Electron transfer in the electrochemistry of metals, metal compounds and metal complexes

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Abstract

Because electron-transfer occurs at the electrode/solution interface, the oxidation of metal electrodes involves electron removal (within the interface) from a solvent molecule or basic constituent (ligand) rather than from the valence-electron shell of the metal (e.g. $Ag + Cl^- \xrightarrow{-e^-} Ag–Cl$, $E°_{Ag/AgCl} = +0.22$ V versus NHE; $Cl^- \xrightarrow{-e^-} Cl^\cdot$, $E°_{Cl^-/Cl^\cdot} = +2.41$ V). The difference in oxidation potential for the free ligand in the absence of the metal electrode and in its presence is a measure of the metal–ligand differential bond energy (e.g. for Ag–Cl, $-\Delta G_{BF} = -\Delta E° \times 23.1$ kcal (eV)$^{-1}$ = 50.6 kcal mol^{-1}). Likewise, oxidation of reduced transition-metal complexes and metalloporphyrins are ligand-centered (or solvent-centered) (e.g. $Fe^{II}Cl_3^- \xrightarrow{-e^-} Fe^{III}Cl_3$), as is the reduction of the oxidized state ($Fe^{III}Cl_3 \rightleftharpoons Fe^{II}Cl_3^-$). In each case the potential for the oxidation of free ligand (or solvent) is decreased in the presence of metal or reduced-metal complex by an amount that is proportional to the metal–ligand bond energy ($-\Delta G_{BF}$).

Keywords: Electron transfer; Electrochemistry; Metals; Metal compounds; Metal complexes
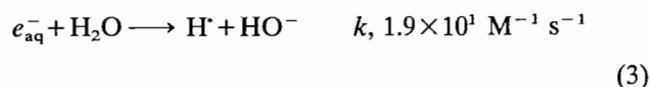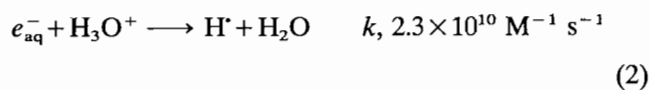
1. Introduction

Electrochemistry is the science of electron transfer across a solution/electrode interface. At the cathode electrons (from the electrode) are transformed within the interface via reaction with ions or molecules to produce reduced molecules or ions (e.g. $H_3O^+ + e^- \rightarrow H^\cdot + H_2O$; $H_2O + e^- \rightarrow H^\cdot + HO^-$; $O_2 + e^- \rightarrow O_2^{\cdot-}$; $Cu^{II}(bpy)_2^{2+} + e^- \rightarrow Cu^I(bpy)_2^+$; $Fe^{III}Cl_3 + e^- \rightarrow Fe^{II}Cl_3^-$). At the anode molecules or ions (from the solution) are transformed within the interface to produce electrons (at the electrode surface) and oxidized ions and molecules (e.g. $2H_2O \rightarrow H_3O^+ + HO^\cdot + e^-$; $Fe^{II}Cl_3^- \rightarrow Fe^{III}Cl_3 + e^-$). The resultant electrons move from the anode through the wires of the external circuit to the cathode as electronic current (amperes; coulombs per second). Within the solution phase the current is carried by the ions of the supporting electrolyte (positive ions towards the cathode and negative ions towards the anode). The limitation of ionic current in the solution phase (between the anode and the cathode), which is the defining difference for electrochemistry and electronics, is due to the incompatibility of electrons and electrolyte solutions.
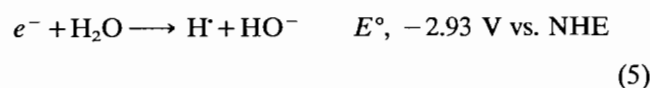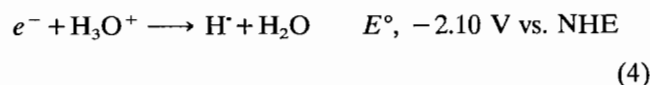
2. The hydrated electron

In aqueous media electrons become hydrated in 10^{-12} s to become the ultimate base, nucleophile and reductant [1].

$$e^- + nH_2O \longrightarrow e^-_{aq} \qquad E°, -3.0 \text{ V vs. NHE} \qquad (1)$$
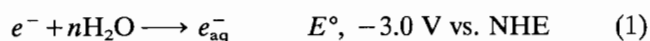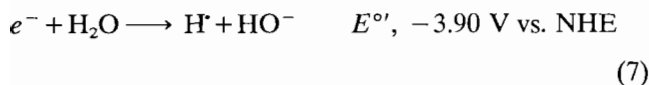
The conjugate acid of the hydrated electron is the hydrogen atom (H$^\cdot$), which is the effective reductant under acidic conditions

$$e^-_{aq} + H_3O^+ \longrightarrow H^\cdot + H_2O \qquad k, 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \qquad (2)$$

$$e^-_{aq} + H_2O \longrightarrow H^\cdot + HO^- \qquad k, 1.9 \times 10^1 \text{ M}^{-1} \text{ s}^{-1} \qquad (3)$$

From electrochemistry the respective standard reduction potentials in water are [2]

$$e^- + H_3O^+ \longrightarrow H^\cdot + H_2O \qquad E°, -2.10 \text{ V vs. NHE} \qquad (4)$$

$$e^- + H_2O \longrightarrow H^\cdot + HO^- \qquad E°, -2.93 \text{ V vs. NHE} \qquad (5)$$

and in acetonitrile [3]

$$e^- + H_3O^+ \longrightarrow H^\cdot + H_2O \qquad E^{\circ\prime}, \ -1.58 \text{ V vs. NHE}$$
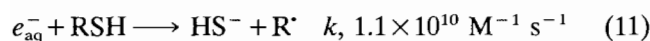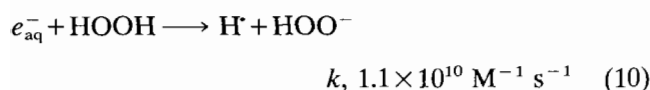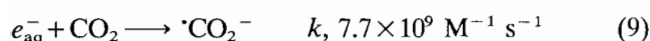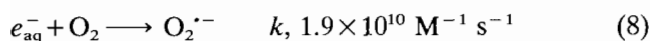
$$(6)$$

$$e^- + H_2O \longrightarrow H^\cdot + HO^- \qquad E^{\circ\prime}, \ -3.90 \text{ V vs. NHE}$$

$$(7)$$
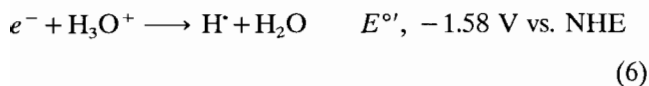
Hydrated electrons also are highly reactive with many components of aqueous biological matrises [1].

$$e_{aq}^- + O_2 \longrightarrow O_2^{\cdot-} \qquad k, \ 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \qquad (8)$$

$$e_{aq}^- + CO_2 \longrightarrow {}^\cdot CO_2^- \qquad k, \ 7.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \qquad (9)$$

$$e_{aq}^- + HOOH \longrightarrow H^\cdot + HOO^-$$

$$k, \ 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad (10)$$

$$e_{aq}^- + RSH \longrightarrow HS^- + R^\cdot \quad k, \ 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad (11)$$

Whereas for the HO–H bond the free energy of formation $(-\Delta G_{BF})$ is 111 kcal mol^{-1} [4], within $(H_3O)^+$ the O–H bond energy is about 70–90 kcal mol^{-1}. The difference accounts for the dramatic increase in the reactivity of e_{aq}^- with the hydronium ion (Eqs. (2) and (3)). On the basis of such considerations the reaction rates of solvated electrons with phenols (RPhO–H; $-\Delta G_{BF}$, 81–84 kcal mol^{-1}) and carbonic acid ((HO)C(O)(O–H); $-\Delta G_{BF}$, 98 kcal mol^{-1}) should be large.

$$e_{aq}^- + RPhOH \longrightarrow H^\cdot + RPhO^-$$

$$k \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad (12)$$

$$e_{aq}^- + (HO)_2C(O) \longrightarrow H^\cdot + HOC(O)O^-$$

$$k \sim 10^7 \text{ M}^{-1} \text{ s}^{-1} \quad (13)$$
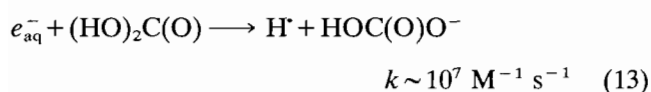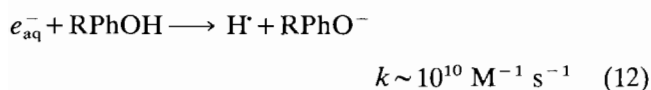
Hence, tyrosine residues (RPhOH) in proteins and biological fluids with 3–5 mM $(HO)_2C(O)$ will be effective traps for hydrated electrons in biological systems. When O_2 reacts with hydrated electrons in aqueous media the product $(O_2^{\cdot-})$ reacts with water at diffusion controlled rates to produce HOO$^\cdot$.

$$e_{aq}^- + O_2 \longrightarrow O_2^{\cdot-} \xrightleftharpoons[pK_{HA}, 4.9]{H_2O} HOO^\cdot + HO^-$$

$$k \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad (14)$$
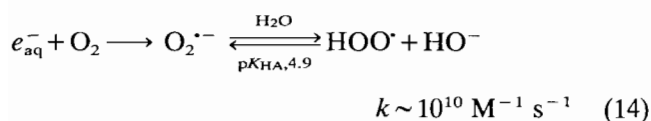
This indicates that any hydrated electrons in aerobic biology that escape trapping by the CO_2, carbonic acid, and tyrosine and cysteine residues will produce finite fluxes of the soft radical, HOO$^\cdot$.
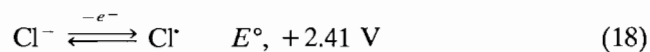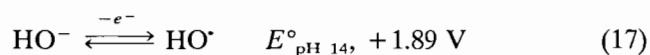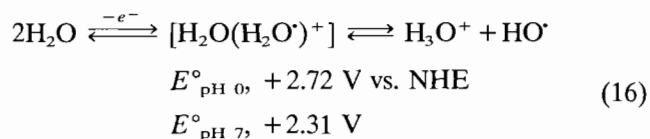
In aqueous solutions the hydrated electron interacts with water to form a hydrogen atom and an hydroxide ion (the conjugate base of H_2O)

$$e_{aq}^- + H_2O \rightleftharpoons H^\cdot + HO^- \qquad K, \ 2 \times 10^5 \quad (15)$$

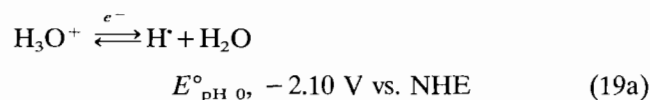which means that H$^\cdot$ is the conjugate acid of e_{aq}^- with a pK_{HA} value of 9.3 [1].

