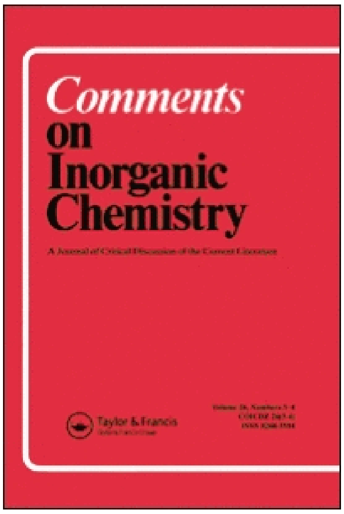

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Electron-Transfer Thermodynamics, Valence-Electron Hybridization, and Bonding for Iron Compounds

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Electron-Transfer Thermodynamics, Valence-Electron Hybridization, and Bonding for Iron Compounds

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The electron-transfer thermodynamics (a) for iron compounds (FeX_m) and complexes (FeL_n) and (b) for their heteroatoms (X/X^-) and ligands (L/L^-) in combination with other physical data provide insight into the valence-electron hybridization and bonding of the iron center. The basic conclusions are: (a) the chemical bonding of iron in its compounds and complexes is covalent and similar to that of carbon, (b) the electron-transfer processes of iron complexes are ligand-centered, and (c) the iron-ligand covalent bond energies can be evaluated from the electrochemically determined redox thermodynamics.

Key Words: *iron complexes, iron porphyrins, electronegativities, covalent bond energies, covalent bonding, iron–oxygen bonds, iron proteins*

Because iron is ubiquitous on earth, is essential to all forms of life, reacts spontaneously in its elemental form with dioxygen, and is the most versatile of the first-row transition metals with respect to compound formation, the chemistry of its compounds has been a primary interest of many scientists. Enzymologists, bioinorganic chemists, and nutritional biochemists have focused on the vital role of iron-proteins for the transport and storage of dioxygen and the catalysis of (a) electron-transfer processes, (b) oxidations and

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dehydrogenations, (c) monoxygenations, and (d) dioxygenations. Likewise, the extensive use of iron in structural steel and its propensity to undergo corrosion by O_2/water systems has prompted extensive engineering studies in search of effective strategies to prevent or inhibit the destructive reactions of dioxygen with metallurgical iron.

In spite of the long and extensive history of iron chemistry, a perusal of contemporary freshman chemistry texts and monographs on inorganic chemistry confirms that there is lack of precision and coherence in the discussion of the bonding, electron-transfer pathways, and valence-electron density and hybridization for iron in its compounds. For example, ferrate ion (FeO_4^{2-}) is universally formulated as an ionic salt $Fe^{6+}(O^{2-})_4$ ($3d^2$, $S = 2/2$, tetrahedral). This, in spite of the fact that O^{2-} is unattainable with electron beams in a vacuum, which would make it a stronger reducing agent than the electron (electrons transform all oxidized iron to Fe^{O}).

Thus, the bonding in transition-metal compounds and complexes has traditionally been viewed as ionic (positive metal center interacting with negative ions; ^{-}OH, O^{2-}, Cl^{-}, ^{-}OAc) and coordinate donor [Lewis acid–base interactions; positive metal center interacting with negative ions and electron-pair Lewis bases

$$(:\mathrm{NH}_3,\ :\mathrm{PPh}_3,\ \mathrm{H}\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\mathrm{H})].$$

Examples of ionic versus covalent bonding illustrate the tradition; $H^{+}Cl^{-}$ vs. H–Cl (1s–3p), $C^{4+}(Cl^{-})_4$ vs. $C(-Cl)_4[2sp^3-(3p)_4]$, $Fe^{3+}(Cl^{-})_3$ vs. $Fe^{O}(-Cl)_3[3d^5sp^2\text{-}(3p)_3]$, $H^{+}\ ^{-}OH$ vs. H–OH (1s–2p), $C^{4+}(O^{2-})$ vs. O═C═O $[2sp^3 = (2p^2)_2]$, and $Fe^{2+}(O^{2-})$ vs. Fe═O $[3d^6sp{=}(2p^2)_2]$. Such ionic formulations for these molecules in an inert matrix are not consistent with their physical and chemical properties. The continued propensity to use ionic bonds with 8-valence-electron oxygen [oxo, oxide, O^{2-} ($2s^2p^6$)] in the formulations of iron compounds is akin to our fondness for an emotional function for the human heart muscle.

The fundamental axiom of the valence-bond theory[1] is that elemental atoms that are connected by covalent bonds are as close to electrical neutrality as is consistent with their respective electronegativities. Hence, uncharged molecules, which consist of uncharged atoms that are held together by covalent bonds, react with each other (in an inert matrix) to give uncharged molecules (with uncharged atoms held together by covalent bonds). For example

$$(\mathrm{Na_2})_g \text{ (Bond Energy, 17.6 kcal)}$$

$$+ (\mathrm{Cl_2})_g \text{ (BE, 59.0 kcal)} \longrightarrow 2\ (\mathrm{NaCl})_g \text{ (BE, 98.5 kcal)} \quad (1)$$

with a charge-excess of 0.66 electron for the chlorine of NaCl on the basis of its gas-phase dipole moment[2] as well as the difference in the electronegativities of Na and Cl (Table I).[3-5] The charge-excesses (δ) for the oxygen in several metal-oxygen diatomic molecules [estimated on the basis of their respective electronegativities (χ)][3-5] are summarized in Table I together with their gas-phase covalent bond energies (ΔH_{DBE}).[6]

The valence-bond concept of chemical bonding[1] begins with the proposition that two neutral atoms combine to form covalent electron-pair bonds via a 1:1 contribution of unpaired valence electrons from the two atoms, e.g.,

$$\mathrm{H}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\!: \longrightarrow \mathrm{H{-}}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cl}}}\!:.$$

Although the term *valence* is used in organic chemistry to indicate the number of covalent bonds for an atom in a molecule [for example, the carbon atoms in diamond (C_n), CH_4, CCl_4, CO_2, and benzene (C_6H_6) have a valence of 4], many inorganic chemists use valence to mean the oxidation state (oxidation number, ionic valence, or charge number) of atoms in molecules. For example, the chemical formula for CrO_3 often is written $Cr^{6+}(O^{2-})_3$ with oxidation numbers of six (VI) and two (II) assigned to Cr and O. However, the bonding in CrO_3 is more reasonably formulated as covalent with 3 σ-bonds and 3 π-bonds between a chromium atom ($d^4s^2 \rightarrow d^3sp^2$) and 3 oxygen atoms ($s^2p^4$), and is similar to that in CO_2(C, sp^3 and O, s^2p^4). In CrO_3 the six covalent bonds mean the valence for chromium is 6 (as it is 4 for carbon in CO_2).

This confusion in nomenclature may be reduced by the use of *covalence* in place of valence and defined as the number of covalent bonds of an atom in a molecule. This term was first suggested by

TABLE I

Bonding, electronegativities, and charge density for metal-chlorine and metal-oxygen molecules

A. Metal-Chlorine		M–Cl		
Element	χ^a	Bond Energy^b ΔH_{DBE}(kcal)	δ^c $(\mathrm{Cl}^{-\delta})$	Valence-Electron Hybridization of M
H	7.18	103 ± 1	0.12(0.18)^d	s
Na	2.84	98 ± 2	0.66(0.66)	s
Cs	2.19	107 ± 2	0.78(0.62)	s
Ba	2.60	104 ± 2	0.70	sp
Zn	4.70	55 ± 5	0.40	$d^{10}sp$
Mn	3.72	86 ± 2	0.52	$d^{5}sp$
Fe	**4.01**	**84**	**0.48**	**$d^{6}sp$**
Co	4.27	93	0.46	$d^{7}sp$
Ni	4.40	89 ± 5	0.44	$d^{8}sp$
Cu	4.48	92 ± 1	0.42	$d^{10}s$
Cl	8.30			

B. Metal-Oxygen

		M=O		
Element	χ^a	Bond Energy[b] ΔH_{DBE}(kcal)	δ^c (O^{-1})	Valence-Electron Hybridization of M
Ba	2.60	34 ± 3	0.60(0.62)[d]	sp
Zn	4.70	65 ± 10	0.30	$d^{10}sp$
Mn	3.72	96 ± 10	0.44	d^5sp
Fe	4.01	93 ± 4	0.40	d^6sp
Co	4.27	92 ± 3	0.36	d^7sp
Ni	4.40	91 ± 4	0.34	d^8sp
Cu	4.48	64 ± 5	0.34	d^9sp
O	7.55			

[a] Electronegativity; $\chi = (IP + EA)/2$ (Refs. 3 and 4).

[b] Dissociative bond energy for M–Cl or M=O; kcal-mol^{-1} (Ref. 6).

