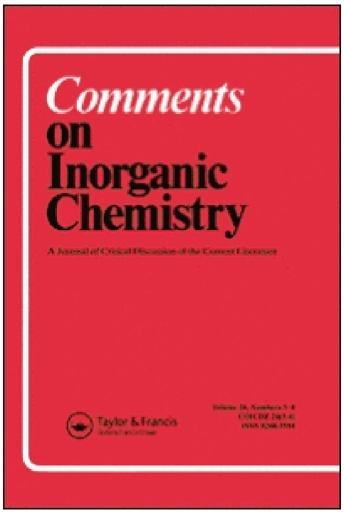

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The Nature of the Bonding and Valency for Oxygen in Its Metal Compounds

Donald T. Sawyer[a]
[a] Department of Chemistry, Texas A&M University, Texas

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The Nature of the Bonding and Valency for Oxygen in Its Metal Compounds

The proposition: Within metal-oxygen compounds the valence of the metal is limited to +3 or less, and unpaired electrons of the zero and minus-one valence states of oxygen are stabilized via pairing to the partially filled d-subshells of transition metals (with formation of d–p covalent bonds). The redox thermodynamics for the various transition metals and for the 0, −1, and −2 valence states of oxygen provide compelling evidence that the electron affinity for the d^5-electrons in manganese(II) is substantially greater than it is for the p^6-electrons in O^{2-}. This prompts the formulation of permanganate ion as $\mathrm{Mn^{II}}(\underset{\cdot}{\dot{\mathrm{O}}})(\mathrm{O^{-}}\cdot)_3^-$ rather than $\mathrm{Mn^{VII}}(\mathrm{O^{2-}})_4^-$; the former formulation is believed to be a more accurate representation of charge density, bond energies, and chemical reactivity. Similar arguments and conclusions are made for the oxygen compounds of other transition metal ions, including the active forms of horseradish peroxidase (Compounds I and II) and of cytochrome P-450. Likewise, the surface compounds of transition metals have properties that are consistent with zero-valent systems and covalent bonds; e.g., $\mathrm{Pd^0}(\cdot\mathrm{OH})_2(\mathrm{s})$, $\mathrm{Ag_2^0}(\underset{\cdot}{\dot{\mathrm{O}}})(\mathrm{s})$, and $\mathrm{Pt^0}(\underset{\cdot}{\dot{\mathrm{O}}})(\mathrm{s})$.

The title prompts the question, "Why bother? We know that the −2 valence for oxygen is just a convenient electron-counting formalism." However, for many this formalism represents chemical and electrostatic truth, and prompts the belief that $\mathrm{Mn^{VII}O_4^-}$ and $\mathrm{Cr_2^{VI}O_7^{2-}}$ are equivalent to $\mathrm{Ce^{4+}}$ in their chemistry and only act as electron-transfer oxidants. In fact, these "oxo" complexes also act as dehydrogenases and monoxygenases. Furthermore, whereas $\mathrm{Ce^{IV}O_2(s)}$ and $\mathrm{Fe_2^{III}O_3(s)}$ in combination with protons yield $\mathrm{Ce^{4+}}$ and $\mathrm{Fe^{3+}}$, respectively, the species $\mathrm{MnO_4^-}$, $\mathrm{Cr_2O_7^{2-}}$, $\mathrm{MnO_2(s)}$, and $\mathrm{MoO_3(s)}$ are unaffected by protons in aqueous media. The for-

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malism of O^{2-} is misleading for the $Mn^{VI}(O^{2-})_4^{2-}$ and $Fe^{VI}(O^{2-})_4^{2-}$ "oxo" complexes; addition of protons promotes the evolution of molecular oxygen and lower valence states for the metals

$$MnO_4^{2-} + 4H^+ \rightarrow Mn^{2+} + 2H_2O + O_2 \qquad (1)$$

$$2FeO_4^{2-} + 10H^+ \rightarrow 2Fe^{3+} + 5H_2O + 3/2O_2 \qquad (2)$$

The formulation[1] for the activated state of cytochrome P-450 as $\dot{+}PFe^{IV}(O^{2-})$ is in chemical conflict with the observed epoxidation of olefins, demethylation of methylanilines, oxidative cleavage of α-diols, and monoxygenation of hydrocarbons. Each of these transformations is characteristic of the electrophilic and biradical nature of atomic oxygen (oxene) rather than of authentic high-valent transition-metal ions [e.g., Ce^{4+}, $Ir^{IV}Cl_6^{2-}$, $Fe^{III}(bpy)_3^{3+}$, $Co^{III}(bpy)_3^{3+}$] that facilitate electron-transfer oxidations.

True ionic oxo salts are unknown in aqueous systems, and the dianions of elements and of small molecules are insoluble in aprotic solvents. For example,

$$Na_2(O^{2-})(s) + H_2O \rightarrow 2Na^+ + 2\,^-OH \qquad (3)$$

$$Ca(O^{2-})(s) + H_2O \rightarrow [(Ca(OH)_2(s) \rightleftharpoons Ca^{2+} + 2\,^-OH] \qquad (4)$$

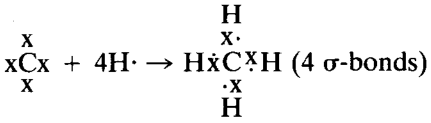
$$Ba(O^{2-})(s) + H_2O \rightarrow Ba^{2+} + 2\,^-OH \qquad (5)$$

$$Fe^{II}(O^{2-})(s) + 2H^+ \rightarrow Fe^{2+} + H_2O \qquad (6)$$

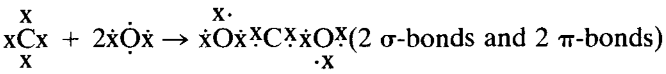
$$Fe_2^{III}(O^{2-})_3(s) + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O \qquad (7)$$

These considerations prompt us to suggest a valence-bond approach for transition-metal bonding to oxygen. Thus, as is true in organic and non-metallic chemistry, covalent bonds are formed by the unpaired d-electrons of the metal with the unpaired p-electrons of oxygen. A guiding principle of the valence-bond theory is that elements connected by covalent bonds are as close to electrical neutrality as is consistent with their respective electron affinities and ionization potentials.[2] For the light elements (H, C, N, O, F, Si, P, S, Cl) the octet rule for electronic valence shells and covalent bond formation are dominant factors after electro-neutrality, ionization-potential, and electron-affinity considerations.