3. Electron transfer in electrochemistry

In electrochemical cells electron transfer occurs within the electrode/solution interface, with electron removal (oxidation) at the anode and electron introduction (reduction) at the cathode. The current through the solution is carried by the ions of the electrolyte, and the voltage limits are those for electron removal (oxidation (positive)) *from* and electron-insertion (reduction (negative)) *into* the solvent/electrolyte (e.g. $H_2O/(H_3O^+)(ClO_4^-)$; $(Na_{aq}^+)(^-OH)$; $(Na_{aq}^+)(Cl^-)$).
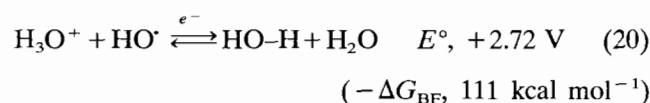
$$2H_2O \xrightleftharpoons{-e^-} [H_2O(H_2O^\cdot)^+] \rightleftharpoons H_3O^+ + HO^\cdot$$

$$E^\circ_{pH \ 0}, \ +2.72 \text{ V vs. NHE}$$
$$E^\circ_{pH \ 7}, \ +2.31 \text{ V} \qquad (16)$$

$$HO^- \xrightleftharpoons{-e^-} HO^\cdot \qquad E^\circ_{pH \ 14}, \ +1.89 \text{ V} \quad (17)$$

$$Cl^- \xrightleftharpoons{-e^-} Cl^\cdot \qquad E^\circ, \ +2.41 \text{ V} \quad (18)$$

In the gas phase electron removal from atoms is limited by their ionization potential (e.g H$^\cdot$, 13.6; K$^\cdot$, 4.3; Na$^\cdot$, 5.1; Cu$^\cdot$, 7.7, 20.3; Ag, 7.6; Fe, 7.9, 16.2, 30.7 eV) [5]. However, in the solution phase electron removal from the solvent (oxidation may be facilitated by the presence of substrate atoms (rather than be from them).
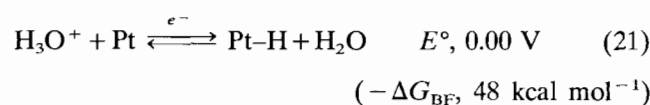
Reductive electron transfer in an electrochemical cell occurs by insertion of an electron from the electrode (cathode) into the solution matrix within the double layer of the electrode/solution interface (e.g. $H_2O/(H_3O^+)(ClO_4^-)$; $(Na_{aq}^+)(ClO_4^-)$).

$$H_3O^+ \xrightleftharpoons{e^-} H^\cdot + H_2O$$

$$E^\circ_{pH \ 0}, \ -2.10 \text{ V vs. NHE} \quad (19a)$$

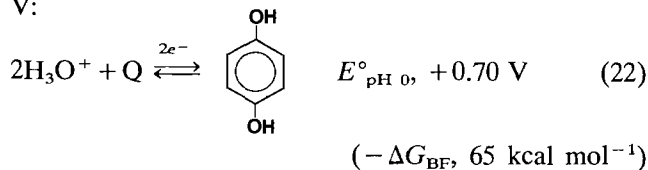$$E^\circ_{pH \ 7}, \ -2.51 \text{ V} \quad (19b)$$

The reductive processes of Eq. (19) may be facilitated by the presence of substrates to stabilize the H-atom product. For example, in pH 0 water the process of Eq. (19a) is shifted by +4.82 V when hydroxyl radicals (HO$^\cdot$) are present

$$H_3O^+ + HO^\cdot \xrightleftharpoons{e^-} HO-H + H_2O \qquad E^\circ, \ +2.72 \text{ V} \quad (20)$$
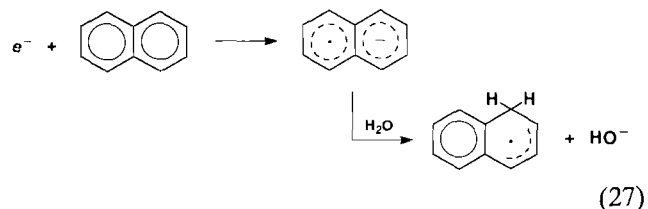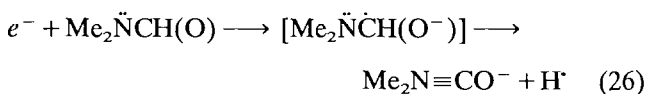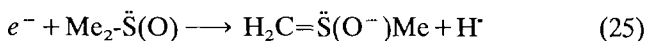
$$(-\Delta G_{BF}, \ 111 \text{ kcal mol}^{-1})$$

and by +2.10 V at a platinum electrode

$$H_3O^+ + Pt \xrightleftharpoons{e^-} Pt-H + H_2O \qquad E^\circ, \ 0.00 \text{ V} \quad (21)$$
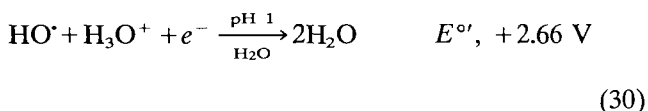
$$(-\Delta G_{BF}, \ 48 \text{ kcal mol}^{-1})$$

In the presence of benzoquinone (Q) the shift is $+2.80$ V:

$$2H_3O^+ + Q \underset{}{\overset{2e^-}{\rightleftharpoons}} \text{(hydroquinone)} \qquad E^\circ_{pH\ 0},\ +0.70\ V \qquad (22)$$

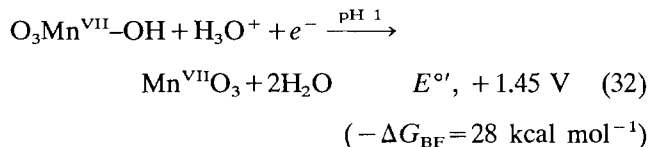$$(-\Delta G_{BF},\ 65\ kcal\ mol^{-1})$$

The free electron interacts with all atoms and molecules that have finite electron affinities to produce anions, and thus is unstable in all but the most inert liquids. Electrochemistry attests to this general axiom and provides a convenient means to evaluate the energetics for the addition of an electron to solvent molecules and other species at the electrode/solution interface, e.g.

$$(23)$$

$$e^- + CO_2(MeCN) \longrightarrow \left[\cdot C\overset{O^-}{\underset{O}{\diagup\!\!\diagdown}} \longleftrightarrow \cdot C\overset{O}{\underset{O^-}{\diagup\!\!\diagdown}} \right]$$

$$E^\circ,\ -1.86\ V\ vs.\ NHE \qquad (24)$$

$$e^- + Me_2\text{-}\ddot{S}(O) \longrightarrow H_2C=\ddot{S}(O^-)Me + H^\cdot \qquad (25)$$

$$e^- + Me_2\ddot{N}CH(O) \longrightarrow [Me_2\ddot{N}CH(O^-)] \longrightarrow$$

$$Me_2N\equiv CO^- + H^\cdot \qquad (26)$$

$$(27)$$
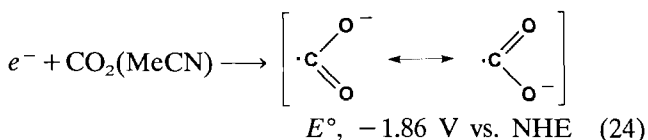
Hence, reductive electrochemistry converts electrons (e^-) via the solution matrix at the interface to atoms and anions. The solution outside the inner double layer is never exposed to an electron. Some examples of such inner-double-layer electron transfer include:

$$H_3O^+ + e^- \longrightarrow H^\cdot + H_2O \qquad E^\circ,\ -2.10\ V\ vs.\ NHE$$

$$(28)$$

$$(H_2O)_5{}^{2+}Fe^{III}(OH) + H_3O^+ + e^- \xrightarrow[H_2O]{pH\ 1}$$

$$Fe^{II}(OH_2)_6{}^{2+} + H_2O \qquad E^{\circ\prime},\ +0.71\ V \qquad (29)$$

$$HO^\cdot + H_3O^+ + e^- \xrightarrow[H_2O]{pH\ 1} 2H_2O \qquad E^{\circ\prime},\ +2.66\ V$$

$$(30)$$
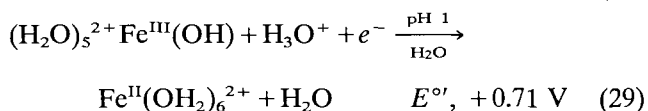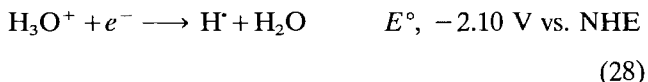
$$-\Delta G_{BF}[(H_2O)_5{}^{2+}Fe^{III}\text{-}OH]$$

$$= [E^{\circ\prime}_{30} - E^{\circ\prime}_{29}] \times 23.1$$

$$= 45\ kcal\ mol^{-1} \qquad (31)$$

$$O_3Mn^{VII}\text{-}OH + H_3O^+ + e^- \xrightarrow{pH\ 1}$$

$$Mn^{VII}O_3 + 2H_2O \qquad E^{\circ\prime},\ +1.45\ V \qquad (32)$$

$$(-\Delta G_{BF} = 28\ kcal\ mol^{-1})$$

An important consideration in the reactions of Eqs. (30) and (32) is that the oxidant in each is the hydronium ion (H_3O^+) and that the reduction potential is determined by the H–OH bond energy $(-\Delta G_{BF})$ of the product H_2O, minus the Mn–OH bond energy (Eq. (32)).