[c] $\Delta N_{MY} = |(\chi_M \times \chi_Y)^{1/2} - \chi_Y|/5.2$ (Ref. 5).

[d] For HCl, dipole moment is 1.08 debyes and interatomic distance is 1.267 Å;

$$\Delta N_{HCl} = \frac{1.08 \times 10^{-18}}{1.27 \times 10^{-8} \times 4.8 \times 10^{-10}} = 0.18 \text{ (Ref. 2).}$$

For BaO, dipole moment is 7.95 debyes and interatomic distance is 2.66 Å;

$$\Delta N_{BaO} = \frac{7.95 \times 10^{-18}}{2.66 \times 10^{-8} \times 4.8 \times 10^{-10}} = 0.62 \text{ (Ref. 2).}$$

Langmuir to give a quantitative measure of the number of covalent bonds for an atom in a molecule.[7] Thus, for the molecules $FeCl_2$, FeO, $Fe(Cp)_2$, (porphyrin)Fe, and $Fe(Me)_2$ the covalence of iron is two; for $FeCl_3$, Fe_2O_3, $Fe(OH)_3$, and (porphyrin)Fe(OH) the covalence of iron is three; for (porphyrin)Fe(O) ("ferryl iron") the covalence of iron is four; for FeO_4^{2-} (ferrate) and $Fe(catecholate)_3$ the covalence of iron is six; and for $Fe(CO)_5$ the covalence of iron is eight. In each of these compounds the iron atom is uncharged and has eight valence electrons ($3d^6 4s^2 \rightarrow d^6sp \rightarrow d^5sp^2$). For these examples, the traditionally used formal oxidation states of the iron [II, III, IV, VI, and VIII (or 0), respectively] are the same as their covalences (number of covalent bonds). However, the iron in $(porphyrin)Fe^+$ (d^5sp) has a covalence of two, a formal oxidation state of three, and a charge of +1. In the present discussion Roman numeral superscripts associated with the iron in the formulas for its compounds and complexes indicate its covalence (number of covalent bonds), *not* its oxidation state or number.

The second axiom of the valence-bond theory is that chemical bonds in metal salts and complexes are a combination of covalent (electron-pair) and ionic (electrostatic positive ion-negative ion attraction) bonding.[8] Thus, for the HCl molecule (ΔH_{DBE}, 103 kcal)[6] the covalent portion of the bond energy is assumed to be equal to the geometric mean of the covalent bond energies for H_2 (ΔH_{DBE}, 104 kcal)[6] and Cl_2 (ΔH_{DBE}, 59 kcal),[6] $(104 \times 59)^{1/2} = 78$ kcal. The difference, $\Delta = (103 - 78) = 25$ kcal, has been assigned to electrostatic interactions between $H^{\delta +}$ and $Cl^{\delta -}$ of the HCl molecule (ionic portion of the bond energy), and is the basis of the Pauling scale of electronegativities,[1] $(\Delta/96) = (\chi_{Cl} - \chi_H)^2$, and the assumption that HCl(g) is 24% ionic [(25/103)100 = 24]. Because this is a circular argument with respect to an estimate of the degree of ionic bonding (and predicts that the bonding of CO is 49% ionic), a more reasonable approach is to use the Mulliken definition of electronegativity, which is one-half of the sum of the element's first ionization potential (IP) and its electron affinity (EA), $\chi = (IP + EA)/2$.[8]

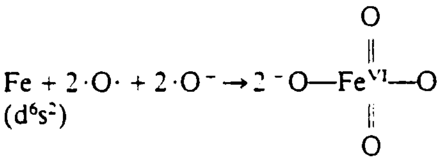
With modern data[3] the electronegativity values can be used to estimate the charge transfer (δ or ΔN) in diatomic molecules, as illustrated in Table I for HCl, metal-chlorine molecules, and metal-oxygen molecules. The gas-phase dipole moments for HCl, CsCl, KCl, and BaO and their interatomic distances provide a direct measure of the metal-chlorine and metal-oxygen charge transfer (ΔN). The use of Mulliken electronegatives to predict ΔN appears consistent with the measured quantities, although the degree of charge transfer is overestimated by up to 25% for CsCl. In any case, the electronegativity differences for CsCl and BaO are the largest of the periodic table (if F is treated as a special case), yet their bonds are 38% covalent. *Hence, to a first approximation all chemical bonds have substantial covalency, and neutral molecules are assembled from neutral atoms (with valence-electron hybridization to give unpaired electrons) via electron-pair formation (covalent bonds).* For example,

$$\underset{(1s)}{2H\cdot} + \underset{(2s^2p^4)}{\cdot O\cdot} \longrightarrow H{-}O{-}H \qquad \text{O covalence. 2} \qquad (2)$$

$$\underset{(2\ sp^3)}{\cdot\dot{\underset{\cdot}{C}}\cdot} + \underset{(2s^2p^4)}{2\ \cdot O\cdot} \longrightarrow O{=}C{=}O \qquad \text{C covalence. 4} \qquad (3)$$

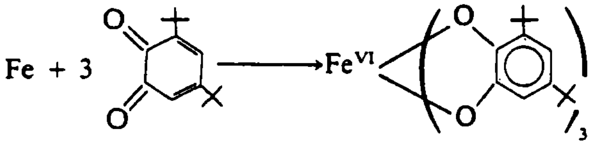
$$\underset{(d^6s^2)}{Fe} + \underset{(s^2p^4)}{\cdot O\cdot} \longrightarrow \underset{(d^6sp)}{Fe^{II}} = O \qquad \text{Fe covalence, 2} \qquad (4)$$

$$\underset{(d^6s^2)}{2\,Fe} + 3\cdot O\cdot \longrightarrow O = \underset{(d^5sp^2)}{Fe^{III}{-}O{-}Fe^{III}} = O \qquad \text{Fe covalence. 3} \qquad (5)$$



$$\underset{(d^6s^2)}{Fe} + 2\cdot O\cdot + 2\cdot O^- \rightarrow 2\ {}^-O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Fe^{VI}}}{-}O \qquad \text{Fe covalence. 6} \qquad (6)$$

(d^5sp^2); $S = 2/2$; 14-e^- system



(d^5sp^2); $S = 2/2$; 14-e^- system

Fe covalence, 6 (7)

(porphyrin)Fe^{II} + $\cdot O \cdot \longrightarrow$ (por)$Fe^{IV}{=}O$ Fe covalence, 4 (8)
(d^6sp) (d^6sp); $S = 2/2$; 16-e^- system
(Fe covalance, 2) (with an axial imidazole it becomes an 18-e^- system)

Fe + 5 CO $\longrightarrow$ (O=C:)Fe^{VIII} = $(C{=}O)_4$ Fe covalence, 8 (9)
(d^5sp^2); $S = 0$; 18-e^- system

Fe + 2 $\cdot C_5H_5$ ($\cdot$Cp) $\longrightarrow$ (Cp)–Fe^{II}–(Cp) Fe covalence, 2 (10)
(d^6sp); $S = 0$; 18-e^- system

ELECTRON-TRANSFER THERMODYNAMICS

The electrochemistry for several iron complexes is illustrated in Fig. 1, and similar data for $Fe(8\text{-}Q)_3$,[10] $Fe(picolinate)_3$,[11] $Fe(DTBC)_3$,[12,13] $[(bpy)_3Fe](ClO_4)_2$,[11] $[(Ph_3PO)_4Fe](ClO_4)_2$,[11] and $[Fe(TDT)_2^{2-}]$[14] have been published. Figure 2 illustrates the cyclic voltammograms for meso-tetrakis(2,6-dichlorophenyl)porphine $[(Cl_8TPP)H_2]$ and its porphyrin complexes with zinc and iron in dimethylformamide (similar data for the tetraphenylporphyrin complexes have been published),[11] and Fig. 3 presents voltammograms for the complexes in H_2CCl_2. In acetonitrile at −35°C the $(Cl_8TPP)Fe(ClO_4)$ complex reacts with O_3 to form a stable oxene adduct $[(Cl_8TPP^{+}\cdot)Fe^{IV}{=}O]$ that (a) is a model for Compound I of horseradish peroxidase,[15] (b) exhibits reversible reduction of its porphyrin cation radical and of the covalently bound oxygen atom, and (c) is reduced by two equivalents of chloride ion to give $(Cl_8TPP)Fe^{III}Cl$ (Fig. 4). In dimethylfor-