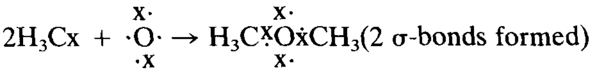
Bonding and Valency of Oxygen in Non-Metallic Compounds. With simple organic compounds covalent bonds result from the combination of the four unpaired electrons in the sp^3 hybridized orbitals of carbon with the unpaired electrons of atomic hydrogen or oxygen



$$\underset{x}{\overset{x}{xCx}} + 4H\cdot \rightarrow H\dot{x}\underset{\underset{H}{\cdot x}}{\overset{\overset{H}{x\cdot}}{C}}{}^{x}_{\cdot}H \text{ (4 }\sigma\text{-bonds)} \qquad (8)$$

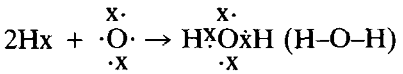


$$\underset{x}{\overset{x}{xCx}} + 2\dot{x}\underset{\cdot}{\overset{\cdot}{O}}\dot{x} \rightarrow \dot{x}O\dot{x}{}^{x}_{\cdot}\underset{\cdot x}{\overset{x\cdot}{C}}{}^{x}_{\cdot}\dot{x}O{}^{x}_{\cdot}\text{(2 }\sigma\text{-bonds and 2 }\pi\text{-bonds)} \qquad (9)$$

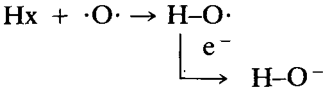


$$2H_3Cx + \underset{\cdot x}{\overset{x\cdot}{\cdot O\cdot}} \rightarrow H_3C{}^{x}_{\cdot}\underset{x\cdot}{\overset{x\cdot}{O}}\dot{x}CH_3\text{(2 }\sigma\text{-bonds formed)} \qquad (10)$$

Similarly, atomic hydrogen forms covalent bonds with atomic oxygen

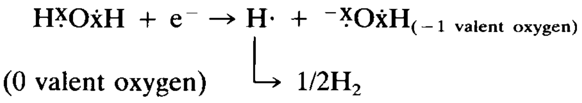


$$2Hx + \underset{\cdot x}{\overset{x\cdot}{\cdot O\cdot}} \rightarrow H{}^{x}_{\cdot}\underset{\cdot x}{\overset{x\cdot}{O}}\dot{x}H \text{ (H–O–H)} \qquad (11)$$



$$Hx + \cdot O\cdot \rightarrow H\text{–}O\cdot \xrightarrow{e^-} H\text{–}O^- \qquad (12)$$

$$\cdot O\cdot + 2e^- \rightarrow \dot{x}O{}^{x}_{\cdot}{}^{2-} \qquad (13)$$



$$\underset{\text{(0 valent oxygen)}}{H{}^{x}_{\cdot}O\dot{x}H} + e^- \rightarrow \underset{\hookrightarrow\ 1/2H_2}{H\cdot} + {}^{-}{}^{x}_{\cdot}O\dot{x}H_{(-1\text{ valent oxygen})} \qquad (14)$$

$$\mathrm{H\dot{x}O\overset{x}{\underset{\cdot}{}}H} + 2e^- \rightarrow \mathrm{H\dot{x}H} + \mathrm{\overset{x}{\underset{\cdot}{}}O\dot{x}}^{2-}_{(-2\ \text{valent oxygen})} \qquad (15)$$

Thus, the oxygen in the water molecule is reduced from the zero-valent state to the -1 state in ^-OH and the -2 state in O^{2-}. The calculated charge density for the oxygen in water is -0.3 electron,[3,4] which is consistent with a near-zero valency.

Such a formulation of oxygen valency prompts the suggestion that the dissolution reaction of Na_2O is driven by valence transfer

$$\begin{array}{ccccccc} Na_2O(s) & + & H_2O & \rightarrow 2Na^+ & + & 2\,^-OH & \\ (-2\ \text{valence}) & & (0\ \text{valence}) & & & (-1\ \text{valence}) & (16) \end{array}$$

Redox Thermodynamics for Oxygen. The electron-transfer potentials for the reduction of ground-state atomic oxygen in water and in acetonitrile are summarized in Table I.[5,6,7] In addition, selected values for the reduction of the zero-valent oxygen in O_3, $HOIO_3$, and HOCl are included.[5] Because the valence of oxygen in water is zero, these reduction processes represent the facilitated reduction of protons via stabilization of the product H-atoms through strong covalent-bond formation with atomic oxygen. Thus, the standard-state reduction of protons,

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0,\ 0.00V\ \text{vs. NHE} \qquad (17)$$

is shifted to a much more favored process in the presence of atomic oxygen

$$\dot{\underset{\cdot}{O}}_{(g)} + 2H^+ + 2e^- \rightarrow H_2O \qquad E^0,\ +2.42V \qquad (18)$$

Likewise, the electron-transfer reduction of H_2O (with zero-valent hydrogen and oxygen), which must overcome the stabilization of the strong O–H bonds, results in a -1 valence for oxygen rather than proton reduction

$$H_2O + e^- \rightarrow 1/2H_2 + {}^-OH \qquad E^0,\ -0.82V\ \text{vs. NHE} \qquad (19)$$

In contrast, an equivalent valence change for the zero-valent oxygen in ·OH is strongly favored[7]

$$\cdot OH + e^- \rightarrow {}^-OH \qquad E^0,\ +1.89V \qquad (20)$$

TABLE I

Reduction potentials for $^3O_{(g)}$ in water and acetonitrile solutions

I. H_2O, pH 0:

$$\begin{tikzcd} O_{(g)} \arrow[r, "+2.1V\ \mathrm{vs\ NHE}", "e^-,\ H^+"'] \arrow[rr, bend right, "+2.4V", "2e^-,\ 2H^+"'] & \cdot OH \arrow[r, "+2.7V", "e^-,\ H^+"'] & H_2O \end{tikzcd}$$

$$O_3 + 2H^+ + 2e^- \xrightarrow{+2.1V} O_2 + H_2O$$

$$HOIO_3 + 2H^+ + 2e^- \xrightarrow{+1.6V} HOIO_2 + H_2O$$

$$HOCl + 2H^+ + 2e^- \xrightarrow{+1.5V} HCl + H_2O$$

$$HOOH + 2H^+ + 2e^- \xrightarrow{+1.8V} 2H_2O$$

II. H_2O, pH 14:

$$\begin{tikzcd} O_{(g)} \arrow[r, "+1.4V", "e^-"'] \arrow[rr, bend right, "+1.6V", "2e^-,\ H_2O"'] & O^-\cdot \arrow[r, "+1.8V", "e^-,\ H_2O"'] & {}^-OH \end{tikzcd}$$