4. Metals

The transformation of metal–electrode surfaces via electro-oxidation to their metallo-oxides, solvated ions and metal complexes is fundamental to most anodic electrochemical processes (batteries, electro-refining, anodic-stripping analysis and reference electrodes). Although this is traditionally represented as the removal of one (or more) valence electrons from a metal atom at the electrode surface to give a metal ion (e.g $Ag(s) \xrightarrow{-e^-} Ag^+$; E°, $+0.80$ V versus NHE), the gas phase ionization potential (e.g. $Ag^\cdot(g) \xrightarrow{-e^-} Ag^+(g)$; IP, 7.6 eV) is far greater than the observed oxidation potential [5]. The difference is attributed to the solvation energy for the metal ion (e.g. $Ag^+ + nH_2O \rightarrow Ag^+(ag)$; $-\Delta G(aq) \approx 70$–100 kcal mol^{-1}). However, such a sequential path would not obviate the 7.6 V energy barrier for the initial step and is in conflict with the observed thermodynamic reversibility for many metal/solvated-metal-ion redox couples.

All reactions, and particularly redox processes, occur via the easiest and lowest energy pathway that is available (mechanistically feasible) to the system. In the case of a metal-electrode/electrolyte interface undergoing anodic transformations, the electrons can come from (a) surface metal atoms (energy limit; first ionization potential), (b) solvent molecules (energy limit; oxidation potential of solvent), (c) electrolyte anions (energy limit; oxidation potential of anions), and (d) base ligands (energy limit; oxidation potential of ligand). All metal electrodes are electrochemically transformed via path b, c or d, but never via path a. This general conclusion is illustrated for silver and copper electrodes in aqueous and acetonitrile (MeCN) solutions that contain inert electrolyte, chloride ion (Cl^-), or bipyridine (bpy).

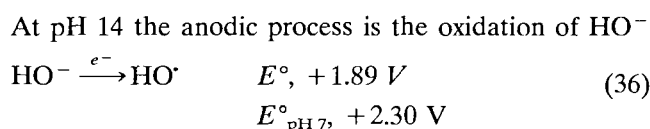In aqueous solutions at pH 0 the silver electrode is oxidized reversibly.

$$Ag(s) + 2H_2O \xrightarrow{-e^-} Ag^I(OH_2)_2{}^+$$

$$E°, \ +0.80 \text{ V vs. NHE} \quad (33)$$
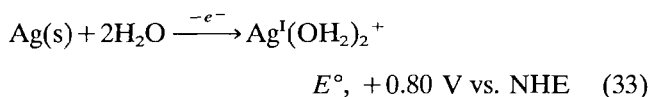
The gas phase ionization potential for a silver atom is 7.6 eV. In contrast, water is oxidized (gives up an electron) at much lower potentials.
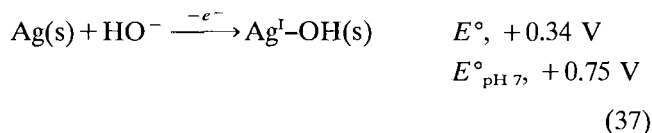
$$2H_2O \xrightarrow{-e^-} [(H_2O)H_2O^{·+}] \longrightarrow H_3O^+ + HO^·$$

$$E°, \ +2.72 \ V \quad (34)$$
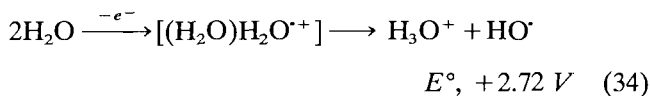
At a silver electrode the latter process is facilitated via formation of an $Ag^I-OH_2{}^+$ bond; the shift in oxidation potential from $+2.72$ to $+0.80$ V is a measure of the bond formation energy $(-\Delta G_{BF})$:

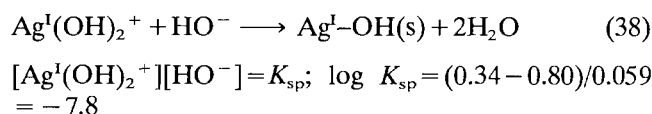$$-\Delta G_{BF} = (+2.72 - 0.80)23.1 = 44.4 \text{ kcal mol}^{-1} \quad (35)$$

At pH 14 the anodic process is the oxidation of HO^-

$$HO^- \xrightarrow{e^-} HO^· \quad \begin{array}{l} E°, \ +1.89 \ V \\ E°_{pH\,7}, \ +2.30 \text{ V} \end{array} \quad (36)$$

which is facilitated via formation of an Ag^I-OH bond $(-\Delta G_{BF} = (1.89 - 0.34) \ 23.1 = 35.8 \text{ kcal mol}^{-1})$:

$$Ag(s) + HO^- \xrightarrow{-e^-} Ag^I-OH(s) \quad \begin{array}{l} E°, \ +0.34 \text{ V} \\ E°_{pH\,7}, \ +0.75 \text{ V} \end{array}$$

$$(37)$$

The data of Eqs. (33) and (36) can be combined to give a value for the solubility product (K_{sp}) for Ag–OH(s).

$$Ag^I(OH)_2{}^+ + HO^- \longrightarrow Ag^I-OH(s) + 2H_2O \quad (38)$$

$[Ag^I(OH)_2{}^+][HO^-] = K_{sp}; \ \log K_{sp} = (0.34 - 0.80)/0.059 = -7.8$

In the presence of chloride ion metal electrodes facilitate its oxidation

$$Cl^- \xrightarrow{-e^-} Cl^· \quad \begin{array}{l} E°, \ +2.41 \text{ V vs. NHE} \\ E°'_{MeCN}, \ +2.24 \text{ V} \end{array} \quad (39)$$
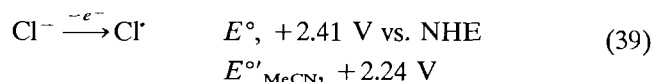
via formation of metal–chlorine covalent bonds, e.g.

$$Ag(s) + Cl^- \xrightarrow{-e^-} Ag-Cl(s) \quad E°, \ +0.22 \text{ V} \quad (40)$$
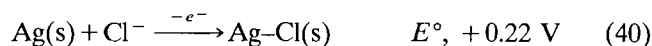
Hence, the differential bond formation energy $(\Delta(-\Delta G_{BF}))$(Ag–Cl bond energy, minus the energy required to break an Ag–Ag bond at the Ag(s) surface) is given by the difference in oxidation potentials (Eqs. (39) and (40)).

$$\Delta(-\Delta G_{BF}) = (2.41 - 0.22)23.1 = 50.6 \text{ kcal mol}^{-1} \quad (41)$$

Because the escape energy for an $Ag^·$ atom from Ag(s) is 68 kcal mol^{-1}, a reasonable approximation for the breakage of a single bond is 22.6 kcal mol^{-1} ((1/3)68) [6]. When combined with Eq. (41), this gives a reasonable value for $-\Delta G_{BF}$.
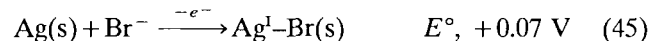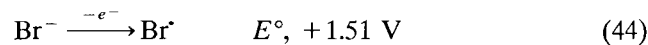
$$Ag^· + Cl^· \longrightarrow Ag-Cl \quad \begin{array}{l} -\Delta G_{BF} = 50.6 + 22.6 \\ = 73.2 \text{ kcal mol}^{-1} \end{array}$$

$$(42)$$

The literature value for the dissociative bond energy (ΔH_{DBE}) of Ag–Cl is 81.6 kcal mol^{-1}, which is equivalent to an estimated $-\Delta G_{BF}$ value of 73.8 kcal mol^{-1} $(-\Delta G_{BF} = \Delta H_{DBE} - T\Delta S = 81.6 - 7.8(\text{est.}) = 73.8$ kcal mol^{-1} [6]. Thus, the proposition that metal-electrode oxidations are solvent- or ligand-centered with potentials that reflect the metal-solvent/ligand bond formation free energies $(-\Delta G_{BF})$ is supported by independent bond energy data. The data of Eqs. (33) and (40) provide a measure of the solubility product for AgCl(s).

$$Ag^I(OH_2)_2{}^+ + Cl^- \longrightarrow Ag^I-Cl(s) + 2H_2O \quad (43)$$
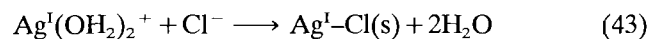
$[Ag^I(OH_2)_2{}^+][Cl^-] = K_{sp}; \ \log K_{sp} = (0.22 - 0.80)/0.059 = -9.8$

Similar results are observed for a silver electrode in the presence of Br^-

$$Br^- \xrightarrow{-e^-} Br^· \quad E°, \ +1.51 \text{ V} \quad (44)$$

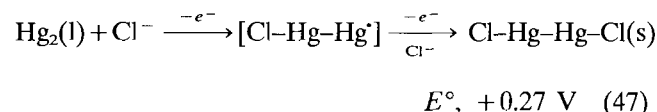$$Ag(s) + Br^- \xrightarrow{-e^-} Ag^I-Br(s) \quad E°, \ +0.07 \text{ V} \quad (45)$$

which gives a measure of the Ag^I-Br bond energy:

$$\Delta(-\Delta G_{BF}) = (1.51 - 0.07)23.1 = 33.6 \text{ kcal mol}^{-1} \quad (46)$$

The latter, when combined with the bond dissociation energy of Ag(s) $(\Delta H_{DBE}/3 = 22.6 \text{ kcal mol}^{-1})$, gives a value for $-\Delta G_{BF}$ of 56.2 kcal (literature, $-\Delta G_{BF} = \Delta H_{DBE} - T\Delta S = (70 \pm 7) - 7.8(\text{est.}) = 62 \pm 7$ kcal mol^{-1}) [6].