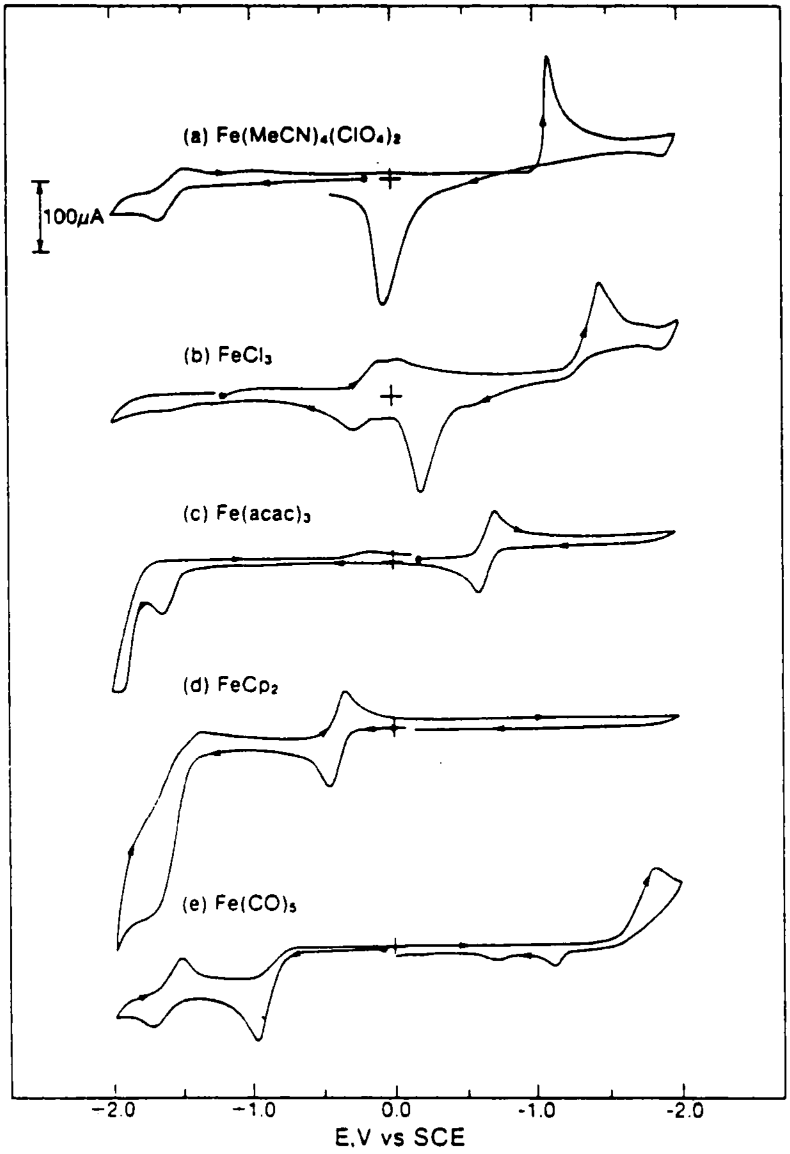


FIGURE 1 Cyclic voltammograms of 3 mM solutions in MeCN (0.1 M TEAP) of (a) [Fe(MeCN)$_4$](ClO$_4$)$_2$, (b) FeCl$_3$, (c) Fe(acac)$_3$, (d) Fe(Cp)$_2$, and (e) Fe(CO)$_5$; scan rate, 0.1 Vs^{-1}, glassy-carbon electrode (GCE) (area, 0.09 cm^2).

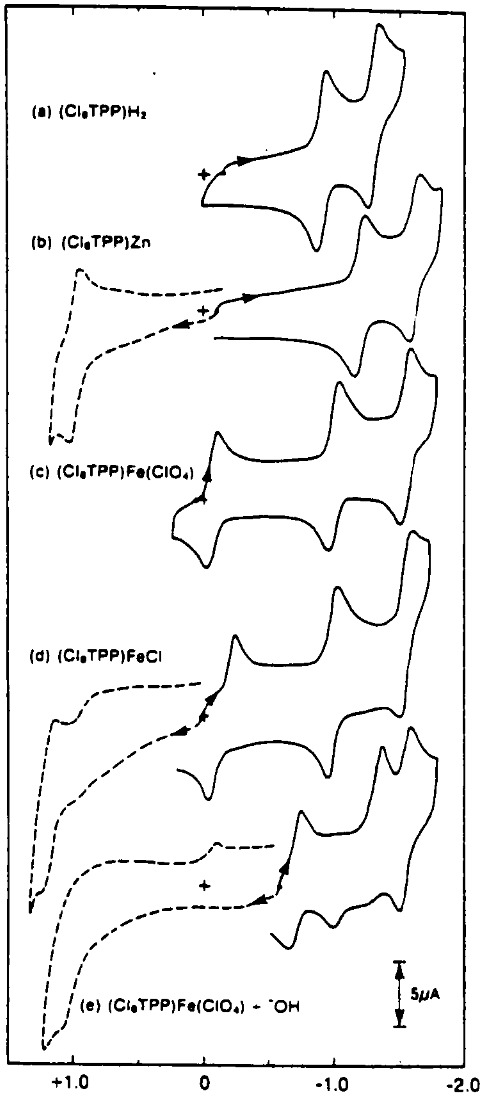


FIGURE 2 Cyclic voltammograms of 0.5 mM solutions in DMF (0.1 M TEAP) of (a) (Cl$_8$TPP)H$_2$, (b) (Cl$_8$TPP)Zn, (c) (Cl$_8$TPP)Fe(ClO$_4$), (d) (Cl$_8$TPP)FeCl, and (e) (Cl$_8$TPP)Fe(ClO$_4$) + 1 equiv. of (Bu$_4$N)OH; scan rate, 0.1 Vs^{-1}, glassy-carbon electrode (GCE) (area, 0.09 cm^2).

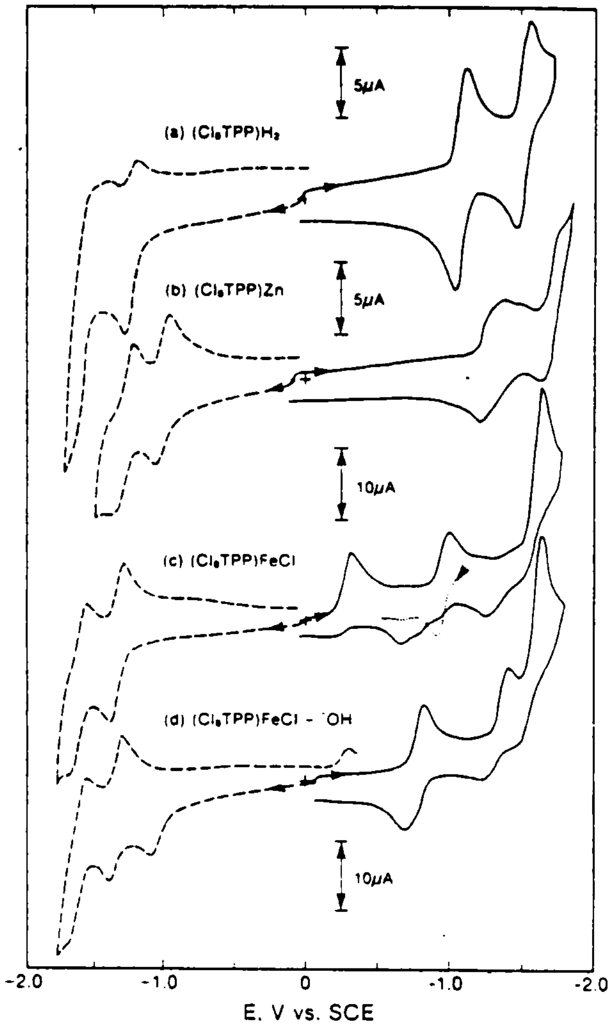


FIGURE 3 Cyclic voltammograms of 0.5 mM solutions in CH_2Cl_2 (0.1 M $(Bu_4N)ClO_4$) of (a) $(Cl_8TPP)H_2$, (b) $(Cl_8TPP)Zn$, (c) (Cl_8TPP) FeCl, and (d) $(Cl_8TPP)FeCl$ + 1 equiv. of $(Bu_4N)OH$; scan rate, 0.1 Vs^{-1}, GCE.