$$O_3 + H_2O + 2e^- \xrightarrow{+1.3V} O_2 + 2\,{}^-OH$$

$$IO_4^- + H_2O + 2e^- \xrightarrow{+0.8V} IO_3^- + 2\,{}^-OH$$

$$ClO^- + H_2O + 2e^- \xrightarrow{+0.9V} Cl^- + 2\,{}^-OH$$

$$HOO^- + H_2O + 2e^- \xrightarrow{+0.9V} 3\,{}^-OH$$

III. MeCN, $HClO_4$:

$$\begin{tikzcd} O_{(g)} \arrow[r, "+2.6V", "e^-,\ H^+"'] \arrow[rr, bend right, "+2.9V", "2e^-,\ 2H^+"'] & \cdot OH \arrow[r, "+3.2V", "e^-,\ H^+"'] & H_2O \end{tikzcd}$$

$$O_3 + 2H^+ + 2e^- \xrightarrow{+2.6V} O_2 + H_2O$$

$$HOIO_3 + 2H^+ + 2e^- \xrightarrow{+2.1V} HOIO_2 + H_2O$$

$$HOCl + 2H^+ + 2e^- \xrightarrow{+2.0V} HCl + H_2O$$

$$HOOH + 2H^+ + 2e^- \xrightarrow{+2.3V} 2H_2O$$

IV. MeCN:

$$\begin{tikzcd} O_{(g)} \arrow[r, "+0.7V", "e^-"'] \arrow[rr, bend right, "+0.6V", "2e^-,\ H_2O"'] & O^-\cdot \arrow[r, "+0.6V", "e^-,\ H_2O"'] & {}^-OH \end{tikzcd}$$

$$O_3 + H_2O + 2e^- \xrightarrow{+0.3V} O_2 + 2\,{}^-OH$$

$$ClO^- + H_2O + 2e^- \xrightarrow{-0.1V} Cl^- + 2\,{}^-OH$$

and reduction of the combination of the zero-valent oxygen of water with -1-valent $O^{-}\cdot$ yields two -1-valent hydroxide ions[7]

$$O^{-}\cdot + H_2O + e^{-} \rightarrow 2\,^{-}OH \qquad E^0,\ +1.77V \qquad (21)$$

Although the chlorine atom is among the strongest one-electron oxidants known[7]

$$Cl\cdot + e^{-} \rightarrow Cl^{-} \qquad E^0,\ +2.41V \qquad (22)$$

when it is stabilized by the covalent bond of the Cl_2 molecule and of the ClO^{-} ion its propensity to change valence is reduced[5,7]

$$Cl_2 + e^{-} \rightarrow Cl_2^{-}\cdot \qquad E^0,\ +0.63V \qquad (23)$$

$$Cl_2 + 2e^{-} \rightarrow 2Cl^{-} \qquad E^0,\ +1.36V \qquad (24)$$

$$ClO^{-} + e^{-} \rightarrow Cl^{-} + O^{-}\cdot \qquad E^0,\ +0.02V \qquad (25)$$

$$ClO^{-} + H_2O + 2e^{-} \rightarrow Cl^{-} + 2\,^{-}OH \qquad E^0,\ +0.89V \qquad (26)$$

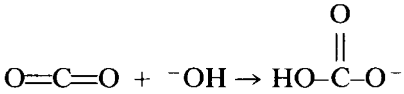
Thus, Cl_2 can transfer an electron from an ^{-}OH because of the stabilization of $\cdot OH$ via bond formation with an $H\cdot$ from another ^{-}OH and of the resulting $O^{-}\cdot$ via bond formation with a $Cl\cdot$ [ΔE^0, $+0.47V$ (Eq. (24) − Eq. (26))]

$$Cl_2 + 2OH^{-} \rightarrow ClO^{-} + Cl^{-} + H_2O \qquad (27)$$

Nucleophilic Attack via Single-Electron Transfer. The facile nucleophilic displacement of chloride ion from alkyl chlorine compounds (all 0-valent atoms) by ^{-}OH (-1-valent O) to give an alcohol (with all atoms zero valent) is a valence-transfer process via electron transfer from the ^{-}OH to the chlorine atom of RCl[8,9]

$$n\text{-BuCl} + \,^{-}OH \rightarrow n\text{-BuOH} + Cl^{-} \qquad (28)$$

Likewise the nucleophilic addition of ^-OH (-1-valent O) to CO_2 gives bicarbonate ion with the valence of the oxygen of the C–OH group changed to zero via electron transfer (and valence transfer) to a zero-valent carbonyl oxygen



$$O{=}C{=}O + {}^-OH \rightarrow HO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^- \qquad (29)$$

The dissolution of $Na_2O(s)$ (-2-valent O) in water occurs via a valence transfer (and electron transfer) from O^{2-} to the zero-valent oxygen of H_2O to give ^-OH (-1-valent O)

$$Na_2O(s) + H_2O \rightarrow 2Na^+ + 2\,{}^-OH \qquad (30)$$

Valency of Oxygen in Halogen Compounds. The minus one- and zero-valence states for oxygen are stabilized by halogen atoms. For example, the oxygen atoms of HOCl, $HOIO_4$, and PhIO all are in the zero-valent state. In turn, the negatively charged oxygens of ClO^-, $^-OIO_3$, and $^-OClO_3$ are at -1 valence. Thus, PhI and ^-OI are transformed to PhIO and $^-OIO_3$ by the addition of one and three zero-valent oxygen atoms, respectively (without a change of valence).

Examples of compounds that contain a -1-valent oxygen include HO^-, MeO^-, HOO^-, $O_3^-\cdot$, $O_2^-\cdot$, ClO_4^-, IO_4^-, and $HOC(O)O^-$. Representive examples of zero-valent O compounds include H_2O, MeOH, MeOMe, HOCl, PhIO, $HOIO_3$, Ph_3PO, and pyridine-N(O).

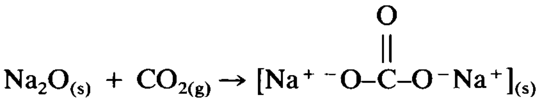
BONDING AND VALENCE FOR METAL-OXYGEN COMPOUNDS

Oxo(-2 Valence) and Hydroxo(-1) Compounds. The extreme electronegativity and basicity of the O^{2-} ion precludes its existence in protic media such as H_2O, and its dissolution in aprotic solvents. As indicated by Eq. (30), the addition of $Na_2O(s)$ to water causes a valence transfer to the zero-valent oxygen of H_2O and results in two ^-OH ions (-1-valent O). The same valence transfer occurs when $Na_2O(s)$ reacts with the zero-valent oxygens of alcohols and carboxylic acids