Another important example is the oxidation of Cl^- at a mercury $(Hg_2(l))$ electrode to form calomel (mercurous chloride, $Hg_2Cl_2(s)$, $Cl-Hg^{II}-Hg^{II}-Cl(s)$).

$$Hg_2(l) + Cl^- \xrightarrow{-e^-} [Cl-Hg-Hg^·] \xrightarrow[Cl^-]{-e^-} Cl-Hg-Hg-Cl(s)$$

$$E°, \ +0.27 \text{ V} \quad (47)$$

the potential shift for the $Cl^-/Cl^·$ couple from $+2.41$ V (Eq. (39)) to $+0.27$ V in the presence of $Hg_2(l)$ is a measure of the [Cl–HgHg] bond energy $(-\Delta G_{BF} = (2.41 - 0.27)23.1 = 49.4 \text{ kcal mol}^{-1})$.

Similar metal-facilitated oxidations of H_2O and of Cl^- occur for all metal electrodes. The respective potentials for the oxidation of each at a copper electrode are
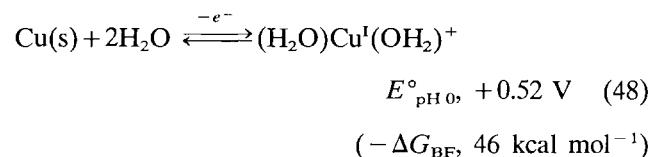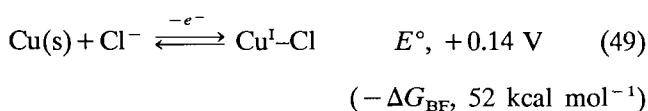
$$Cu(s) + 2H_2O \xrightleftharpoons{-e^-} (H_2O)Cu^I(OH_2)^+$$

$$E°_{pH\,0}, \ +0.52 \text{ V} \quad (48)$$

$$(-\Delta G_{BF}, \ 46 \text{ kcal mol}^{-1})$$

Table 1

Redox potentials ($E^{\circ\prime}$) for the $M^I(OH_2)_2{}^+/M$ and $M^IOH/M,HO^-$ couples of Cu, Ag and Au in H_2O and in MeCN (0.1 M tetraethylammonium perchlorate)

|	M	E° (V vs. NHE)[a]	
		$M^I(solv)_n{}^+/M$	$M^IOH/M, HO^-$
H_2O[b]	Cu	+0.52	−0.36
	Ag	+0.80	+0.34
	Au	+1.7	
	$H_2O^{\cdot+}/H_2O$; $HO^{\cdot}/HO^-$ (GC)	+2.72	+1.89
MeCN[c]	Cu	+0.19	−0.79
	Ag	+0.54	−0.30
	Au	+1.58	−0.19
	$H_2O^{\cdot+}(MeCN)/H_2O$; $HO^{\cdot}/HO^-$ (GC)	+3.2	+0.92

[a] SCE = +0.24 V vs. NHE.
[b] Ref. [7].
[c] Ref. [8].

$$Cu(s) + Cl^- \xrightarrow[\;]{-e^-} Cu^I\text{-}Cl \qquad E^{\circ}, \;+0.14 \text{ V} \qquad (49)$$

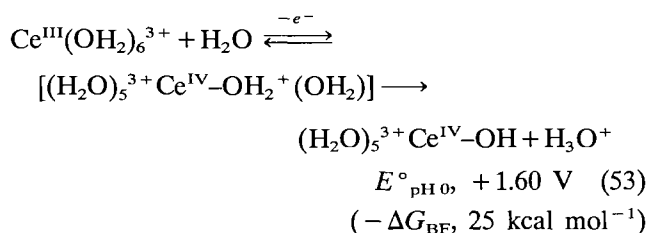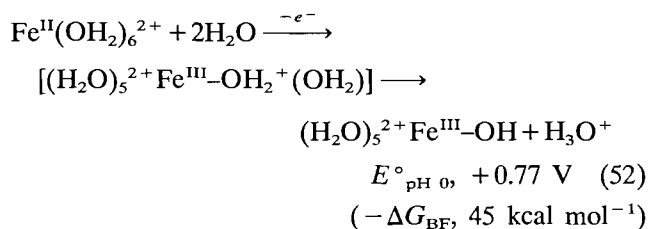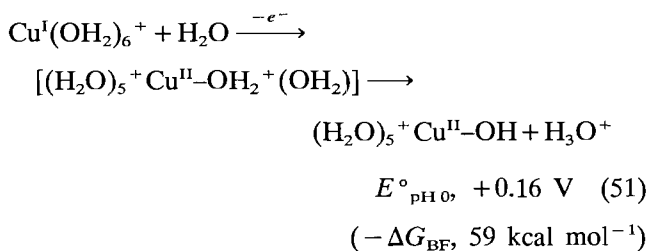$$(-\Delta G_{BF}, \; 52 \text{ kcal mol}^{-1})$$

Additional redox data for oxidations of H_2O/HO^- at Cu, Ag and Au electrodes in aqueous and acetonitrile (MeCN) solutions are summarized in Table 1 [7, 8]. At pH 0 with an iron electrode the water oxidation of Eq. (34) is shifted by -3.12 V
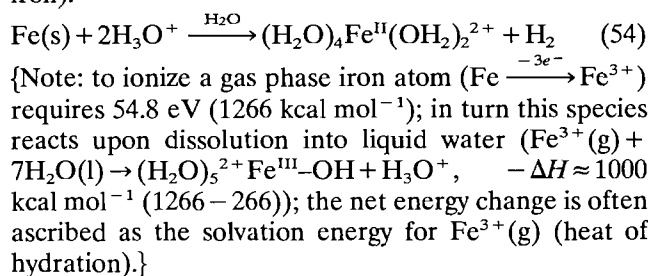
$$Fe(s) + 4H_2O \xrightarrow[\;]{-2e^-} [(H_2O)_2Fe^{II}(OH_2)_2]^{2+}$$

$$E^{\circ}_{pH\,0}, \; +0.40 \text{ V} \qquad (50)$$
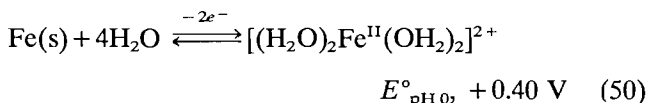
which indicates that the $[H_2O(H_2O^{\cdot})^+]$ species is stabilized by a strong $(H_2O)_2(H_2O)^+Fe^{II}\text{-}OH_2{}^+$ covalent bond ($-\Delta G_{BF}$, ~71 kcal mol^{-1}).

5. Metal complexes

In an analogous fashion, the removal of an electron (oxidation) from water via Eq. (34) is aided by the presence of transition-metal ions (e.g. $Cu^I(OH_2)_6{}^+$, $Fe^{II}(OH_2)_6{}^{2+}$ and $Ce^{III}(OH_2)_6{}^{3+}$, each with one, two and three $M\text{-}OH_2{}^+$ covalent bonds, respectively).