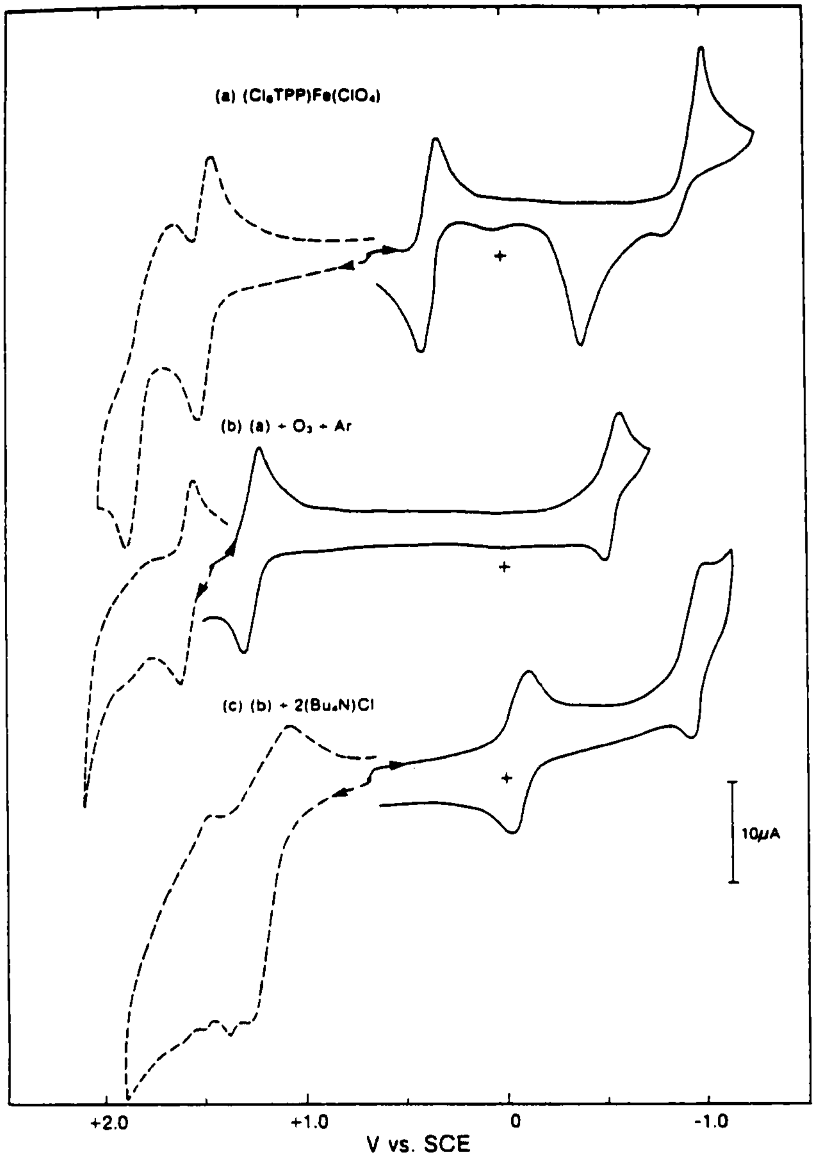


FIGURE 4 Cyclic voltammograms at a glassy-carbon electrode (area, 0.09 cm^2) in MeCN (0.1 M TEAP) at −35°C of (a) 1 mM [(Cl$_8$TPP)Fe](ClO$_4$), (b) the product from its exposure for 10 s to 0.03 atm O$_3$ in O$_2$ (1 atm) (followed by a purge with Ar), and (c) solution (b) plus two equivalents of (Bu$_4$N)Cl; scan rate, 0.1 Vs^{-1}.

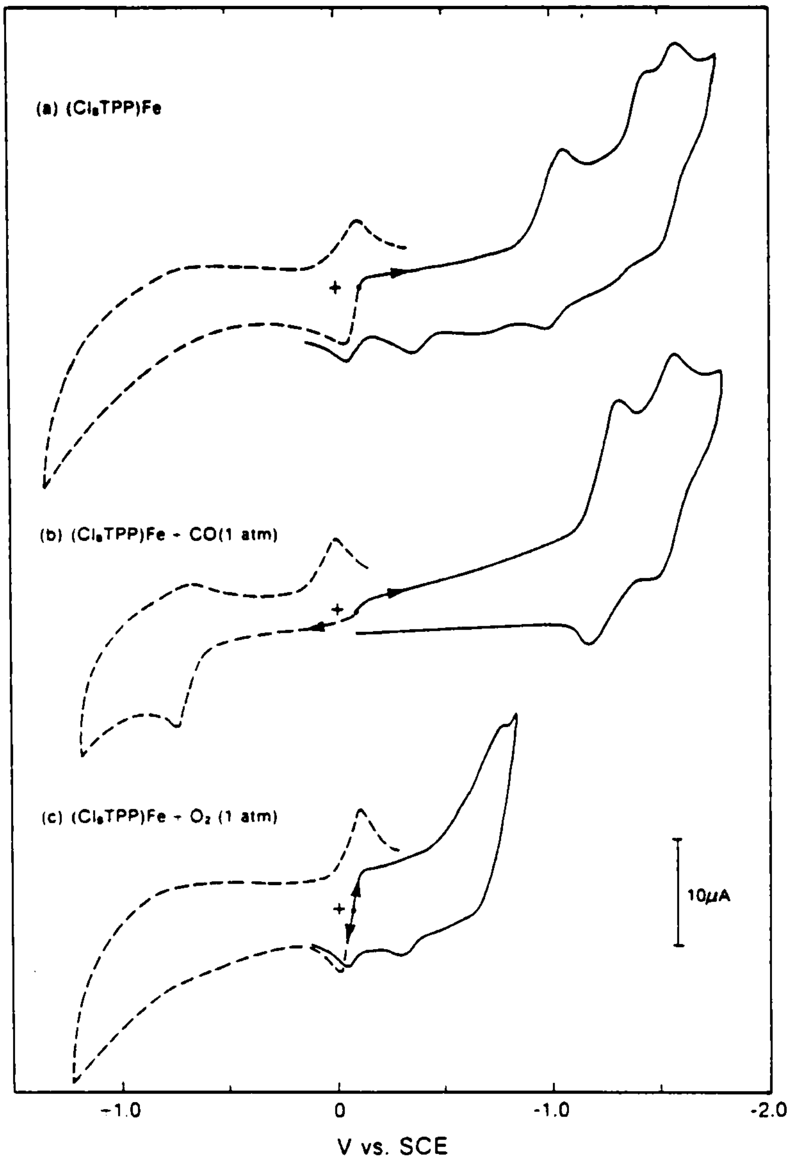


FIGURE 5 Cyclic voltammograms at a glassy-carbon electrode (area, 0.09 cm^2) in dimethylformamide (0.1 M TEAP) at (a) 0.5 mM (Cl$_8$TPP)Fe, (b) 0.5 mM (Cl$_8$TPP)Fe in the presence of CO (1 atm), and (c) 0.5 mM (Cl$_8$TPP)Fe in the presence of O$_2$ (atm); scan rate, 0.1 Vs^{-1}.

mamide at ambient temperature the anodic electrochemistry of the reduced iron porphyrin [$(Cl_8TPP)Fe^{II}$)] is markedly changed by the presence of carbon monoxide, and the initial oxidation is shifted about +0.03 V by the presence of dioxygen (Fig. 5). The redox reactions and potentials for this group of iron compounds are summarized in Table II.[6,11,12,14-16]

Table III summarizes the redox thermodynamics for several iron-porphyrin complexes and iron organo-metallic compounds in acetonitrile. Although most of the redox processes of Tables II and III are ligand-centered, the oxidations of Fe(s) [−0.26 V vs. NHE (+0.26 V−0.52 V for ½(Fe−Fe) bond energy), Fig. 1)], $Fe(Cp)_2$(+0.70 V, Fig. 1), $Fe(CO)_5$ (+0.95 V, Fig. 1), $(Cl_8TPP)Fe$ (+0.20 V, Fig. 5), and $(Cl_8TPP)Fe(CO)$ (+0.99 V, Fig. 5) are metal-centered. The shifts to more positive potentials for the oxidation of $Fe(Cp)_2$ and $Fe(CO)_5$ relative to Fe(s) and of $(Cl_8TPP)Fe(CO)$ relative to $(Cl_8TPP)Fe$ represent the stabilization of the valence electrons of Fe (d^6s^2) and $(Cl_8TPP)Fe$ (d^6sp) by the covalent bonds with Cp· and CO; respectively.

BONDING AND VALENCE-ELECTRON HYBRIDIZATION

The electron-transfer thermodynamics for protons, water, hydroxide, and several iron compounds in aqueous media and in acetonitrile are summarized in Table IV.[16] In acetonitrile the reduction of H_2O requires that the H−OH covalent bond be broken to give a hydrogen atom and a hydroxide ion

$$\mathrm{H{-}OH} + e^- \rightarrow \mathrm{H}\cdot + {}^-\mathrm{OH} \qquad E^{0\prime},\ -3.90\ \mathrm{V\ vs.\ NHE.} \qquad (11)$$

In contrast the reduction of ·OH to ⁻OH does not have this barrier.

$$\cdot\mathrm{OH} + e^- \rightarrow {}^-\mathrm{OH} \qquad E^{0\prime},\ +0.92\ \mathrm{V\ vs.\ NHE.} \qquad (12)$$

Hence, the difference in reduction potentials, $\Delta E^{0\prime}$, is a measure of the covalent bond energy[11,17]

$$\Delta G_{\mathrm{DBE}} = -\Delta G_{\mathrm{BF}}$$

$$= [+0.92 - (-3.90)]\ 23.1\ \mathrm{kcal\ (eV)^{-1}} = 111\ \mathrm{kcal}.$$

If the entropy contribution ($T\Delta S_{\mathrm{DBE}}$) is assumed to be 7.8 kcal, then ΔH_{DBE} for the H–OH bond is 119 kcal ($\Delta H_{\mathrm{DBE}} = \Delta G_{\mathrm{DBE}} + T\Delta S\Delta_{\mathrm{BE}}$), which is identical to the literature value.[6]

Analogous arguments are used to estimate the iron-oxygen covalent bond energies for the compounds in Table IVC.[11,15,18–20] In the case of $(\mathrm{Cl_8TPP})\mathrm{Fe^{IV}{=}O}$, addition of an electron breaks the π-bond, which represents about one-third of the double bond energy.[5,15] The redox data of Table II have been used to estimate the respective iron-ligand covalent bond energies ($-\Delta G_{\mathrm{BF}}$). Table IVD notes the parallels in covalent bonding of H·, LFe, and $\mathrm{Me_3C}$· with ·OH, ·O·, ·OOH, and $\cdot\mathrm{OO^-}$.

