Intermetal Oxygen, Sulfur, Selenium, and Nitrogen Atom Transfer Reactions

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Intermetal Oxygen, Sulfur, Selenium, and Nitrogen Atom Transfer Reactions

Abstract
The importance of electron-transfer reactions is clearly indicated by the extensive literature describing this field and the present research emphasis devoted toward understanding these fundamental processes.1 The intricacies of electron-transfer reactions have been vigorously examined experimentally and theoretically for over 40 years.2·3 Because of continuing, intensive effort, fundamental aspects of these vital processes are still being elaborated.

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Comments
Intermetal Oxygen, Sulfur, Selenium, and Nitrogen Atom Transfer Reactions

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I. Introduction

The importance of electron-transfer reactions is clearly indicated by the extensive literature describing this field and the present research emphasis devoted toward understanding these fundamental processes. The intricacies of electron-transfer reactions have been vigorously examined experimentally and theoretically for over 40 years. Because of continuing, intensive effort, fundamental aspects of these vital processes are still being elaborated.

The unambiguous demonstration of atom-transfer reactions was a major advance in the development and understanding of electron transfer between metal complexes. The elucidation of two classes of electron transfer—inner sphere and outer sphere mechanisms—remains an important distinction in redox processes. A great deal is known about one-electron redox reactions mediated by halogen atom transfer or group transfer of univalent ligands. Today, atom-transfer reactions continue to be an area of fundamental importance. This is particularly apparent in biological systems. For example, a number of metalloenzymes mediate the transfer of an atom and one or more electrons to a substrate. Perhaps most notable among these is the cytochrome P-450 class of enzymes. These enzymes utilize an iron porphyrin complex in the catalytically active site and are believed to operate via an oxygen atom transfer from an iron oxo intermediate to the substrate. In addition, a variety of molybdoenzymes are believed to catalyze oxygen atom transfer to/from a variety of substrates such as xanthine (to uric acid), sulfite (to sulfate), nitrate (to nitrite), and amine N-oxides (to amines). In the majority of these cases, information on reaction pathways is lacking. As a result, a large number of studies have focused on the transfer of an oxygen atom between a metal center and organic or nonmetal substrates. Significant progress in understanding the mechanism of cytochrome P-450 has been achieved in this manner. Furthermore, a great deal of effort has centered on using metal-oxo complexes as selective oxidants in industrial processes and laboratory practices. A recent comprehensive review discusses the range of metal complexes and substrates that have been studied.

In addition to metal oxo complexes, a great deal of research focuses on the chemistry of other metal-ligand multiply-bonded functional groups. Of particular importance are metal-sulfido complexes, which are relevant models for intermediates in hydrodesulfurization and metal-nitrido complexes, possible intermediates in hydrodenitrification and nitrogen fixation. In contrast to the large number of metal-mediated oxygen atom transfer reactions, much less is known about atom-transfer processes of other multiply bonded ligands. For metal sulfide complexes, this may be attributable in part to the lack of terminal sulfide species. On the other hand, a large number of terminal metal nitride compounds are known.

The paucity of nitrogen atom transfer processes may reflect an intrinsic difficulty in matching the trivalency requirement of nitrogen on transfer between a metal complex and substrate. In general, inner-sphere electron transfer mediated by formation of a $\mu$-nitrido

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intermediate typically results in the formation of a derivatized nitrogen compound which is still N-bonded to the metal complex.

Although atom transfer processes are a very common class of reactions, they are not always explicitly recognized or described as such. A large number of these reactions involve atom transfers to and from carbon-based or non-metal substrates. Epoxidations and hydroxylation of organic molecules fall into this category. These oxygen atom transfer reactions, many of which are synthetically useful, have been summarized elsewhere. Analogsulfur-based chemistry also exists as illustrated by sulfur atom transfer from phosphine sulfides to acceptor complexes to form transition metal terminal sulfide complexes. In related chemistry, sulfur atom abstraction by nucleophiles such as phosphines, cyanide, and sulfite have also been documented. In general, few sulfur atom transfer reactions involving the terminal $M=S$ group are known.

