mM phosphate buffer pH 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{3-} + e^- = Mo(CN)_8^{4-}$	0.6096	0.0043±0.002	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0×10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2×10^4	2×10^9	1
2b	$Mo(CN)_8^{4-} + GS^- = Mo(CN)_8^{3-} + GS^{\bullet}$	2.6558	$(4.0 \pm 0.2) \times 10^4$	$(1.5 \pm 0.9) \times 10^4$
5	$Mo(CN)_8^{4-} + GS^{\bullet} = Mo(CN)_8^{3-}$ + GS”	1×10^6	2×10^5	0.2
4	$GS^{\bullet} + GS^{\bullet} = GSSG$	5.0×10^9	1.0×10^5	2.0×10^5
6	$Mo(CN)_8^{4-} = P$	2.00×10^3	1.00×10^{-4}	5.00×10^{-8}

1.0 mM $K_4Mo(CN)_8$ + 1.0 mM GSH + 50 mM deuterated phosphate buffer pD 10.00 + 1.0 M NaCl

#	**Electrochemical Reactions**	**E**	**k_s**	**α**
1	$Mo(CN)_8^{3-} + e^- = Mo(CN)_8^{4-}$	0.5906	0.06±0.02	0.5
3	$GS^{\bullet}$ + e- = GS^-	0.5845	1.0×10^{-4}	0.5
	Chemical Reactions	**K**	**k_f**	**k_b**
2a	$GSH + PO_4^{3-} = GS^- + HPO_4^{2-}$	2×10^4	2×10^9	1
2b	$Mo(CN)_8^{4-} + GS^- = Mo(CN)_8^{3-} + GS^{\bullet}$	1.2679	$(5.3 \pm 0.3) \times 10^3$	$(4.0 \pm 0.4) \times 10^3$
5	$Mo(CN)_8^{4-} + GS^{\bullet} = Mo(CN)_8^{3-}$ + GS”	1×10^5	1×10^5	1
4	$GS^{\bullet} + GS^{\bullet} = GSSG$	2.0×10^5	1.0×10^6	5
6	$Mo(CN)_8^{4-} = P$	4.00×10^3	1.00×10^{-4}	2.50×10^{-8}

References

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