Although the uncharged tris 3,5-di-t-butyl-catecholate complex of iron $[\mathrm{Fe(DTBC)_3}]$ has been extensively studied,[3,12,13,21] the proposed bonding in these reports is unclear. The most common formulation is as an ionic salt between iron(3^+) and three semiquinone anion radicals, $\mathrm{Fe^{3+}(DTBSQ^{-}\cdot)_3}$. However, the magnetic moment is 2.9 B.M. (consistent with an S = 2/2 spin state)[12,21] and the electrochemistry indicates a ligand-centered reduction.[12] Both of these characteristics are analogous to ferrate dianion $\mathrm{Fe^{VI}(O)_4^{2-}}$ ($\mathrm{d^5sp^2}$; S = 2/2; covalence 6). Thus, the iron center ($\mathrm{d^5sp^2}$, eight unpaired electrons) forms six covalent Fe–O bonds with three catechols (equivalent to the six H–O bonds in three $\mathrm{DTBCH_2}$ molecules), which leaves two unpaired electrons at the iron center (S = 2/2).

The thermodynamic data of Table IV also can be used to estimate the formation constants (K_f) for ion-ion redox reactions [$\mathrm{H^+ + {}^-OH \rightarrow HOH}$ and $\mathrm{(Cl_8TPP)^{II}Fe^+ + {}^-OH \rightarrow (Cl_8TPP)Fe^{III}{-}OH}$], which is illustrated in Table IVE.

The results from the estimation of covalent bond energies from ligand-centered redox potentials for several iron and manganese compounds are compared to gas-phase values in Table V.[6,15,22,23] The self-consistency is impressive with the iron-ligand bond energy

TABLE II

Redox potentials for iron complexes and their apparent metal–ligand covalent-bond-formation free energies ($-\Delta G_{BF}$)

Complex (FeL_n)[a]	$E_{1/2}$, V vs. NHE[b]		Bond	$-\Delta G_{BF}$, kcal[c]
	$\cdot L/L^-$	FeL_n/FeL_n^-		
A. MeCN[d]				
$Fe^{III}Cl_3$ (d^5sp^2)	+2.11	+0.34	Cl_2Fe-Cl	41
$Fe^{III}(8Q)_3$[e]	+0.21	−0.41	$(8Q)_2Fe-O$(of 8Q)	14
$Fe^{III}(acac)_3$[e]	+0.55	−0.42	$(acac)_2Fe-O$(of acac)	18
$Fe^{III}(PA)_3$[e]	+1.50	+0.20	$(PA)_2Fe-O$(of PA)	30
$Fe^{III}(DTBC)_2^-$[f]	+0.12	−0.24	$^-(DTBC)Fe-O$(of DTBC)	8
$Fe^{III}(TDT)_2^-$[g]	+0.19	−0.59	$^-(TDT)Fe-S$(of TDT)	18
$Fe^{III}(bpy)_3^{3+}$[e]	+2.32(+/0)	+1.30	$^{2+}(bpy)_2Fe-N$(of bpy)$^+$	24
$Fe^{III}(OPPh_3)_4^{3+}$[e]	>+2.5(+/0)	+1.27	$^{2+}(Ph_3PO)_3Fe-(OPPh_3)^+$	>28
$Fe^{III}(OPPh_3)_4^{3+}$[e]	>+2.5(+/0)	+1.85	$^{2+}(MeCN)Fe-(MeCN)^+$	>15
$(Cl_8TPP)Fe^{III}Cl$[e]	+2.11	−0.02	$(Cl_8TPP)Fe-Cl$	49
$(Cl_8TPP)Fe^{III}(OH)$[e]	+0.92($\cdot OH/^-OH$)	−0.48	$(Cl_8TPP)Fe-OH$	32
$(Cl_8TPP)Fe^{IV}(O)$[h]	+0.67($\cdot O/O^{-}\cdot$)	−0.30	$(Cl_8TPP)Fe{=}O \rightarrow (Cl_8TPP)Fe-O^-$	22 (π-bond)
$Fe^{VI}(DTBC)_3$[f] (d^5sp^2; S = 2/2)	+0.12	−0.29	$(DTBC)_2Fe-O$(of DTBC)	9

B. Aqueous, pH 14[d,i]				
$Fe^{VI}(O)_2(O^{-})_2^{2-}$ (d^5sp^2; S = 2/2	+1.43 ($\cdot O\cdot/O^{-}\cdot$)	+0.55	$(^{-}O)_2(O)Fe{=}O$	20 (π-bond)
$Fe^{III}(O)(O^{-})^{-}$ (d^5sp^2)	+1.77($O^{-}\cdot/2\ OH$)	−0.7	$(O)Fe-O$	57
$Fe^{II}(OH)(O^{-})^{-}$ (d^6sp)	+1.89 ($\cdot OH/^{-}OH$)	+0.8	$(^{-}O)Fe-OH$	62
$Fe^{III}(CN)_6^{3-}$ (d^5sp^2)	+2.4	+0.36	$^{3-}(CN)_5Fe-CN$	47
C. Aqueous, pH 0[d,i]				
$^{2+}(H_2O)_2Fe^{III}(OH)$ (d^5sp^2)	+2.72 ($\cdot OH,H^{+}/H_2O$)	+0.77	$^{2+}(H_2O)_2Fe-OH$	45

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[a] Key: 8Q, 8-quinolinate; acac, acetylacetonate; PA, picolinate; DTBC, 3,5-di-t-butyl-catecholate; TDT, 3,4-toluene-dithiolate; bpy, 2,2-bipyridine.

[b] $E_{NHE} = E_{SCE} + 0.24$ V.

[c] Ref. 6.

[d] The superscript Roman numerals indicate the covalence (number of covalent bonds) for the metal, *not* the oxidation state.

[e] Ref. 11.

[f] Ref. 12.

[g] Ref. 14.

[h] Ref. 15.

[i] Ref. 16.

TABLE III

Redox potentials for iron porphyrin complexes and organometallics in acetonitrile

A. Porphyrins and Porphine[a]

	$E^{\circ\prime}$, V vs. NHE[b]				
	$MP^{+\cdot} \rightarrow MP^{2+}$	$MP \rightarrow MP^{+\cdot}$	$Fe^{+}P \rightarrow FeP(d^{5}sp \rightarrow d^{6}sp)$	$MP \rightarrow MP^{-\cdot}$	$MP^{-\cdot} \rightarrow MP^{2-}$
H_2TPP	+1.53	+1.29	–	−0.90	−1.23
Zn(TPP)	+1.37	+1.07	–	−1.06	−1.44
$(TPP)^{II}Fe^{+}$	+1.64	+1.37	+0.47	−0.81 ($MP \rightarrow M^{-}P$)	−1.59
$(Cl_8TPP)^{II}Fe^{+}$	+1.96	+1.70	+0.56 (+0.20, DMF)	−0.83 ($MP \rightarrow M^{-}P$)	−1.39
			$PFeL \rightarrow PFe + L$ (ligand-centered)		
$(Cl_8TPP)Fe^{III}Cl$	–	+1.44	−0.02	−0.81 ($MP \rightarrow M^{-}P$)	−1.59
$(Cl_8TPP)Fe^{III}(SCH_2Ph)$		+1.13	−0.21	−0.81 ($MP \rightarrow M^{-}P$)	−1.59
$(Cl_8TPP)Fe^{III}(OH)$	–	+1.34	−0.48	−1.06	−1.59
$(Cl_8TPP)Fe^{IV}{=}O$ ($d^{6}sp$)	+1.84	+1.51	−0.30, −0.52		

B. Organometallics[a]

	$E^{\circ\prime}$, V vs. NHE[b]	
	$FeL_n \rightarrow FeL_n^{+}$	$LFeX_m \rightarrow LFe^{+} + mX$
$Fe^{VIII}(CO)_5(d^{5}sp^{2})$ (18-electron system)		+1.24
$[Fe(CO)_5 + e^{-} + 2\,H_2O \rightarrow Fe + 2\,^{-}OH + H_2CO + 4\,CO$, −1.51 V vs. NHE]		
$(Cl_8TPP)Fe^{IV}(CO)$		+0.99 (DMF)
$Fe^{II}(Cp)_2(d^{6}sp)$ (18-electron)		+0.70
$(TPP)Fe^{II}(py)_2(d^{6}sp)$ (18-electron) (TPP, tetraphenylporphyrin biradical)	+0.41	
$Fe^{II}(TDT)_2^{2-}$ ($d^{6}sp$) (14-electron) (TDT, 3,4-toluenedithiolate anion radical)	−0.56	

[a] The superscript Roman numerals indicate the covalence (number of covalent bonds) for the metal, *not* the oxidation state.