Until recently, transfers involving a nitrogen atom were extremely rare. Early examples involved the reaction of terminal transition metal nitride complexes and phosphines. These reactions produced phosphiniminate complexes as shown in eq 1. Such products exemplify the derivatization of nitrogen, as discussed earlier.

$$L_n M = N + PR_3 \rightarrow L_n M = N = PR_3 \quad (1)$$

**II. Definition and Scope**

**A. Atom-Transfer Reactions**

In the manner of Taube, atom-transfer reactions will be defined as processes in which an atom originating on either the oxidizing or reducing agent is transferred to the reaction partner so that in the activated complex both oxidizing and reducing centers are bridged by the atom being transferred. Transfer reactions involving a univalent atom typically mediate a formal one-electron redox process and have been intensively studied. In these cases, much is known about how the nature of the bridging atom affects the rate of electron transfer in inner-sphere reactions. However, when the valency of the transferring atom is greater than one, much less information exists for these types of processes.

**B. Scope**

The focus of this paper is on inner-sphere electron transfer or atom-transfer reactions in which the transferring atom is oxygen, sulfur, selenium, or nitrogen. In addition, emphasis will be placed on reactions between two metal complexes—intermetal atom transfer processes. Accordingly, reactions in which a group 16 element is transferred from a nonmetallic reactant as represented by the sulfur atom abstraction from a thiol by WCl$_4$(PMe$_3$)$_2$ to form an alkane and $S=\text{WCl}_2$(PMe$_3$)$_2$ will not be surveyed. Furthermore, the large body of literature which involves oxygen atom transfer between transition metal complexes and nonmetal reagents will not be covered because this topic was recently and thoroughly reviewed. The growing body of literature on imido transfer involving the $M=NR$ fragment will also not be covered since this involves a group transfer. In addition, atom-transfer reactions which do not involve a net redox process, such as the intermetal pairwise exchange of oxo, imido, and alkyliden ligands reported by Gibson, will not be discussed. These will be considered formally as ligand scrambling processes.

When dealing with intermetal atom transfer reactions, one must make the distinction between complete and incomplete atom transfer processes. Complete atom transfer involves situations in which the transferring atom completely severs all of its bonds with the donor complex and is only bonded to the acceptor species after reaction (eq 2). Incomplete atom transfer will be defined as reactions which yield a bridged species as the final product (eq 3). Note that the terms incomplete and complete do not pertain to the extent of equilibrium but refer to whether or not a stable bridged complex is formed.

In addition to the above qualifications, it is also useful to classify atom-transfer reactions into categories which are metal-based or ligand based. Reactions illustrated by eqs 2 and 3 are metal-centered atom-transfer processes and will be designated as primary atom transfer reactions. Atom-transfer reactions which involve redox at a ligand will be classified as secondary atom transfer processes (see section IV).

An intriguing aspect of complete atom-transfer reactions involves the number of redox equivalents transferred between the oxidant and the reductant. In what might be considered the simplest cases, transfer of a species typically is accompanied by an exchange of a number of electrons which matches the valence of the transferred ligand. Thus, in the classic inner-sphere example of Taube (eq 4), transfer of chlorine is attended by [Cl-Cr(H$_2$O)$_5$]$^{2+}$ and [Cr(H$_2$O)$_6$]Cl$^+$.

$$[(H_2O)_5Cr^+\text{-}Cl]^+ + [Cr(H_2O)_6]^{2+} \rightleftharpoons [(H_2O)_5Cr^+ \text{-} Cl]^{2+} + [Cl-Cr(H_2O)_6]^{2+} \quad (4)$$

by a formal one-electron reduction of Cr$^+$ (III) and a formal one-electron oxidation of Cr(II). However, the valency requirement of the transferring atom does not always dictate the number of redox equivalents involved during the reaction. For example, in the reduction of [Cp$_2$M(IV)X]$^+$ with Cp$_2$M (eq 5, $M=\text{Ru, Os}; X=\text{I, Br}$), transfer of the univalent halogen atom mediates a formal two-electron redox reaction.

$$\text{Cp}_2\text{M(IV)X}}^+ + \text{Cp}_2\text{M(II)} = \text{Cp}_2\text{M(II)} + [\text{Cp}_2\text{M(IV)X}}^+ \quad (5)$$

The fact that atom-transfer reaction can mediate multielectron changes is also a noteworthy aspect. One-electron redox reactions can occur by either an inner-sphere or an outer-sphere mechanism. In contrast, few multielectron reactions, in which all of the electrons are transferred in the same step, occur by an outer-sphere process. Most redox reactions involving a multielectron step seem to be atom-transfer processes.