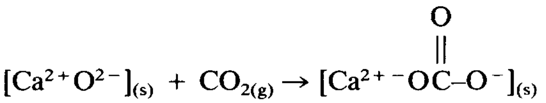
$$Na_2O_{(s)} + MeOH \rightarrow MeO^- + {}^-OH + 2Na^+ \qquad (31)$$

$$Na_2O_{(s)} + MeC(O)OH \rightarrow MeC(O)O^- + {}^-OH + 2Na^+ \qquad (32)$$

Even with gas–solid reactions there can be valence transfer from O^{2-} to give two −1-valent oxygens



$$Na_2O_{(s)} + CO_{2(g)} \rightarrow [Na^+ \, {}^-O\text{–}\overset{\overset{O}{\|}}{C}\text{–}O^- Na^+]_{(s)} \qquad (33)$$



$$[Ca^{2+}O^{2-}]_{(s)} + CO_{2(g)} \rightarrow [Ca^{2+} \, {}^-O\overset{\overset{O}{\|}}{C}\text{–}O^-]_{(s)} \qquad (34)$$

$$[Ca^{2+}O^{2-}]_{(s)} + H_2O_{(g)} \rightarrow [Ca^{2+}({}^-OH)_2]_{(s)} \qquad (35)$$

Formation of Oxene(0 Valent) and $O^- \cdot (-1)$ Compounds with Transition Metal Ions. A convenient means to the formation of metal-oxygen compounds is the combination of atomic oxygen with the elemental metal. The usual sources of atomic oxygen for these reactions are compounds in which it is held by weak covalent bonds. Examples include:

$$m\text{-}ClPhC(O)OOH \rightarrow ClPhC(O)OH + [O] \qquad (36)$$

$$H_2O_2 \rightarrow H_2O + [O] \qquad (37)$$

$$O_3 \rightarrow O_2 + [O] \qquad (38)$$

$$HOCl \rightarrow HCl + [O] \qquad (39)$$

$$IO_4^- \rightarrow IO_3^- + [O] \qquad (40)$$

$$PhIO \rightarrow PhI + [O] \qquad (41)$$

$$p\text{-}NCPhN(Me)_2(O) \rightarrow NCPhNMe_2 + [O] \qquad (42)$$

The dissolution and oxidation of the elemental manganese in steel alloys to MnO_4^- by IO_4^- illustrates the nature of such oxygen-atom-transfer chemistry and the valence changes for the oxygen

$$Mn_{(s)} + \overset{(0)}{[O]} \rightarrow Mn^{II}\overset{(-2)}{O}_{(s)} \xrightarrow{H_2O} \overset{(0)\quad(-1)}{Mn^{II}(OH)_{2(s)}} \tag{43}$$

$$\underset{d^5(S = 5/2)}{Mn^{II}\overset{(-2)}{O}_{(s)}} + [O] \rightarrow \underset{\text{“}d^7\text{”}(S = 3/2)}{Mn^{II}\overset{(-1)}{(O^-\cdot)}_{2(s)}} \tag{44}$$

$$Mn^{II}(O^-\cdot)_{2(s)} + [O] \rightarrow \underset{\text{“}d^9\text{”}(S = 1/2)}{Mn^{II}\overset{(-1)}{(O^-\cdot)}_2\overset{(0)}{(O)}_{(s)}}$$

$$\xrightarrow[]{\overset{(-1)}{2^-OH}} \underset{\text{“}d^9\text{”}(S = 1/2)}{Mn^{II}\overset{(-1)}{(O^-\cdot)}_4^{2-}} + \overset{(0)}{H_2O} \tag{45}$$

$$2Mn^{II}(O^-\cdot)_2(O)_{(s)} + [O]$$

$$\rightarrow Mn^{II}\overset{(-1)}{(O^-\cdot)}_2\overset{(0)}{(\cdot O\cdot)}_3Mn^{II}\overset{(-1)}{(O^-\cdot)}_{3(s)}$$

$$\xrightarrow{2^-OH} 2\,\underset{\text{“}d^{10}\text{”}(S = 0)}{Mn^{II}\overset{(-1)}{(O^-\cdot)}_3\overset{(0)}{(O)}^-} + H_2O \tag{46}$$

The instability of the Mn^{3+} ion in basic media results from its exceptional electron affinity, which facilitates electron transfer from ^-OH.

$$2Mn^{3+} + 6\,^-OH \rightarrow Mn^{II}(OH)_{2(s)} + Mn^{II}(O^-\cdot)_{2(s)} + 2H_2O \tag{47}$$

The assignment of an invariant valence of +2 for the manganese in all of these manganese-oxygen compounds may appear arbitrary, but follows from (a) the redox thermodynamics for oxygen (Table I) and manganese compounds (Table II),[10,11] (b) the evidence that covalent bond formation by zero-valent and −1-valent oxygen strongly moderates its redox potentials, and (c) the belief that such covalent bond formation occurs with the electrons of partially filled d-subshells of transition metals. Thus, I suggest that the formulations of Eqs. (44)–(47) are more reasonable representations of the bonding, charge distribution, chemical reactivity, and redox thermodynamics than the classical high-valent metal-oxo formulas. Specifically, $\mathrm{Mn^{II}(O^{-}\cdot)_2}$ is proposed rather than $\mathrm{Mn^{IV}(O^{2-})_2}$, $\mathrm{Mn^{II}(O^{-}\cdot)_4^{2-}}$ rather than $\mathrm{Mn^{VI}(O^{2-})_4^{2-}}$, and $\mathrm{Mn^{II}(O)(O^{-}\cdot)_3^{-}}$ rather than $\mathrm{Mn^{VII}(O^{2-})_4^{-}}$; these represent systems with 2, 4, and 5 metal d-oxy radical covalent bonds. Such covalent bonding accounts for the inertness of $\mathrm{MnO_{2(s)}}$ and $\mathrm{MnO_4^-}$ to reactivity with protons, whereas true oxo systems $[\mathrm{Ba^{2+}(O^{2-})_{(s)}}$, $\mathrm{(Fe^{3+})_2(O^{2-})_{3(s)}}$, and $\mathrm{(Ce^{4+})(O^{2-})_{2(s)}}]$ yield free metal cations upon acidification ($\mathrm{Ba^{2+}}$, $\mathrm{Fe^{3+}}$, and $\mathrm{Ce^{4+}}$).