[b] $E_{NHE} = E_{SCE} + 0.24$ V.

TABLE IV

Energetics of hydrogen-oxygen and iron-oxygen bonds and formation constants

A. Aqueous Media	$E^{0\prime}$, V vs. NHE
$H^+ + \cdot OH + e^- \rightarrow HOH$	+2.72
$\cdot OH + e^- \rightarrow {}^-OH$	+1.89
$H^+ + e^- \rightarrow H\cdot$	−2.10
$HOH + e^- \rightarrow H\cdot + {}^-OH$	−2.93
$O + e^- \rightarrow O^-\cdot$	+1.43
$O^-\cdot + HOH + e^- \rightarrow 2\ {}^-OH$	+1.77
B. MeCN[a]	
$H^+ + \cdot OH + e^- \rightarrow HOH$	+3.24
$\cdot OH + e^- \rightarrow {}^-OH$	+0.92
$O + e^- \rightarrow O^-\cdot$	+0.67
$H^+ + e^- \rightarrow H\cdot$	−1.58
$HOH + e^- \rightarrow H\cdot + {}^-OH$	−3.90
$O^-\cdot + H_2O + e^- \rightarrow 2\ {}^-OH$	+0.59
$O_2 + e^- \rightarrow O_2^-\cdot$	−0.65 (DMF)
$(Cl_8TPP)^{II}Fe^+ + e^- \rightarrow (Cl_8TPP)Fe^{II}$	+0.56[b]
$(Cl_8TPP)Fe^{III}\text{-}OH + e^- \rightarrow (Cl_8TPP)Fe^{II} + {}^-OH$	−0.48[b]
$(Cl_8TPP)Fe^{IV}{=}O + e^- \rightarrow (Cl_8TPP)Fe^{III}O^-$	−0.30[c]
$(Cl_8TPP)Fe^{II} + O_2 + e^- \rightarrow (Cl_8TPP)Fe^{III}\text{-}OO^-$	−0.12 (DMF)[d]
$(Salen)Fe^{III}\text{-}OH + e^- \rightarrow (Salen)Fe^{II} + {}^-OH$	−0.46[e]
$(Salen)Fe^{III}\text{-}O\text{-}Fe^{III}(Salen) + e^- \rightarrow (Salen)Fe^{II} + (Salen)Fe^{III}O^-$	−0.90[c]
$(TPP)Fe^{III}\text{-}O\text{-}Fe^{III}(TPP) + e^- \rightarrow (TPP)Fe^{II} + (TPP)Fe^{III}O^-$	−1.26[f]

TABLE IV

(cont.)

C. Bond Energies[a]	
H-OH	$\Delta G_{DBE} = [+0.92-(-3.90)]23.1 = 111$ kcal
	$\Delta H_{DBE} = \Delta G_{DBE} + 7.8 = \mathbf{119\ kcal}$
$(Cl_8TPP)Fe^{IV}=O$	$\Delta G_{DBE} = [+0.67-(-0.30)23.1 = 22.4$
	$\Delta H_{DBE} = (3 \times 22.4 + 7.8) = \mathbf{75\ kcal}$
$(Cl_8TPP)Fe^{III}$-OH	$\Delta G_{DBE} = [+0.92-(-0.48)]23.1 = 32.3$
	$\Delta H_{DBE} = 32.3 + 7.8 = \mathbf{40.1\ kcal}$
$(Cl_8TPP)Fe^{III}$-OO^-	$\Delta G_{DBE} = -0.12-(-0.65)]23.1 = 12.2$
	$\Delta H_{DBE} = 12.2 + 7.8 = \mathbf{20.0\ kcal}$
$(Salen)Fe^{II}$-OH	$\Delta G_{DBE} = [+0.92-(-0.40)]23.1 = 30.5$
	$\Delta H_{DBE} = 30.5 + 7.8 = \mathbf{38.3\ kcal}$
$(Salen)Fe^{III}$-OFe(Salen)	$\Delta G_{DBE} = [+0.67-(-0.90)]23.1 = 36.3$
	$\Delta H_{DBE} = 36.3 + 7.8 = \mathbf{44.1}$
$(TPP)Fe^{III}$-OFe(TPP)	$\Delta G_{DBE} = +0.67-(-1.26)]23.1 = 44.6$
	$\Delta H_{DBE} = 44.6 + 7.8 = \mathbf{52.4\ kcal}$

D. Parallels in Bonding

1. H-OH, $(Cl_8TPP)Fe$-OH, Me_3C-OH
2. H-O-H, (TPP)Fe-O-Fe(TPP), Me_3C-O-CMe_3
3. OC=O, $(Cl_8TPP)Fe$=O, $(Me_3C)_2C$=O
4. H-OOH, $(Cl_8TPP)Fe$-OOH, Me_3C-OOH
5. H-OO^- $(Cl_8TPP)Fe$-OO^-, Me_3C-OO^-

E. Formation Constants

1. $H^+ + {}^-OH \rightarrow HOH, K_f$

a. Aqueous:

$$\begin{array}{ll} H^+ + e^- \rightarrow H\cdot & E^{\circ\prime},\ -2.10\ \text{V vs. NHE} \\ -(\cdot OH + e^- \rightarrow {}^-OH) & E^{\circ\prime},\ +1.89\ \text{V}) \\ \hline H^+ + {}^-OH \rightarrow H\cdot + \cdot OH & \Delta E^{\circ}_{\mathrm{rxn}} = -3.99\ \text{V} \end{array}$$

$$H\cdot + \cdot OH \rightarrow HOH \qquad -\Delta G_{\mathrm{BF}} = \Delta G_{\mathrm{DBE}} = 111\ \text{kcal}$$

$$\log K_f = \left(\Delta E^{\circ}_{\mathrm{rxn}} + \frac{\Delta G_{\mathrm{DBE}}}{23.1}\right)/0.05915 \qquad = (-3.99 + 4.82)/0.05915$$

$$= 14.0$$

b. MeCN:

$$\log K_f = (-2.50 + 4.82)/0.05915 = 39.2$$

2. MeCN:

$$\begin{array}{ll} (Cl_8(TPP)Fe^+ + {}^-OH \rightarrow Cl_8TPPFe\text{–}OH & K_f \\ (Cl_8TPP)Fe^+ + e^- \rightarrow Cl_8TPPFe & E^{\circ\prime},\ +0.56\ \text{V} \\ -(\cdot OH + e^- \rightarrow {}^-OH & E^{\circ\prime},\ +0.92\ \text{V}) \\ \hline CL_8TPPFe^+ + {}^-OH \rightarrow Cl_8TPPFe + \cdot OH & \Delta E_{\mathrm{rxn}} = -0.36\text{V} \\ (Cl_8TPP)Fe + \cdot OH \rightarrow (Cl_8TPP)Fe\text{–}OH & -\Delta G_{\mathrm{BF}} = 32.2\ \text{kcal} \end{array}$$

$$\log K_f = \left(\Delta E^{\circ}_{\mathrm{rxn}} + \frac{\Delta G_{\mathrm{DBE}}}{23.1}\right)/0.05915 = (-0.36 + 1.40)/0.05915$$

$$= 1.04/0.05915 = 17.6$$

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[a] The superscript Roman numerals indicate the covalence (number of covalent bonds) for the metal, *not* the oxidation state.

[b] Ref. 11.

[c] Ref. 15.

[d] Ref. 18.

[e] Ref. 19.

[f] Ref. 20.