$$Cu^I(OH_2)_6{}^+ + H_2O \xrightarrow[\;]{-e^-}$$

$$[(H_2O)_5{}^+Cu^{II}\text{-}OH_2{}^+(OH_2)] \longrightarrow$$

$$(H_2O)_5{}^+Cu^{II}\text{-}OH + H_3O^+$$

$$E^{\circ}_{pH\,0}, \; +0.16 \text{ V} \qquad (51)$$

$$(-\Delta G_{BF}, \; 59 \text{ kcal mol}^{-1})$$

$$Fe^{II}(OH_2)_6{}^{2+} + 2H_2O \xrightarrow[\;]{-e^-}$$

$$[(H_2O)_5{}^{2+}Fe^{III}\text{-}OH_2{}^+(OH_2)] \longrightarrow$$

$$(H_2O)_5{}^{2+}Fe^{III}\text{-}OH + H_3O^+$$

$$E^{\circ}_{pH\,0}, \; +0.77 \text{ V} \qquad (52)$$

$$(-\Delta G_{BF}, \; 45 \text{ kcal mol}^{-1})$$

$$Ce^{III}(OH_2)_6{}^{3+} + H_2O \xrightarrow[\;]{-e^-}$$

$$[(H_2O)_5{}^{3+}Ce^{IV}\text{-}OH_2{}^+(OH_2)] \longrightarrow$$

$$(H_2O)_5{}^{3+}Ce^{IV}\text{-}OH + H_3O^+$$

$$E^{\circ}_{pH\,0}, \; +1.60 \text{ V} \qquad (53)$$

$$(-\Delta G_{BF}, \; 25 \text{ kcal mol}^{-1})$$

In none of these examples has the potential for removal of an electron approached the ionization potentials of the metals. Although traditional treatments attribute the potentials of Eqs. (33), (48) and (50)–(53) to the removal of electrons from the metals, coupled with large ionic solvation energies, this requires a pathway with the ionization potential as a kinetic barrier. Furthermore, the spontaneous reaction of iron with acidified water is driven by the formation of $Fe\text{-}OH_2{}^+$ and H–H covalent bonds that facilitate hydrogen atom transfer from water (rather than electron transfer from iron).
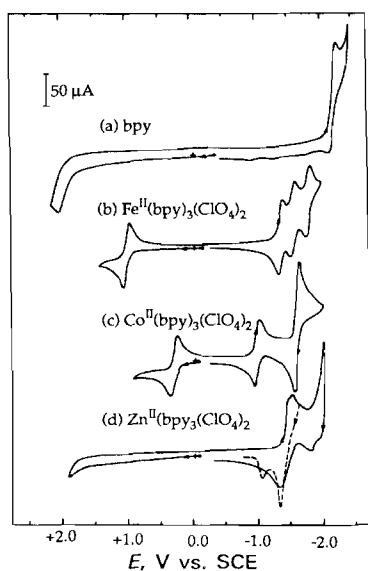
$$Fe(s) + 2H_3O^+ \xrightarrow[\;]{H_2O} (H_2O)_4Fe^{II}(OH_2)_2{}^{2+} + H_2 \qquad (54)$$

{Note: to ionize a gas phase iron atom ($Fe \xrightarrow{-3e^-} Fe^{3+}$) requires 54.8 eV (1266 kcal mol^{-1}); in turn this species reacts upon dissolution into liquid water ($Fe^{3+}(g) + 7H_2O(l) \rightarrow (H_2O)_5{}^{2+}Fe^{III}\text{-}OH + H_3O^+$, $-\Delta H \approx 1000$ kcal mol^{-1} (1266 − 266)); the net energy change is often ascribed as the solvation energy for $Fe^{3+}(g)$ (heat of hydration).}

Fig. 1. Cyclic voltammograms of 3 mM solutions in MeCN (0.1 M tetraethylammonium perchlorate): (a) bpy; (b) Fe(bpy)$_3^{2+}$; (c) Co(bpy)$_3^{2+}$; (d) Zn(bpy)$_3^{2+}$. Conditions: scan rate, 0.1 V s^{-1}; 25 °C; glassy carbon working electrode (0.09 cm^2); SCE vs. NHE, +0.242 V.

Table 2
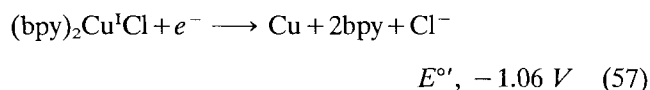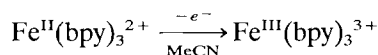Oxidation potentials for ligands (L) and their ML$_3$ complexes with Zn(II), Mn(II), Fe(II) and Co(II) in MeCN (0.1 M tetraethylammonium perchlorate)

Ligand (L or L$^-$)[a]	$E_{1/2}$[b] (V vs. NHE)[c]				
	L/L$^{·+}$ (L$^-$/L$^·$)	Zn^{II}L$_3$	Mn^{II}L$_3$	Fe^{II}L$_3$	Co^{II}L$_3$
H$_2$O	+2.8	+2.8	+2.8	+1.84	+2.8
bpy	+2.32	> +2.5	+1.55	+1.30	+0.58
PA$^-$	+1.50	+1.54	+0.60	+0.20	+0.04
acac$^-$	+0.55	+0.58	+0.18	-0.42	-0.35
8-Q$^-$	+0.21	+0.22	-0.06	-0.41	-0.57

[a]Key: bpy, 2,2'bipyridine; PA$^-$, picolinate (2-carboxylate pyridine); acac$^-$, acetylacetonate; 8-Q$^-$, 8-quinolinate.
[b]$E_{1/2}$ taken as $(E_{p,a}+E_{p,c})/2$ for reversible couples of Mn^{II}L$_3$ and Fe^{II}L$_3$ complexes; as $E_{p,a/2}$+0.03 V for L (or L$^-$) and Zn^{II}L$_3$; and as $E_{p,c/2}$-0.03 V for Co^{II}L$_3$ complexes that exhibit separated redox couples.
[c]SCE vs. NHE; +0.242 V.

$$Fe^{II}(bpy)_3^{2+} \xrightarrow[MeCN]{-e^-} Fe^{III}(bpy)_3^{3+}$$

$$E^{o\prime}, +1.30 \text{ V} \quad (58)$$

(Noteworthy are the three reversible one-electron reductions of this complex.) The electron that is removed from the Fe^{II}(bpy)$_3^{2+}$ complex comes from the ligands to give bpy$^{·+}$, which couples with one of the four unpaired electrons of the iron(II) center (d^{6}sp) to give a third covalent bond (Fe^{III}(bpy)$_3^{3+}$, d^{5}sp^2; $S=5/2$). The difference in oxidation potentials for Fe^{II}(bpy)$_3^{2+}$ and free bpy (Eq. (55)) is a measure of the Fe^{III}–bpy$^+$ bond energy ($-\Delta G_{BF}=(2.32-1.30)23.1=23.6$ kcal mol^{-1}). The potential that would be required to remove an electron from the d^{6}sp manifold of the iron(II) center of Fe^{II}(OH$_2$)$_6^{2+}$ or Fe^{II}(bpy)$_3^{2+}$ would be greater than the first ionization potential of atomic iron (7.9 eV) [5].

Table 2 summarizes the oxidation potentials for ligands (L) and their M^{II}L$_3$ complexes with zinc(II), manganese(II), iron(II) and cobalt(II). The difference in the potentials for the free and complexed ligands is a measure of the metal(III)–ligand bond formation energies ($-\Delta G_{BF}$); these are summarized in Table 3 [9]. For this group of complexes the order of metal(III)–nitrogen bond energies, Co^{III}(bpy)$_3^{3+}$ > Fe^{III}(bpy)$_3^{3+}$ > Mn^{III}(bpy)$_3^{3+}$, and of metal(III)–oxygen bond energies, Fe^{III}(acac)$_3$ > Co^{III}(acac)$_3$ > Mn^{III}(acac)$_3$, is consistent with their relative stability constants. With the picolinate (PA$^-$) ligand there is a combination metal–oxygen covalent bonding and nitrogen-base donor interaction, which shifts the bond energy order, Co^{III}(PA)$_3$ > Fe^{III}(PA)$_3$ > Mn^{III}(PA)$_3$. All of the data are consistent with ligand-centered redox processes.

Table 4 summarizes the oxidation potentials for a variety of ligands (L) in acetonitrile (MeCN) [11]. Their

Within an aprotic solvent (e.g. MeCN) oxidation of metals and metal complexes is also ligand-centered with the potential determined by the oxidation potential of the ligand and the metal–ligand covalent bond formation free energy ($-\Delta G_{BF}$). For example, the free bipyridine (bpy) ligand in acetonitrile is oxidized near the solvent limit at a glassy carbon electrode (GC) (Fig. 1) [9]

$$(bpy) \xrightarrow[MeCN]{} bpy^{·+} \quad E^{o\prime}, +2.32 \text{ V vs. NHE} \quad (55)$$
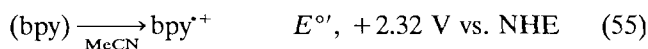
but at a copper electrode the oxidation occurs at a negatively potential [10]:

$$Cu(s) + 2bpy \xrightarrow{-e^-} Cu^I(bpy)_2^+ \quad E^{o\prime}, -0.16 \text{ V} \quad (56)$$
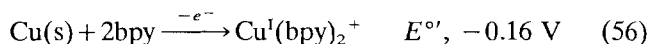
Even more striking is the reduction of [(bpy)$_2$Cu^I(OH$_2$)]$^+$ at a glassy carbon electrode, which occurs at -1.04 V versus NHE. The difference (-0.88 V) is due to the Cu–Cu bond energy (20.3 kcal mol^{-1}) that must be overcome in the metal oxidation process. Reduction of (bpy)$_2$Cu^{I}Cl occurs at essentially the same potential as that for Cu^I(MeCN)$_4$Cl (-1.01 V versus NHE) [11]:

$$(bpy)_2Cu^ICl + e^- \longrightarrow Cu + 2bpy + Cl^-$$

$$E^{o\prime}, -1.06 \text{ V} \quad (57)$$

The difference between this value and that for the Cl$^·$/Cl$^-$ couple (Eq. (39), +2.24 V versus NHE) is a measure of the (bpy)$_2$Cu^I–Cl bond energy ($-\Delta G_{BF}=[2.24-(-1.06)]23.1=76.2$ kcal mol^{-1} (the value for gas phase Cu–Cl(g) is 84±1 kcal mol^{-1}) [6]).