TABLE II

Redox potentials for manganese ions and complexes

A. Aqueous solutions (each ion is at unit activity)	E°, V vs. NHE
$\mathrm{Mn^{3+} + e^- \rightarrow Mn^{2+}}$ (5M $\mathrm{HClO_4}$)	+1.54
$\mathrm{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$	+1.51
$\mathrm{MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^-}$	+0.59
$\mathrm{MnO_4^- + e^- \rightarrow MnO_4^{2-}}$ (>pH 12)	+0.56
$\mathrm{MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2(s) + 4OH^-}$	+0.60
$\mathrm{MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O}$	+1.24
$\mathrm{MnO_2(s) + 4H^+ + e^- \rightarrow Mn^{3+} + 2H_2O}$	+1.0
$\mathrm{MnO_2(s) + H_2O + e^- \rightarrow Mn(OH)(O)(s) + OH^-}$	+0.1
$\mathrm{Mn(OH)(O)(s) + H_2O + e^- \rightarrow Mn(OH)_2(s) + OH^-}$	+0.2
B. Acetonitrile (0.1M tetraethylammonium perchlorate)	
$\mathrm{Mn(MeCN)_4^{3+} + e^- \rightarrow Mn(MeCN)_4^{2+}}$	>+2.54
$\mathrm{Mn(bpy)_3^{3+} + e^- \rightarrow Mn(bpy)_3^{2+}}$	+1.61
$\mathrm{Mn(bpyO_2)_3^{4+} + e^- \rightarrow Mn(bpyO_2)^{3+}}$	+1.86
$\mathrm{Mn(bpyO_2)_3^{3+} + e^- \rightarrow Mn(bpyO_2)_3^{2+}}$	+1.11
$\mathrm{(bpy)_4Mn_2(\mu\text{-}O)_2^{4+} + e^- \rightarrow (bpy)_4Mn_2(\mu\text{-}O)_2^{3+}}$	+1.57
$\mathrm{(bpy)_4Mn_2(\mu\text{-}O)_2^{3+} + e^- \rightarrow (bpy)_4Mn_2(\mu\text{-}O)_2^{2+}}$	+0.62

Additional support for the formulation of permanganate ion as a d^5-oxene-tri-oxy radical $[Mn^{II}(O)(O^{-}\cdot)_3^{-}]$ is provided in a recent theoretical evaluation of the bonding and valence transfer within the elemental adducts of d^5-Cr^{I} (CrC^+, CrN^+, CrO^+, and CrF^+).[12] The estimated charge transfer from the Cr^{I}-d^5 manifold to C, N, O, and F is 0.07, 0.2, 0.5, and 0.7 electron, respectively. Thus, the CrO^+ species is best represented as a resonance hybrid $[Cr^{I}(\dot{\underset{\cdot}{O}})^+ \leftrightarrow Cr^{II}(O^{-}\cdot)^+]$. Given that the electron affinity of Cr^{I} for its d^5 electrons is related to the redox potential for the Cr^{II}/Cr^{I} couple

$$Cr^{II} + e^- \rightarrow Cr^{I} \qquad E^0 = -1.5V \text{ vs. NHE (estimated)} \qquad (48)$$

and that the comparable d^4/d^5 transformation for the Mn^{III}/Mn^{II} couple is favored by about 3.0V (~70 kcal)

$$Mn^{III} + e^- \rightarrow Mn^{II} \qquad E^0 = +1.5V \text{ vs. NHE} \qquad (49)$$

a reasonable estimate for the valence transfer in the d^5-$Mn^{II}(\dot{\underset{\cdot}{O}})^{2+}$ system is less than 0.2 electron. An extension of this argument to the d^5-$Fe^{III}(\dot{\underset{\cdot}{O}})^{3+}$ system (with the redox potential for the Fe^{IV}/Fe^{III} couple estimated to be $> +4.0V$ vs. NHE) indicates that the valence transfer to the zero-valent O should be less than 0.1 electron.

The incompatibility of high-valent manganese [such as Mn(VII) in MnO_4^-] with oxidizable anionic ligands is confirmed in a recent paper.[13] Formation of nominal $Mn^{IV}F_4$ from neutralization of nominal $Mn^{IV}F_6^{2-}$ results in a spontaneous decomposition to MnF_3 and F_2. Given the observed chemistry a more reasonable formulation for the decomposition reaction would involve a +3 valence with a covalently bound fluorine atom.

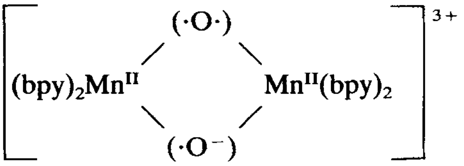
$$2Mn^{III}(\cdot F)(F^-)_3 \rightarrow 2Mn^{III}F_3 + F_2 \qquad (50)$$

If F^- holds its valence electron less firmly than Mn^{III}, then O^{2-} and $O^{-}\cdot$ can not withstand the electron affinities of Mn(VIII), Mn(VI), Mn(V), and Mn(IV). Indeed, the preceding section demonstrates that even Mn(II) has a higher electron affinity than does $O^{-}\cdot$. This is further supported by a recent report,[14] which concludes that the bonds in MnF_2 are only 49% ionic and that the net charge per F is -0.32 electron.

The apparent hydrolytic disproportionation of Mn(III) in water to Mn(II) and Mn(IV) becomes reasonable as a metal-to-hydrogen atom (of H_2O) valence-transfer process

$$\begin{aligned} 2Mn^{3+} + 2H_2O &\rightarrow 2Mn^{II}(\cdot OH)^{2+} + 2H^+ \\ &\rightarrow Mn^{II}(O^-\cdot)_2(s) + Mn^{2+} + 4H^+ \qquad (51) \end{aligned}$$

Another extensively studied metal-oxygen complex is the Nyholm complex, $[(bpy)_4Mn_2^{III,IV}(\mu\text{-}O)_2^{3+}]$,[15] which often is suggested as a model for the water-oxidation center of photosystem II in green-plant photosynthesis.[16] In line with the proposition that oxo ions are incompatible with higher valent manganese, a more reasonable formulation is



The redox transformations and potentials for this complex (Table II) are in accord with the oxygen redox processes of Table I rather than for valence changes of manganese. That is, the oxidation of the complex ($+1.57$V vs. NHE) involves the removal of an electron from the $O^-\cdot$ ion to give a 4+ complex, and its reduction ($+0.62$V) involves the addition of an electron to the covalently bound oxygen atom to give a 2+ complex.

The argument that high-valent transition metal ions are incompatible with the electronegative oxo group, particularly when electron transfer results in unpaired valence electrons that can stabilize each other via bond formation, prompts the reformulation of other metal-oxygen compounds. Table III lists the traditional electronic formulation and the suggested representation.