TABLE V

Comparison of gas-phase and solution-phase bond energies (ΔH_{DBE}) for iron and manganese compounds[a]

Gas Phase	ΔH_{DBE}, kcal[b]	Solution Phase	ΔH_{DBE}, kcal[c]
$Fe^{II}{=}O$ (d^6sp)	93.3	$(Cl_8TPP)Fe^{IV}{=}O$ (d^4sp)	75
$^{+}Fe^{II}{=}O$ (d^5sp)	69	$(Cl_8TPP^{+\cdot})Fe^{IV}{=}O$ (d^4sp)	54
$^{+}Fe^{I}{-}OH$ (d^6s)	73	$(Cl_8TPP)Fe^{III}{-}OH$ (d^5sp^2)	40
		$^{2+}(H_2O)_5Fe^{III}{-}OH$ (d^5sp^2)	53
$Mn^{II}{=}O$ (d^5sp)	96.3	$(Cl_8TPP)Mn^{IV}{=}O$ (d^5sp)	95
$^{+}Mn^{II}{=}O$ (d^5s)	57	$(Cl_8TPP^{+})Mn^{V}{=}O$ (d^5sp)	43
$Fe^{I}{-}Cl$ (d^6sp)	84	$(Cl_8TPP)Fe^{III}{-}Cl$ (d^5sp^2)	57
		$Cl_2Fe^{III}{-}Cl$ (d^5sp^2)	49
$(CO)_4Fe^{VIII}{-}(CO)$	41	$(CO)_4Fe^{VIII}{-}(CO)$	42
		$(Cl_8TPP)Fe^{IV}{-}(CO)$	26

[a] The superscript Roman numerals indicate the covalence (number of covalent bonds) for the metal, *not* the oxidation state.
[b] Refs. 6 and 22.
[c] $\Delta H_{DBE} = -\Delta G_{BF} + T\Delta S_{DBE} = [(\Delta E_{ox})\, 23.1 + 7.8]$; Refs. 15 and 23.

reduced (a) by about 20 kcal when a given neutral molecule loses an electron, and (b) by about 10 kcal per unit increase in covalence.

The formation of the same iron-oxygen covalent bonds from either (a) oxidized iron plus oxy anions via electron-transfer (redox) reactions or (b) radical-radical coupling reactions is summarized in Table VI. The valence-electron hybridization for the iron center is included as well as the spin state and estimated covalent bond energy (ΔH_{DBE}). A similar set of reactions of and data for iron-porphyrin compounds is presented in Table VII. Table VIIA emphasizes that just as the combination of a proton with a hydroxide ion yields a covalent H–OH bond (Table VI), (a) the combination of protons and porphyrin dianion (Por^{2-}) yields covalent porphine (H_2Por) and (b) the addition of Lewis acids (Zn^{2+} or Fe^{2+}) to porphine (H_2Por) oxidatively displaces protons to give covalent-bonded $Zn^{II}Por$ and $Fe^{II}Por$.

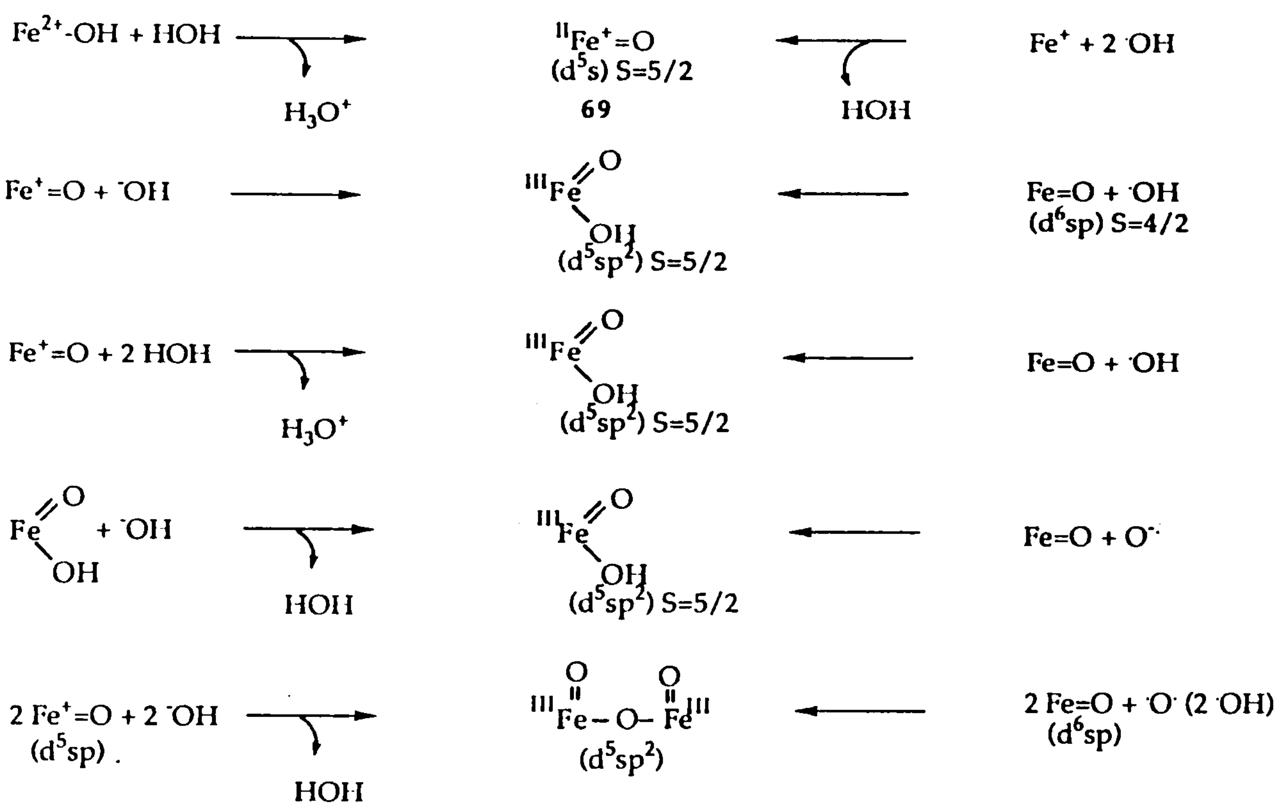
Although this discussion has focussed on iron compounds (with an emphasis on the nature of iron-oxygen bonds), closely similar arguments and conclusions can be made for all transition-metal compounds. To the extent that a convincing case has been made that all neutral and negatively charged iron-oxygen compounds have covalent bonds with elemental iron ($d^6s^2 \rightarrow d^6sp \rightarrow d^5sp^2$ hybridization, and covalency 2, 3, 4, 6, or 8) and oxygen-centered redox chemistry, the same conclusions are in order for iron-sulfur compounds (including the iron-sulfur proteins).[24,25] However, the covalency of iron is limited to two or three in such compounds {d^6sp and d^5sp^2 hybridization; $Fe^{II}(SR)_4^{2-}$ and $Fe^{III}(SR)_4^{-}$ $[(RS)_2Fe(\mu\text{-}S)_2\text{-}Fe(SR)_2]^{3-,2-}$ and $[(RS)_4Fe_4S_4]^{3-,2-,-}$}, and they have negative redox potentials [-0.6 V vs. NHE for $Fe^{III}(TDT)_2^{-}$.

The "bottom lines" are (a) the chemical bonds of iron compounds are covalent, (b) the oxidation numbers (II, III, IV, V, VII, and VIII) that are associated with iron in its compounds represent (in most cases) the number of covalent bonds ("covalence") rather than the charge number (oxidation state) of the iron center, (c) the valence-electron hybridization of iron in its compounds determines the bond geometry and has a strong effect on the covalent bond energies, (d) in its bonding with non-metals iron ($d^6sp \rightarrow d^5sp^2$) is closely similar to hydrogen (1s) and carbon (sp^3), and (e) the bond energies ($-\Delta G_{BF}$) for Fe–Y covalent bonds can

TABLE VI

Bonding and valence-electron hybridization for iron-oxygen compounds

Lewis Acid-Base Electron Transfer		Covalent Product Species (Valence Electrons) S = Spin State, ΔH_{DBE}, kcal		Radical-Radical Coupling
$H^+ + {}^-OH$	$\xrightarrow[K_f,\ 10^{14}]{}$	H-OH (1s) S=0 **119**	$\longleftarrow$	$H^\cdot + {}^\cdot OH$
$Fe^{3+} + {}^-OH$ (d^5)	$\longrightarrow$	${}^{I}Fe^{2+}$-OH (d^5s) S=5/2 **53**	$\longleftarrow$	$Fe^{2+} + {}^\cdot OH$ (d^6)
$Fe^{3+} + 2\,HOH$ (d^5)	$\xrightarrow[H_3O^+]{}$	${}^{I}Fe^{2+}$-OH (d^5s) S=5/2 **53**	$\longleftarrow$	$Fe^{2+} + {}^\cdot OH$
Fe^{2+}-OH + ${}^-OH$ (d^5s)	$\xrightarrow[HOH]{}$	${}^{II}Fe^+$=O (d^5sp) S=5/2 **69**	$\xleftarrow[HOH]{}$	$Fe^+ + 2\,{}^\cdot OH$ (d^5s^2)



Fe²⁺-OH + HOH
H₃O⁺
IIFe⁺=O
(d⁵s) S=5/2
69
HOH
Fe⁺ + 2 ·OH
Fe⁺=O + ⁻OH
IIIFe=O, OH
(d⁵sp²) S=5/2
Fe=O + ·OH
(d⁶sp) S=4/2
Fe⁺=O + 2 HOH
H₃O⁺
IIIFe=O, OH
(d⁵sp²) S=5/2
Fe=O + ·OH
Fe=O, OH + ⁻OH
HOH
IIIFe=O, OH
(d⁵sp²) S=5/2
Fe=O + O·⁻
2 Fe⁺=O + 2 ⁻OH
(d⁵sp) .
HOH
IIIFe(=O)–O–Fe(=O)III
(d⁵sp²)
2 Fe=O + ·O· (2 ·OH)
(d⁶sp)

TABLE VI

(cont.)