Fig. 1 illustrates that the oxidation of the Fe^{II}(bpy)$_3^{2+}$ complex is reversible and ligand-centered [9]:

Table 3
Apparent metal–ligand covalent bond formation free energies $(-\Delta G_{BF})$ for several manganese, iron and cobalt complexes

Complex	$-\Delta G_{BF}^a$ (kcal mol^{-1})
Manganese	
$(8Q)_2Mn^{III}$–8Q	6
$(acac)_2Mn^{III}$–acac	9
$(PA)_2Mn^{III}$–PA	22
$[(bpy)_2Mn^{III}$–bpy]$^{3+}$	$> 23^b$
Iron	
$(8Q)_2Fe^{III}$–8Q	15
$(acac)_2Fe^{III}$–acac	23
$(PA)_2Fe^{III}$–PA	31
$[(bpy)_2Fe^{III}$–bpy]$^{3+}$	$> 29^b$
$[(Ph_3PO)_3Fe^{III}$–OPPh$_3$]$^{3+}$	$> 30^b$
$[(MeCN)_4Fe^{III}$–OH$_2$]$^{3+}$	23
Cobalt	
$(8Q)_2Co^{III}$–8Q	16
$(acac)_2Co^{III}$–acac	21
$(PA)_2Co^{III}$–PA	35
$[(bpy)_2Co^{III}$–bpy]$^{3+}$	$> 46^b$

$^a(-\Delta G_{BF}) = [E_{1/2}[ZnL_3^-/ZnL_2(L^.)] - E_{1/2}(ML_3^-/M(^.L)L_2] \times 23.1$ kcal mol^{-1}.

$^b(-\Delta G_{BF}) = [E_{p,a}(ZnL/ZnL^{.+}) - E_{p,a}(ML/M^{.}L^+)] \times 23.1$ kcal mol^{-1}; L = (bpy)$_3$ or (Ph$_3$PO)$_4$.

Table 4
Redox potentials for ligands in acetonitrile (0.1 M (Et$_4$N)ClO$_4$)

Ligand (L)^a	$E_{p,a}^{b,c}$ (V vs. SCE)	$E_{p,c}^b$ (V vs. SCE)
H$_2$O	2.80	
py	2.30	-2.75
bpy	2.15	-2.25
tpy	2.00	-2.15, -2.5
Cl$^-$	2.00	
PhC(O)O$^-$	1.45	
PA$^-$	1.34	
AcO$^-$	1.30	
DPAH$^-$	1.20	
HOC(O)O$^-$	1.15, 1.55	
HO$^-$	0.68	
PhCH$_2$O$^-$	0.50	
DPA^{2-}	0.25, 1.25	
TDTH$^-$	-0.05	

^{a}Key: bpy, 2,2′-bipyridine; tpy, 2,2′:6′,2″-terpyridine; PA$^-$, picolinate anion; DPAH$^-$, 2,6-carboxyl, carboxylato-pyridine anion; DPA^{2-}, 2,6-dicarboxylato-pyridine dianion; HOC(O)O$^-$, bicarbonate anion; TDTH$^-$, toluene-3,4-dithiol anion.

$^b E_{p,a}$, anodic peak potential; $E_{p,c}$, cathodic peak potential; glassy carbon electrode (GCE); scan rate, 0.1 V s^{-1}.

^{c}Saturated calomel electrode (SCE); E_{SCE}, +0.242 V vs. NHE.

relative Lewis basicity (nucleophilicity) increases as their oxidation potential becomes less positive. However, the potential at which L is oxidized (and L$^.$ is reduced) within an ML$_x$ complex is shifted by the M–L covalent bond energy $(-\Delta G_{BF})$. Figs. 2 and 3 illustrate the electrochemistry for several copper(II) and copper(I) complexes in MeCN. The redox potentials for these
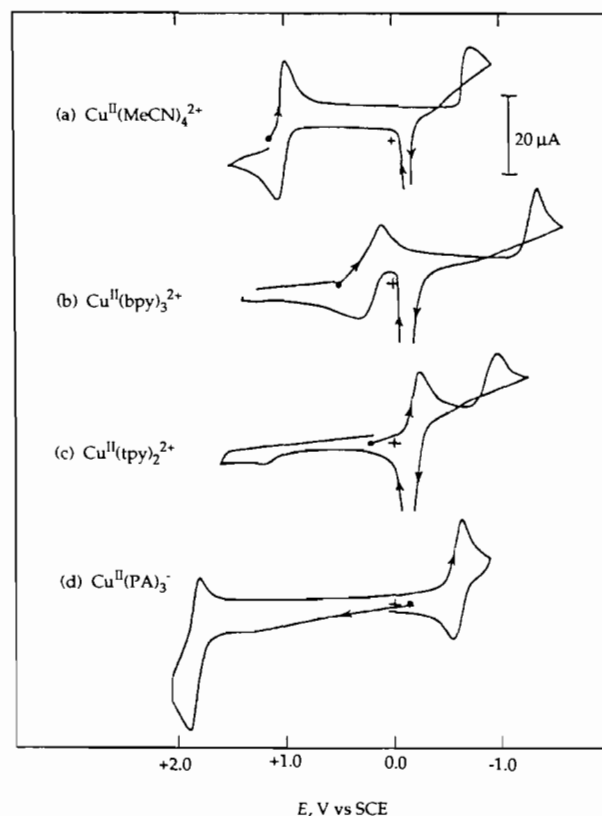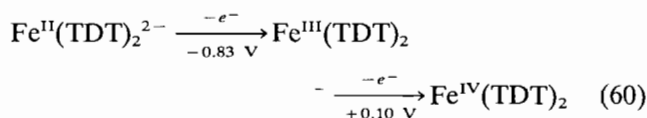

Fig. 2. Cyclic voltammograms of: (a) 1 mM [Cu^{II}(MeCN)$_4$](ClO$_4$)$_2$; (b) (a) plus 3 equiv. of bpy; (c) (a) plus 2 equiv. of tpy; (d) (a) plus 3 equiv. of PA$^-$ in MeCN (0.1 M (Et$_4$N)ClO$_4$). Scan rate, 0.1 V s^{-1}; GCE (0.09 cm^2); SCE vs. NHE, +0.242 V.

copper complexes and their ligands are summarized in Table 5. In addition, the shift in redox potential (ΔE) for the free ligand (L) and when bonded in a complex (CuL$_x$) is tabulated. This quantity is a measure of the apparent copper–ligand covalent bond formation free energy $(-\Delta G_{BF})$ (Table 6).

$$-\Delta G_{BF} = (\Delta E)23.1 \text{ kcal mol}^{-1} \qquad (59)$$

Table 6 summarizes the copper–ligand bond energies for the various complexes.

The dianion of toluene-3,4-dithiol (TDT^{2-}) forms unique complexes [M^{II}(TDT)$_2^{2-}$] with transition metals that are readily oxidized via a ligand-centered process to M^{III}(TDT)$_2^-$ [12]. Fig. 4 illustrates the cyclic voltammetry for the latter complexes of Cu, Ni, Co and Fe. Not only do each of the M^{III}(TDT)$_2^-$ complexes undergo a reversible one-electron reduction, but the Ni(III), Co(III) and Fe(III) complexes also exhibit a somewhat reversible oxidation to the M(IV) valence state. For example,
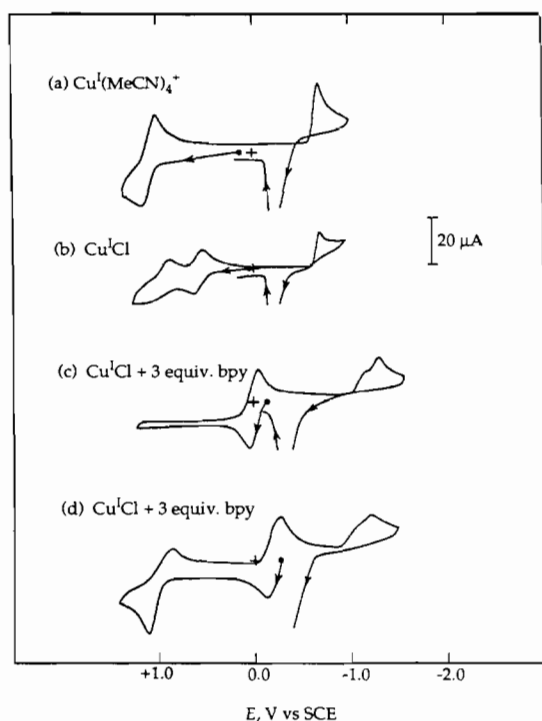
$$Fe^{II}(TDT)_2^{2-} \xrightarrow[-0.83 \text{ V}]{-e^-} Fe^{III}(TDT)_2$$

$$^- \xrightarrow[+0.10 \text{ V}]{-e^-} Fe^{IV}(TDT)_2 \qquad (60)$$

Fig. 3. Cyclic voltammograms of: (a) 1 mM $Cu^I(MeCN)_4^+$; (b) 1 mM Cu^ICl; (c) (b) plus 3 mM bpy; (d) (b) plus 3 mM tpy in MeCN (0.1 M $(Et_4N)ClO_4$). Scan rate, 0.1 V s^{-1}; GCE (0.09 cm^2); SCE vs. NHE, +0.242 V.

Table 7 summarizes the redox potentials for this group of complexes and the estimated M–S bond energies $(-\Delta G_{BF})$ in the $M^{III}(TDT)_2^-$ and $M^{IV}(TDT)_2$ complexes. These are based on the oxidation potential difference (ΔE) between the $M^{II}(TDT)_2^{2-}$ complex and $Zn^{II}(TDT)_2^{2-}$ (not able to form a third covalent bond) and the ΔE between $M^{III}(TDT)_2^-$ and $Cu^{III}(TDT)_2^-$ (filled valence-electron shell and unable to form a fourth covalent bond), respectively $(-\Delta G_{BF} = (\Delta E)\ 23.1$ kcal mol^{-1}).