The formulation of a zero-valent oxygen in permanganate

TABLE III

Reformulation of metal-oxygen complexes with $O^{-}\cdot$ and O atoms

Traditional Formula	Proposed Formula[a]
$Fe^{VI}(O^{2-})_4^{2-}$ (d^2, S = 2/2)	$Fe^{III}(O^{-}\cdot)_3(OH)_2^{2-}$ ("d^8", S = 2/2)
$Cr^{VI}(O^{2-})_4^{2-}$ (d^0, S = 0)	$Cr^{III}(O^{-}\cdot)_3(OH)_2^{2-}$ ("d^6", S = 0)
$Cr^{VI}(O^{2-})_2Cl_2$ (d^0, S = 0)	$Cr^{III}(\dot{\underset{\cdot}{O}})(O^{-}\cdot)Cl_2$ ("d^6", S = 0)
$Ni^{IV}(O^{2-})_2$ (d^6, S = 4/2)	$Ni^{II}(O^{-}\cdot)_2$ ("d^{10}", S = 0)
$Co^{III}(O^{2-})_2^{-}$ (d^6, S = 4/2)	$Co^{II}(O^{-}\cdot)(OH)$ ("d^8", S = 2/2)
$V^{V}(O^{2-})_2^{+}$ (d^0, S = 0)	$V^{III}(O^{-}\cdot)_2^{+}$ ("d^4", S = 0)
$V^{IV}(O^{2-})^{2+}$ (d^1, S = 1/2)	$V^{III}(O^{-}\cdot)^{2+}$ ("d^3", S = 1/2)
$Mo^{VI}(O^{2-})_3(s)$ (d^0, S = 0)	$Mo^{III}(O^{-}\cdot)_3(s)$ ("d^6", S = 0)
$Mo^{VI}(O^{2-})_2^{2+}$ (d^0, S = 0)	$Mo^{III}(\dot{\underset{\cdot}{O}})(O^{-}\cdot)^{2+}$ ("d^6", S = 0)
$Mo^{V}(O^{2-})Cl_3$ (d^1, S = 1/2)	$Mo^{III}(\dot{\underset{\cdot}{O}})Cl_3$ ("d^5", S = 1/2)
$Pb^{IV}(O^{2-})_2(s)$	$Pb^{II}(O^{-}\cdot)_2(s)$
$Pt^{II}(O^{2-})(s)$ (d^8, S = 2/2)	$Pt^{0}(\dot{\underset{\cdot}{O}})(s)$ ("d^{10}", S = 0)
TPP $Fe^{V}(O^{2-})^{+}$ (d^3, S = 3/2)	TPP $Fe^{III}(\dot{\underset{\cdot}{O}})^{+}$ ("d^7", S = 3/2)
$(TPP^{-}\cdot)Fe^{IV}(O^{2-})^{+}$ ("d^5", S = 5/2,3/2) (Compd. I)	TPP $Fe^{III}(\dot{\underset{\cdot}{O}})^{+}$ ("d^7", S = 3/2)
TPP $Fe^{IV}(O^{2-})$ (d^4, S = 4/2) (Compd. II)	TPP $Fe^{III}(O^{-}\cdot)$ ("d^6", S = 4/2)
$(RS^{-})(TPP^{-}\cdot)Fe^{IV}(O^{2-})$ ("d^5", S = 5/2,3/2)	$(RS\cdot)$TPP $Fe^{II}(\dot{\underset{\cdot}{O}})$ ("d^9", S = 1/2) (active form of Cytochrome P-450)

[a] "d^8" represents the sum of d-electrons plus covalently coupled oxy-radical electrons.

(MnO_4^-) and in chromyl chloride (CrO_2Cl_2) is consistent with their electrophilic oxidation of diols and alcohols, respectively.[17]

$$6H^+ + 2Mn^{II}(\dot{\underset{\cdot}{O}})(O^{-}\cdot)_3^{-} + 5RCH(OH)CH(OH)R' \rightarrow 5RCH(O) + 5R'CH(O) + 3H_2O + 2Mn^{2+} \quad (52)$$

$$2H^+ + 2Cr^{III}(\dot{\underset{\cdot}{O}})(O^{-}\cdot)Cl_2 + 3RCH_2OH \rightarrow 3RCH(O) + 4H_2O + 2Cr^{III}Cl_2^{+} \quad (53)$$

With the traditional formulation for chromyl chloride [$Cr^{VI}(O^{2-})_2Cl_2$] a metal-directed electrophilic activation of a carbon to a carbonium ion must be invoked to accomodate subsequent attack by the nucleophilic oxo groups. With the oxene of the $Cr^{III}(O)(O^{-}\cdot)Cl_2$ formulation, direct electrophilic abstraction of a hydrogen atom can occur to give an $\cdot OH$, which can then combine with the just formed carbon radical (the so-called "rebound mechanism").[18]

Thus, the proposed formulation for the active form of cytochrome P-450 (Table III) accomodates the redox thermodynamics of the components and the electrophilic nature of the oxygenation chemistry, and does not invoke carbon activation by a high-valent iron center that is inaccessible (surrounded by porphinato, thiolato, and oxo nucleophiles in contemporary formulations).

$$(RS\cdot)TPP\ Fe^{II}(\underset{\cdot}{\dot{O}}) + RCH(O) \rightarrow \{(RS\cdot)TPP\ Fe^{II}(\cdot OH)[R\underset{\cdot}{C}(O)]\} \rightarrow (RS\cdot)TPP\ Fe^{II} + RC(O)OH \quad (54)$$

Such an electronic distribution for the active form of cytochrome P-450 follows from the redox thermodynamics of Table I, and from the recent observation that the removal of an electron from a bound thiolate ion is favored over the alternative removal from the iron(II) center (the resulting sulfur radical is stabilized by covalent bond formation with an iron(II) d-electron).[19]

The proposition that ligand-centered electron-transfer oxidations occur in transition-metal complexes with oxo and hydroxo ligands has been confirmed in a series of electrochemical studies.[6] Preliminary results are summarized in Table IV, and demonstrate that the stabilization of the oxy-radical products via bond formation with the unpaired d-electrons of iron(II) and iron(III) shifts the oxidation potential by approximately -0.6V. This is comparable to the shifts in potential that are observed for the ligand-centered oxidation of the bis(3,4-toluene dithiolate) complexes of Fe(II), Cu(II), Mn(II), and Co(II).[19]

On the basis of the data of Tables I and IV and the preceding discussion, the redox reactions and potentials for Compound I and Compound II of horseradish peroxidase are formulated in terms of $Fe^{III}TPP\ Cl$ in a model matrix of acetonitrile buffered with picolinate/picolinic acid (PA^{-}/PAH).