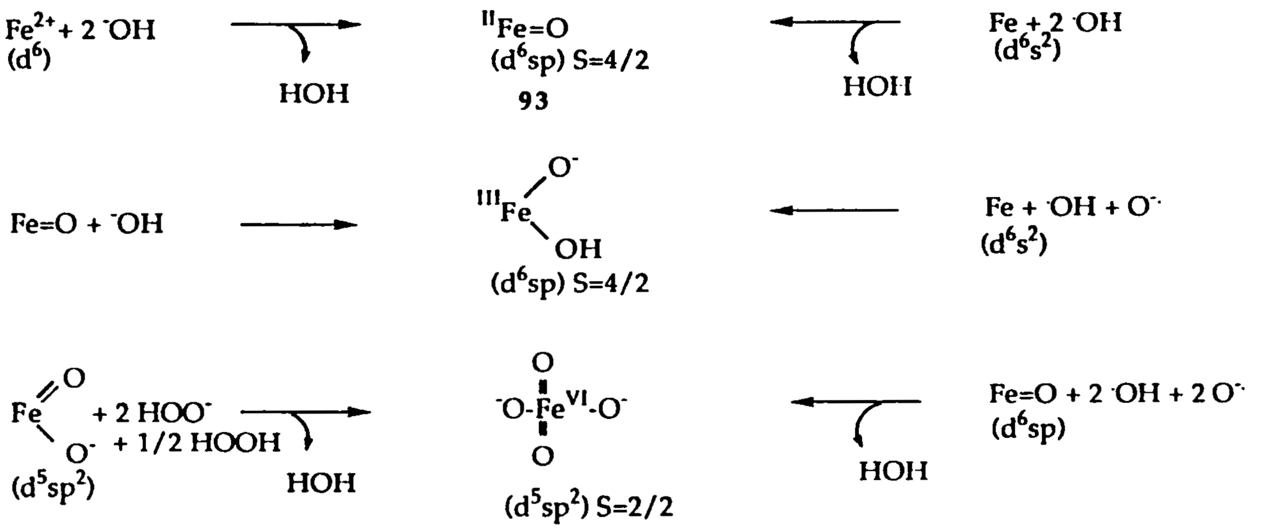


TABLE VII

Bonding, electron-transfer reactions, and valence-electronics for iron-porphyrin

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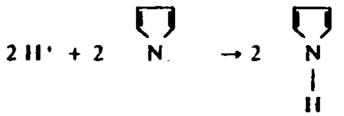
A. Bonding and Synthesis in Metal Porphyrins



$2\,H^{+} + Por^{2-} \rightarrow (H\text{-})_2Por[H_2Por]$
(1s)

$H_2Por + Zn^{2+} \rightarrow {}^{II}Zn{=}Por[ZnPor] + 2\,H^{+}$
(d^{10}) $(d^{10}sp)$

$H_2Por + Fe^{2+} \rightarrow {}^{II}FePor + 2\,H^{+}$
(d^{6}) $(d^{6}sp)$

$H_2Por + Fe^{3+} \rightarrow {}^{II}Fe^{+}Por + 2\,H^{+}$
(d^{5}) $(d^{5}sp)$

B. Redox Thermodynamics in Acetonitrile

	$E^{0\prime}$, V vs. NHE
1. Oxidizing agents	
$H^{+} + e^{-} \rightarrow H\cdot$	−1.58
$(Cl_8TPP)^{II}Fe^{+} + e^{-} \rightarrow (Cl_8TPP)Fe^{II}$ $(d^{5}sp)$ $(d^{6}sp)$	+0.56
2. Reducing agents	
$^{-}OH \rightarrow \cdot OH + e^{-}$	+0.92
$^{-}OOH \rightarrow \cdot OOH + e^{-}$	−0.16
$O_2^{-}\cdot \rightarrow \cdot O_2\cdot + e^{-}$	−0.66
$O_2^{2-} \rightarrow O_2^{-}\cdot + e^{-}$	−2.3
$O^{-}\cdot \rightarrow \cdot O\cdot + e^{-}$	+0.46

TABLE VII

(cont.)

$Cl^- \rightarrow Cl\cdot + e^-$	+2.24
$PhCH_2S^- \rightarrow PhCH_2S\cdot + e^-$	+0.24
$Bu^- \rightarrow Bu\cdot + e^-$	−2.8

C. Covalent Bond Formation and Valence-Electron Hybridization

Lewis Acid-Base Electron Transfer		Product Species (Valence Electrons), S = Spin State ΔH_{DBE}, kcal		Radical-Radical Coupling
$H^+ + {}^-OH$	⟶	H–OH (1s) S = 0 **119**	⟵	$H\cdot + \cdot OH$
$PorFe^+ + {}^-OH$ (d^5sp)	⟶	$PorFe^{III}$–OH (d^5sp^2) S = 5/2 **40**	⟵	$PorFe + \cdot OH$ (d^6sp)
$H^+ + O_2^{2-}$	⟶	$H–OO^-$ (1s) S = 0 **80**	⟵	$H\cdot + O_2^-\cdot$
$PorFe^+ + O_2^{2-}$ (d^5sp)	⟶	$PorFe^{III}$–OO^- (d^5sp^2) S = 5/2 **21**	⟵	$PorFe + O_2^-\cdot$ (d^6sp)
$H^+ + O_2^-\cdot$	⟶	H–OO· (1s) S = 1/2 **59**	⟵	$H\cdot + \cdot O_2\cdot$
$PorFe^+ + O_2^-\cdot$ (d^5sp)	⟶	$PorFe^{IV}(O_2)$ (d^6sp) S = 0 **25 (DMF)**	⟵	$PorFe + \cdot O_2\cdot$ (d^6sp)

H^+ + OOH	$\longrightarrow$	$H-OOH$ (1s) $S = 0$ **89**	$\longleftarrow$	$H\cdot$ + $\cdot OOH$
$PorFe^+$ + OOH (d^5sp)	$\longrightarrow$	$PorFe^{III}-OOH$ (d^5sp^2) $S = 5/2$ **16**	$\longleftarrow$	$PorFe$ + $\cdot OOH$ (d^6sp)
H^+ + $O\ \cdot$	$\longrightarrow$	$H-O\cdot$ (1s) $S = 1/2$ **102**	$\longleftarrow$	$H\cdot$ + $\cdot O\cdot$
$PorFe^+$ + $O\ \cdot$	$\longrightarrow$	$PorFe^{IV}=O$ (d^4sp) $S = 2/2$ **74**	$\longleftarrow$	$PorFe$ + $\cdot O\cdot$
H^+ + Cl^-	$\longrightarrow$	$H-Cl$ (1s) $S = 0$ **103**	$\longleftarrow$	$H\cdot$ + $\cdot Cl$
$PorFe^+$ + $Cl\cdot$ (d^5sp)	$\longrightarrow$	$PorFe^{III}-Cl$ (d^5sp^2) $S = 5/2$ **56**	$\longleftarrow$	$PorFe$ + $\cdot Cl$ (d^6sp)
H^+ + $PhCH_2S^-$	$\longrightarrow$	$H-SCH_2Ph$ (1s) $S = 0$ **87**	$\longleftarrow$	$H\cdot$ + $PhCH_2S\cdot$
$PorFe^+$ + $PhCH_2S^-$ (d^5sp)	$\longrightarrow$	$PorFe^{III}-SCH_2Ph$ (d^5sp^2) $S = 5/2$ **30**	$\longleftarrow$	$PorFe$ + $PhCH_2S\cdot$ (d^6sp)
H^+ + Bu	$\longrightarrow$	$H-Bu$ (1s) $S = 0$ **99**	$\longleftarrow$	$H\cdot$ + $Bu\cdot$
$PorFe^+$ + Bu d^5sp	$\longrightarrow$	$PorFe^{III}-Bu$ (d^5sp^2) $S = 5/2$ **20–40**	$\longleftarrow$	$PorFe$ + $Bu\cdot$ (d^6sp)

be evaluated from their redox potentials [e.g., $-\Delta G_{BF} = (E^{0'}{}_{\cdot Y/Y^-} - E^{0'}{}_{FeY/Fe,Y^-})\ 23.1$ kcal].

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