Although most iron(II) complexes are oxidized by hydrogen peroxide (HOOH) via Fenton chemistry

$$2Fe^{II}L_x + HOOH \longrightarrow 2L_xFe^{III}OH \qquad (61)$$

within MeCN the combination of $Fe^{II}(OPPh_3)_4^{2+}$ and HOOH (1:10) yields a unique purple complex (λ_{max}, 576 nm (ϵ, 1770 M^{-1} s^{-1})), $(Ph_3PO)_4^{2+}Fe^{III}OOH$ [13]. The reversible one-electron, ligand-centered oxidation of $Fe^{II}(OPPh_3)_4^{2+}$ at +1.2 V versus SCE is replaced by an irreversible two-electron oxidation at +1.9 V (Fig. 5).

$$(Ph_3PO)_4^{2+}Fe^{III}OOH + 2H_2O \xrightarrow{-2e^-}$$
$$(Ph_3PO)_4^{2+}Fe^{III}OH + O_2 + 2H_3O^+ \qquad (62)$$
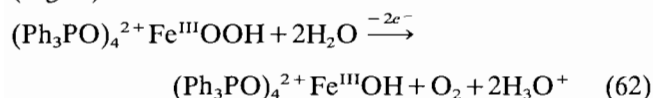
Whereas $Fe^{II}(OPPh_3)_4^{2+}$ is reduced by two electrons at −1.1 V to give metallic iron, the $(Ph_3PO)_4^{2+}$-$Fe^{III}OOH$ complex is reduced in several steps to give an iron oxide.
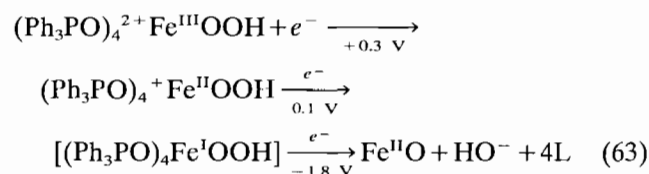
Table 5
Redox potentials for copper complexes and their ligands in MeCN

Electrode reaction	$E_{1/2}$[a] (V vs. SCE)[b]	ΔE[c] (V)
$bpy - e^- \rightarrow bpy^{\cdot+}$	2.1	
$Cu^{II}(bpy)_2^{2+} + e^- \rightarrow Cu^I(bpy)_2^+$	0.1	2.0
$Cu^{II}(OH)(bpy)_2^+ + e^- \rightarrow Cu^I(OH)(bpy)_2$	−0.1	2.2
$Cu^{II}(OAc)(bpy)_2^+ + e^- \rightarrow Cu^I(OAc)(bpy)_2$	−0.1	2.2
$tpy - e^- \rightarrow tpy^{\cdot+}$	1.9	
$Cu^{II}(tpy)_2^{2+} + e^- \rightarrow Cu^I(tpy)_2^+$	−0.2	2.1
$Cu^I(tpy)_2^+ + e^- \rightarrow Cu + 2tpy$	−0.9	2.8
$PA^- - e^- \rightarrow PA^{\cdot}$	1.3	
$Cu^{II}(PA)_3^- + e^- \rightarrow Cu^I(PA) + 2PA^-$	−0.6	1.9
$Cu^I(PA) + e^- \rightarrow Cu + PA^-$	−1.6	2.9
$AcO^- - e^- \rightarrow AcO^{\cdot}$	1.2	
$Cu^I(OAc)(MeCN)_4 + e^- \rightarrow Cu + 4MeCN + AcO^-$	−1.2	2.4
$Cu^I(OAc)(bpy)_2 + e^- \rightarrow Cu + 2bpy + AcO^-$	−1.3	2.5
$PhC(O)O^- - e^- \rightarrow PhC(O)O^{\cdot}$	1.4	
$Cu^{II}[OC(O)Ph]_2 + e^- \rightarrow Cu^I[OC(O)Ph] + PhC(O)O^-$	−0.25	1.65
$Cu^I[OC(O)Ph] + e^- \rightarrow Cu + PhC(O)O^-$	−1.3	2.7
$PhCH_2O^- - e^- \rightarrow PhCH_2O^{\cdot}$	0.4	
$Cu^{II}(OCH_2Ph)_2(bpy)_2 - e^- \rightarrow Cu^I(OCH_2Ph)_2^-(bpy)_2$	−0.4	0.8
$DPAH^- - e^- \rightarrow DPAH^{\cdot}$	1.2	
$Cu^{II}(DPAH)(DPA)^- + e^- \rightarrow Cu^I(DPA)^- + DPAH^-$	−0.5	1.7
$DPA^{2-} - e^- \rightarrow DPAH^{\cdot-}$	0.2	
$Cu^I(DPA)^- + e^- \rightarrow Cu + DPA^{2-}$	−1.8	2.0
$Cl^- - e^- \rightarrow Cl^{\cdot}$	2.0	
$Cu^{II}Cl_2(MeCN)_4 + e^- \rightarrow Cu^ICl(MeCN)_4 + Cl^-$	0.56	1.44
$Cu^{II}Cl_2(bpy)_2 + e^- \rightarrow Cu^ICl(bpy)_2 + Cl^-$	0.02	1.98
$Cu^{II}Cl_2(tpy) + e^- \rightarrow Cu^ICl(tpy) + Cl^-$	−0.1	2.1
$Cu^ICl(MeCN)_4 + e^- \rightarrow Cu + 4MeCN + Cl^-$	−1.2	3.2
$Cu^ICl(bpy)_2 + e^- \rightarrow Cu + 2bpy + Cl^-$	−1.25	3.25
$Cu^ICl(tpy) + e^- \rightarrow Cu + tpy + Cl^-$	−1.15	3.15
$HO^- - e^- \rightarrow HO^{\cdot}$ (at pH 7 in H_2O)	2.1	
$Cu^I(OH)(H_2O)_3 + e^- \rightarrow Cu + 3H_2O + HO^-$	−0.3	2.4
$Cu^I(OH)(bpy)_2 + e^- \rightarrow Cu + 2bpy + HO^-$	−1.3	3.4

[a]$E_{1/2}$ taken as $E_{p,a/2}$ +0.03 V for the irreversible reduction and $E_{p,c/2}$ −0.03 V for the irreversible oxidation.
[b]Saturated calomel electrode (SCE) vs. NHE, +0.242 V.
[c]$\Delta E = E_{1/2}(L^+/L) - E_{1/2}(Cu^{II}/Cu^I)$ or $\Delta E = E_{1/2}(L^+/L) - E_{1/2}(Cu^I/Cu^{\cdot})$.

$$(Ph_3PO)_4^{2+}Fe^{III}OOH + e^- \xrightarrow[+0.3\ V]{}$$
$$(Ph_3PO)_4^+Fe^{II}OOH \xrightarrow[0.1\ V]{e^-}$$
$$[(Ph_3PO)_4Fe^IOOH] \xrightarrow[-1.8\ V]{e^-} Fe^{II}O + HO^- + 4L \qquad (63)$$

The electrochemical reduction of permanganic acid $[HOMn^{VII}(O)_3]$, which is traditionally represented as a metal-centered electron transfer to change Mn^{7+} to Mn^{6+}, is another example of a ligand-centered process.
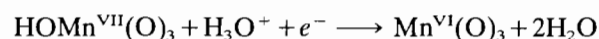
$$HOMn^{VII}(O)_3 + H_3O^+ + e^- \longrightarrow Mn^{VI}(O)_3 + 2H_2O$$
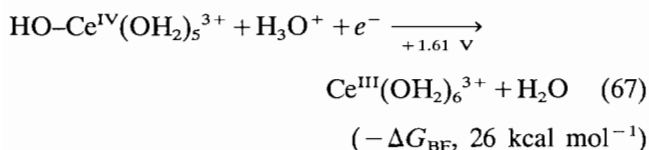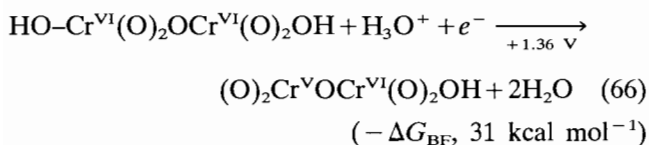$$E^\circ,\ +1.51\ V\ vs.\ NHE \qquad (64)$$

Table 6
Apparent metal–ligand covalent bond formation free energies $(-\Delta G_{BF})$ for several copper complexes

Metal–ligand bond	$-\Delta G_{BF}$ (kcal mol^{-1})
(bpy)$^+$–Cu^{II}(bpy)$_2^+$	46
(bpy)$^+$–Cu^{II}(OH)(bpy)	51
(bpy)$^+$–Cu^{II}(OAc)(bpy)	51
(tpy)$^+$–Cu^{II}(tpy)$^+$	48
(tpy)$^+$–Cu^I(tpy)	64
PA–Cu^{II}(PA)$_2^-$	43
PA–Cu^I	67
AcO–Cu^I(MeCN)$_4$	55
AcO–Cu^I(bpy)$_2$	57
PhC(O)O–Cu^{II}[OC(O)Ph]	37
PhC(O)O–Cu^I	62
PhCH$_2$O–Cu^{II}(OCH$_2$Ph)(bpy)$_2$	18
DPAH–Cu^{II}(DPA)$^-$	39
DPA$^-$–Cu^I	46
Cl–Cu^{II}Cl(MeCN)$_4$	33
Cl–Cu^{II}Cl(bpy)$_2$	46
Cl–Cu^{II}Cl(tpy)	48
Cl–Cu^I(MeCN)$_4$	74
Cl–Cu^I(bpy)$_2$	75
Cl–Cu^I(tpy)	73
HO–Cu^I(H$_2$O)$_3$	55
HO–Cu^I(bpy)$_2$	78