TABLE IV

Electrochemical redox potentials in acetonitrile for hydroxide-ion and phenoxide-ion oxidations in the absence and presence of $Fe^{II}(OPPh_3)_4^{2+}$ and $Zn^{II}(OPPh_3)_4^{2+}$, and of zinc(II)$^-$ and iron(II,III)-tetraphenylporphyrin(TPP^{2-})

Redox Couple	$E^{0\prime}$, V. vs. NHE
$H^+ + \cdot OH + e^- \leftarrow H_2O$	+2.7
$H_2O + O^-\cdot + e^- \leftarrow 2\,^-OH$	+0.8
$H^+ + PhO\cdot + e^- \leftarrow HOPh$	+1.7
$PhO\cdot + e^- \leftarrow \,^-OPh$	+0.3
$Fe^{III}(OPPh_3)_4^{3+} + e^- \rightleftharpoons Fe^{II}(OPPh_3)_4^{2+}$	+1.5
$H_2O + Zn^{II}(OPPh_3)_4(O^-\cdot)^+ + e^- \leftarrow Zn^{II}(OPPh_3)_4^{2+} + 2\,^-OH$	+0.9
$H_2O + Fe^{II}(OPPh_3)_4(O^-\cdot)^+ + e^- \leftarrow Fe^{II}(OPPh_3)_4^{2+} + 2\,^-OH$	+0.3
$Fe^{III}TPP(ClO_4) + e^- \rightleftharpoons Fe^{II}TPP + ClO_4^-$	+0.3
$Fe^{III}TPP(^-OH) + e^- \rightleftharpoons Fe^{II}TPP(^-OH)^-$	−0.4
$Fe^{III}TPP(\cdot OH)^+ + e^- \leftarrow Fe^{III}TPP(^-OH)$	+1.2
$H_2O + Fe^{III}TPP(O^-\cdot) + e^- \leftarrow Fe^{III}TPP(^-OH) + \,^-OH$	+0.0
$\xrightarrow{-e^-} Fe^{III}TPP(O)^+$	<0.0
$Fe^{III}TPP(\cdot OPh)^+ + e^- \leftarrow Fe^{III}TPP(^-OPh)$	+1.2
$Zn^{II}TPP + \cdot OPh + e^- \leftarrow Zn^{II}TPP(^-OPh)^-$	+0.4

$$\begin{array}{ccc} \text{TPP Fe}^{III}(\dot{\underset{\cdot}{O}})\text{Cl} + e^- & \rightarrow & \text{TPP Fe}^{III}(O^-\cdot) + \text{Cl}^- \\ \text{Compound I, “d}^7\text{” } (S = 3/2) & & \text{Compound II, “d}^6\text{” } (S = 4/2) \end{array}$$

$$E^{0\prime}, +0.7\text{V vs. NHE} \quad (55)$$

$$\text{TPP Fe}^{III}(O^-\cdot) + 2\text{PAH} + e^- \rightarrow \text{TPP Fe}^{III}(\text{PA}^-) + H_2O + \text{PA}^- \qquad E^{0\prime}, +0.9\text{V} \quad (56)$$

$$\text{TPP Fe}^{III}(\dot{\underset{\cdot}{O}})\text{Cl} + 2\text{PAH} + 2e^- \rightarrow \text{TPP Fe}^{III}(\text{PA}^-) + H_2O + \text{PA}^- + \text{Cl}^- \qquad E^{0\prime}, +0.8\text{V} \quad (57)$$

These reduction potentials are compatible with the proposition that activation by H_2O_2 yields Compound I

$$\text{Fe}^{III}\text{TPP Cl} + H_2O_2 \rightarrow \text{TPP Fe}^{III}(\text{O})\text{Cl} + H_2O \quad (58)$$

and with the reduction energetics for H_2O_2 in a PA^-/PAH-MeCN matrix.

$$H_2O_2 + 2PAH + 2e^- \rightarrow 2H_2O + 2PA^- \qquad E^{0\prime},\ +1.0V \text{ vs. NHE} \qquad (59)$$

A two-electron reduction potential for Compound I that is greater than that for H_2O_2 is precluded by thermodynamics.

For the proposed active form of cytochrome P-450, the estimated one-electron reduction potential is much less positive than it is for Compound I,

$$\underset{\text{“}d^9\text{” } (S\,=\,1/2)}{(RS\cdot)Fe^{II}TPP(\overset{\cdot}{\underset{\cdot}{O}})} + e^- \rightarrow (RS\cdot)Fe^{II}TPP(O^-\cdot)^- \qquad E^{0\prime},\ +0.2V \text{ vs. NHE} \qquad (60)$$

which precludes undesirable one-electron processes. The two-electron reduction potential within the model matrix (PA^-/PAH-MeCN) is estimated to be similar to that for Compound I.

$$(RS\cdot)Fe^{II}TPP(O) + 2PAH + 2e^- \rightarrow (RS\cdot)Fe^{II}TPP + H_2O + 2PA^- \qquad E^{0\prime},\ +0.7V \text{ vs. NHE} \qquad (61)$$

Another consideration is the auto-oxidation of reduced heme. The kinetic analysis[20] clearly requires a mechanism that is second-order in heme and first-order in dioxygen, with an initial reversible binding of dioxygen

$$Fe^{II}P + O_2 \rightleftharpoons Fe^{II}P(O_2) \qquad (62)$$

This, in turn, reacts with a second heme in an apparent irreversible electron-transfer process

$$Fe^{II}P(O_2) + Fe^{II}P \rightarrow PFe^{III}(O_2^{2-})Fe^{III}P \qquad (63)$$

The latter μ-peroxide dimer reacts with two additional reduced hemes to give two μ-oxo dimers

$$\mathrm{PFe^{III}(O_2^{2-})Fe^{III}P + 2Fe^{II}P \rightarrow 2PFe\text{–}O\text{–}FeP} \qquad (64)$$

which are formulated as $\mathrm{PFe^{III}(O^{2-})Fe^{III}P}$. However, in view of the present discourse and the strong electron-donating propensity of oxo dianion, a more chemically reasonable formulation would involve an oxene bridging via two covalent bonds with two reduced hemes.

The electrostatic equivalent of the μ-oxo$\mathrm{(Fe^{III}P)_2}$ formulation is the TPP $\mathrm{Fe^{III}(^{-}OH)}$ species, which is reversibly reduced.

$$\mathrm{TPP\ Fe^{III}(^{-}OH) + e^{-} \rightleftharpoons TPP\ Fe^{II}(^{-}OH)^{-}}$$

$$E^{0\prime},\ -0.4\mathrm{V\ vs.\ NHE} \qquad (65)$$

However, the reduction of the μ-oxo system occurs at much more negative potentials and is an apparent irreversible two-electron process. This behavior is strongly supportive of the proposition that this is a ligand-centered reduction of an oxene-bridged $\mathrm{Fe^{II}TPP}$ dimer.

$$\mathrm{TPP\ Fe^{II}(\overset{\cdot}{\underset{\cdot}{O}})Fe^{II}TPP + 2e^{-} + H_2O \rightarrow 2Fe^{II}TPP(^{-}OH)^{-}}$$

$$E^{0\prime},\ -0.9\mathrm{V\ vs.\ NHE} \qquad (66)$$

The product species of the reduction has the electrochemical and spectroscopic characteristics of $\mathrm{Fe^{II}TPP(^{-}OH)^{-}}$. Again, an oxene formulation for the oxygen-bridged dimer is consistent with its (a) limited solubility in acidic media, (b) inertness to one-electron transfer processes, (c) significant covalent character [about −0.2 electron charge on oxygen if the electronegativities for iron(III) and oxygen are 2.2 and 3.4, respectively],[14] and (d) small magnetic moment (μ_{eff} = 1.6B.M.).[21]

The "oxides" that are formed on the surfaces of transition-metal electrodes and heterogeneous catalysts via anodization and autooxidation represent another class of metal-oxygen compounds.

Similar arguments to those of the preceding paragraphs lead to the conclusion that covalent interactions of zero-valent elements dominate the bonding of surface compounds such as $Pd(OH)_2(s)$, $Ag_2O(s)$, and $PtO(s)$. If electronegativities of 2.20 [Pd(II)], 1.93 [Ag(I)], 2.28 [Pt(II)], and 3.44 (O) are used,[2,14] then the estimated charge-density on the oxygen atoms of $Pd(OH)_2$ is 0.15 electron, of Ag_2O is 0.26 electron, and of PtO is 0.20 electron. As a result of such covalent-bond stabilization the redox couple for the $\cdot OH/{}^-OH$ couple is shifted from +1.9V vs. NHE (aqueous, Table I) to +0.1V for $Pd(OH)_2$,[5]

$$\begin{array}{ll} Pd^0(\cdot OH)_2(s) + H_2O + 2e^- \rightarrow Pd^0 + 2\,{}^-OH & \\ s^2d^8 \qquad\qquad\qquad\qquad E^{0\prime},\ +0.1V \text{ vs. NHE} & (67) \end{array}$$

which represents an apparent covalent bond-energy of 41 kcal for Pd–OH. Similarly the $O(g)/{}^-OH$ couple is shifted from +1.6V to +0.34V for Ag_2O and to +0.15V for PtO,[5]

$$\begin{array}{l} Ag_2^0(\overset{\cdot}{\underset{\cdot}{O}})(s) + H_2O + 2e^- \rightarrow 2Ag^0 + 2\,{}^-OH \\ s^2d^9 \qquad\qquad\qquad\qquad E^{0\prime},\ +0.34V \end{array} \qquad (68)$$

$$\begin{array}{ll} Pt^0(\overset{\cdot}{\underset{\cdot}{O}})(s) + H_2O + 2e^- \rightarrow Pt^0 + 2\,{}^-OH & \\ s^2d^8 \qquad\qquad\qquad\qquad E^{0\prime},\ +0.15V & (69) \end{array}$$

which represent apparent covalent-bond energies of 30 kcal for Ag–O and of 67 kcal for Pt═O. Such covalent bonding appears to account for the resistance of these surface compounds to attack and dissolution by strong acids, and for their ability to facilitate O-atom transfer reactions.

Finally, a closing thought for future discussion. If high-valent transition-metal ions are incompatible with the −2 and −1 valence states of oxygen on the basis of their respective redox thermodynamics, then are the +2 valence states of Pd(II) and Pt(II) capatible with the minus −1 valence states of H^- and carbanions (R_2CH^-)? The respective redox potentials are[5]: $Pd^{II/0}$, +1.0V; $Pt^{II/0}$, + 1.0V; H_2/H^-, −2.2V; and R_2CH_2/R_2CH^-, ~−2V. Given this and the stabilization afforded by valence transfer with d-s and d-p covalent-bond formation, $L_2Pd^0(\cdot H)(\cdot CHPh_2)$ appears to be a more realistic representation than the conventional formalism of $L_2Pd^{II}(^-H)(^-CHPh_2)$ that is used in reaction mechanisms for organometallic chemistry. Indeed, a recent paper[22] makes a strong case for $L_2Pd^0(\cdot CH_3)_2$ and $L_2Pd^0(\cdot H)(\cdot CH_3)$ instead of $L_2Pd^{II}(CH_3^-)_2$ and $L_2Pd^{II}(H^-)(CH_3^-)$.

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DONALD T. SAWYER
Department of Chemistry,
Texas A&M University,
College Station, Texas 77843

References

1. P. F. Guengerich and T. L. McDonald, Acc. Chem. Res. **17**, 9 (1984).
2. L. C. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (Cornell Univ. Press, Ithaca, NY, 1960).
3. K. Jug, N. D. Epiotis and S. Buss, J. Am. Chem. Soc. **108**, 3640 (1986).
4. J. Mullay, J. Am. Chem. Soc. **108**, 1770 (1986).
5. R. Parsons, *Handbook of Electrochemical Constants*, (Butterworths Scientific Publications, London, 1959), pp. 69–73.
6. P. Cofré, P. K.-S. Tsang and D. T. Sawyer, Inorg. Chem. (submitted).
7. H. A. Schwarz and R. W. Dodson, J. Phys. Chem. **88**, 3643 (1984).
8. J. L. Roberts, Jr. and D. T. Sawyer, J. Am. Chem. Soc. **103**, 712 (1981).
9. J. L. Roberts, Jr., T. S. Calderwood and D. T. Sawyer, J. Am. Chem. Soc. **105**, 7691 (1983).
10. K. Yamaguchi and D. T. Sawyer, Inorg. Chem. **24**, 971 (1985).
11. K. Yamaguchi and D. T. Sawyer, Israel J. Chem. **25**, 164 (1985).
12. J. F. Harrison, J. Phys. Chem. **90**, 3313 (1986).
13. K. O. Christe, Inorg. Chem. **25**, 3721 (1986).
14. R. T. Sanderson, Inorg. Chem. **25**, 3518 (1986).
15. R. S. Nyholm and A. Turco, Chem. Ind. (London), 74 (1960).
16. K. Sauer, Acc. Chem. Res. **11**, 257 (1978).
17. J. March, *Advanced Organic Chemistry*, 3rd ed. (McGraw-Hill, New York, 1985), pp. 1057–1066.
18. J. T. Groves and G. A. McClusky, J. Am. Chem. Soc. **98**, 859 (1976).
19. D. T. Sawyer, G. S. Srivatsa, M. E. Bodini, W. P. Shaefer and R. M. Wing, J. Am. Chem. Soc. **108**, 936 (1986).
20. J. P. Collman, Acc. Chem. Res. **10**, 265 (1977).
21. K. Jayaraj, A. Gold, G. E. Toneg, J. H. Helms and W. E. Hatfield, Inorg. Chem. **25**, 3516 (1986).
22. J. J. Low and W. A. Goodard III, J. Am. Chem. Soc. **108**, 6115 (1986).