Comparison of this with the reduction of free hydroxyl radical (HO$^•$)

$$HO^• + H_3O^+ + e^- \longrightarrow 2H_2O \qquad E°, +2.72 \text{ V} \qquad (65)$$
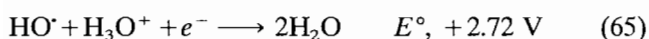
provides a measure of the HO–Mn^{VII}(O)$_3$ bond energy $(-\Delta G_{BF} = (2.72 - 1.51)23.1 = 28$ kcal mol^{-1}). The other strong oxidants ((HO)$_2$Cr$_2^{VI}$(O)$_5$ and HOCe^{IV}(OH$_2$)$_5^{3+}$) that are used for aqueous redox titrations are reduced by a similar path.

$$HO–Cr^{VI}(O)_2OCr^{VI}(O)_2OH + H_3O^+ + e^- \xrightarrow[+1.36 \text{ V}]{}$$

$$(O)_2Cr^VOCr^{VI}(O)_2OH + 2H_2O \quad (66)$$

$$(-\Delta G_{BF}, 31 \text{ kcal mol}^{-1})$$

$$HO–Ce^{IV}(OH_2)_5^{3+} + H_3O^+ + e^- \xrightarrow[+1.61 \text{ V}]{}$$

$$Ce^{III}(OH_2)_6^{3+} + H_2O \quad (67)$$

$$(-\Delta G_{BF}, 26 \text{ kcal mol}^{-1})$$

An important point in these electron-transfer reductions is that the primary electron acceptor is the hydronium ion (H$_3$O$^+$), which is transformed to a hydrogen atom (H$^•$) that reacts with HO$^•$ (either free or bound via a covalent bond to the metal center).

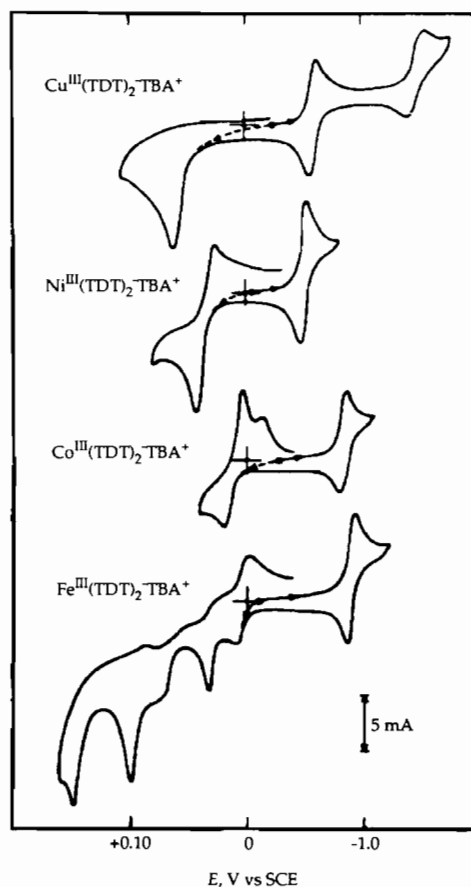Under alkaline conditions Mn^{VII}O$_4^-$ is reduced via direct electron addition to one of the bound oxygen atoms.

Fig. 4. Cyclic voltammograms in MeCN (0.1 M TEAP) of [M^{III}(TDT)$_2^-$][Bu$_4$N] complexes (M = Cu, Ni, Co and Fe). Scan rate, 0.1 V s^{-1}; Pt electrode surface area, 0.11 cm^2.

Table 7
Electrochemical oxidation potentials for M^{II}(TDT)$_2^{2-}$ complexes in MeCN (0.1 M TEAP)

Metal (M)	$E_{p,a}$ (V vs. SCE)		$-\Delta G_{BF}$ (kcal mol^{-1})	
	First oxidation	Second oxidation	M^{III}–S	M^{IV}–S
(TDTH$^-$)	−0.05 (irrev.)			
Zn	+0.18 (irrev.)			
Cu	−0.53	+0.62	16.4	
Ni	−0.47	+0.44	15.0	4.2
Co	−0.73	+0.20	21.0	9.7
Fe	−0.83	+0.10, +0.32	23.3	12.0
Mn	−0.63	+0.22 (irrev.)	18.7	9.2

$$^-OMn^{VII}(O)_3 + e^- \longrightarrow \; ^-OMn^{VI}(O)_2O^-$$

$$E°, +0.55 \text{ V vs. NHE} \quad (68)$$
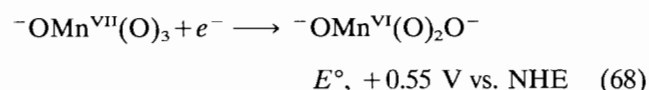
The extent of the stabilization of the oxygen atom in Mn^{VIII}O$_4^-$ is indicated by the reduction potential for a free $^•$O$^•$ atom:
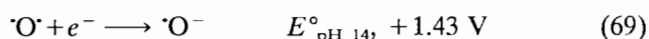
$$^•O^• + e^- \longrightarrow \; ^•O^- \qquad E°_{pH\ 14}, +1.43 \text{ V} \quad (69)$$

Table 8
Redox potentials for $(Cl_8TPP)M$ porphyrins (M = Zn, Mn, Fe, Co) and their complexes in H_2CCl_2

	$E^{\circ\prime}$ (V vs. SCE)				
	$MP^{2+} \leftarrow MP^{\bullet+}$	$MP^{\bullet+} \leftarrow MP$	$PML \leftarrow PM + L^-$	$MP \rightarrow MP^{\bullet-}$	$MP^{\bullet-} \rightarrow MP^{2-}$
$(Cl_8TPP)H_2$	+1.63	+1.23		-1.10	-1.54
$(Cl_8TPP)Zn^{II}$	+1.34	+1.02		-1.27	-1.72
$(Cl_8TPP)Mn^{III}Cl^a$	+1.49	-0.06	-0.23	-1.34	
$(Cl_8TPP)Fe^{III}Cl$	+1.64	+1.35	-0.29	-0.97 (M→M⁻)	-1.63
$(Cl_8TPP)Co^{II}$	+1.25	+0.82		-0.86 (M→M⁻)	-1.29
$(Cl_8TPP)Fe^{III}OH^b$	+1.64	+1.35	-0.75	-1.31	-1.63

[a] $(Cl_8TPP)Mn^{III}Cl \rightarrow [(Cl_8TPP)Mn^{IV}Cl]^+ + e^-$, $E^{\circ\prime} = +0.88$ V vs. SCE.

[b] $(Cl_8TPP)Fe^{III}OH \rightarrow [(Cl_8TPP)Fe^{IV}(O)] + e^-$, $E^{\circ\prime} = +1.00$ V vs. SCE; generated from $(Cl_8TPP)Fe^{III}Cl$ plus 1 equiv. of $(Bu_4N)OH$.
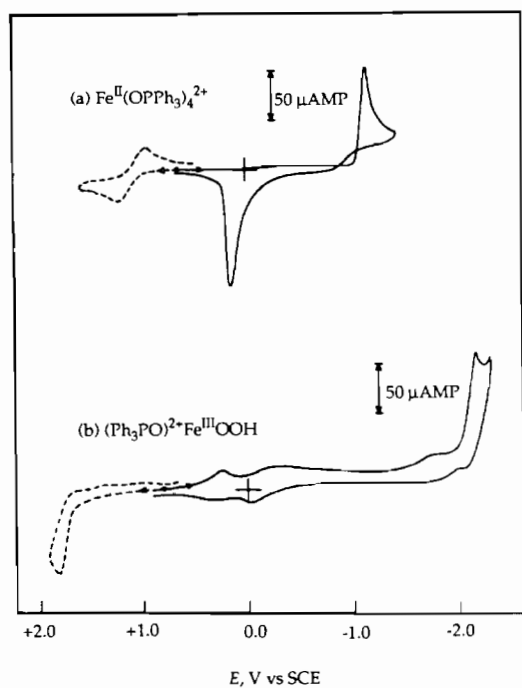

Fig. 5. Cyclic voltammograms in MeCN of (a) 3 mM $Fe^{II}(OPPh_3)_4(ClO_4)_2$ and (b) 3 mM $(Ph_3PO_4^{2+}Fe^{III}OOH$. Scan rate, 0.1 V s⁻¹; glassy carbon working electrode (area 0.11 cm²).

6. Metalloporphyrins

Although metalloporphyrins often are classified as coordination complexes, they are much closer to organometallic compounds with their strong metal–nitrogen covalent bonds. Table 8 summarizes the redox potentials for several neutral porphyrins and their chloro and hydroxo derivatives [9]. Again the electron-transfer processes are ligand- or porphyrin-centered. However, the reductions of $(Cl_8TPP)Co^{II}$ and $(Cl_8TPP)Fe^{II}$ are unique because they are metal-centered to give $(Cl_8TPP)Co^-$ and $(ClTPP)Fe^-$ [11]. The latter are nucleophiles that react with alkyl halides, e.g.

$$(Cl_8TPP)Fe^- + n\text{-}BuBr \longrightarrow$$

$$(Cl_8TPP)Fe^{III}\text{-}(n\text{-}Bu) + Br^- \quad (70)$$
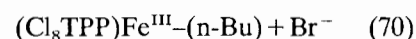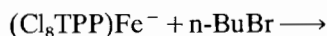
In summary, the electron-transfer reactions for metals, metal complexes and metalloporphyrins are ligand-centered (or solvent-centered). In each case the potential for the oxidation of free ligand is decreased in the presence of metal or reduced-metal complex by an amount that is proportional to the metal–ligand bond energy $(-\Delta G_{BF})$.

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