**III. Oxygen Atom Transfer Reactions**

**A. Incomplete Oxygen Atom Transfer**

As indicated above, early work on atom transfer reactions involved extensive studies of inner-sphere
processes mediated by the transfer of a halogen atom. Use of oxygen in analogous work was primarily limited to discussions involving water as a bridging species. Oxygen atom transfer processes generally involve terminal metal oxo complexes as the oxidant. The terminal oxo ligand is typically found in complexes in which the metal exists in a high formal oxidation state (≥4+) and has four or fewer d electrons. As a result of these restrictions, stable terminal transition metal oxo complexes have been limited to groups 4–8. Furthermore, molecular orbital considerations indicate that strong π-donation from oxygen to metal can lead to metal–oxo triple bond interactions for octahedral d^0 metal complexes and tetrahedral d^4 metal complexes. An increased contribution by the triple bond resonance

\[ \text{O} \equiv \text{M} \equiv \text{O}^* \]

form correspondingly decreases the Lewis basicity of the terminal oxo ligand. Despite potentially low Lewis basicity, the oxo ligand of transition metal complexes can bind to nonmetal and transition metal Lewis acids. For example, treatment of a tetraazoc macrocyclic complex (C_2H_2N_4)TiO with Fe(salen)Cl produces a species containing a Ti–O–Fe linkage. Single-crystal X-ray diffraction studies indicate that the Ti–O distance is 1.701(6) Å and the Fe–O distance is 1.935(6) Å. Comparisons with Ti–O = 1.613(5) – 1.626(7) Å, Ti–O–Ti (1.838 Å), and Fe–O–Fe bond distances suggest that the μ-oxo interaction consists of a Ti=O double bond and an Fe–O single bond, Ti=O–Fe–O. Consequently, no redox change has occurred and the μ-oxo product is formally a Lewis acid–base adduct.

Bridged μ-oxo Lewis acid–base adducts are clearly important intermediates in redox reactions mediated by oxygen atom transfer. When electron transfer does occur, the most common result is a formal net one-electron change attended by formation of a stable μ-oxo product. Since this class of reactions have been reviewed recently, only relevant aspects and new developments will be presented here.

An early example of incomplete oxygen atom transfer germane to metallomacrocyclic chemistry involves the oxidation of simple ferrous hemoporphyrins by dioxygen. This reaction leads to the formation of a thermodynamic product, μ-oxo ferric porphyrin dimers \([\text{POR} \text{Fe} (\text{III}) \text{OFe} (\text{III}) \text{POR}] \) (eq 6).

\[
2 \text{Fe(POR)} + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe(POR)OFe(POR)}
\]  

for the formation of the μ-oxo product which involved formation of a μ-peroxo diiron intermediate. Several years later, evidence in support of this intermediate was reported. Using low-temperature H NMR, La Mar, Balch, and co-workers were able to spectroscopically observe the μ-peroxo bridged species at −80 °C. The μ-peroxo bridge could be homolitically cleaved by the addition of nitrogenous bases such as pyridine or 1-methylimidazole to form a high valent oxoiron porphyrin monomer according to eq 7. Treatment of \([\text{POR} \text{Fe} (\text{III}) \text{OFe} (\text{III}) \text{POR}] \) with an excess of ligated monomeric complexes. For example, exposure of solutions of \([\text{POR} \text{Cr} (\text{III}) \text{OFe} (\text{L}) \) to oxygen results in formation of \([\text{L} \text{FeOFe} (\text{L})] \) and spectroscopic detection of \([\text{POR} \text{Cr} (\text{IV}) \text{OFe} (\text{L})] \).

The equilibrium for reactions such as those shown in eqs 8 and 9 lie far to the right. However, the reversibility of incomplete oxygen atom transfer in these systems is suggested by the subsequent reactivity of the μ-oxo complex. For example, exposure of solutions of \([\text{POR} \text{Cr} (\text{III}) \text{OFe} (\text{L}) \) to oxygen results in formation of \([\text{L} \text{FeOFe} (\text{L})] \) and spectroscopic detection of \([\text{POR} \text{Cr} (\text{IV}) \text{OFe} (\text{L})] \).

The μ-oxo iron dimer presumably forms from the oxidation of \([\text{Fe} (\text{III}) \text{OFe} (\text{III}) \text{POR}] \) (Scheme 1) which was produced by the disproportionation of the initial CrOFe complex (eq 10). Also, nitrogenous bases such as pyridine have been shown to convert \([\text{Fe} (\text{Pc})_2 \text{O}] \) to bisligated monomeric complexes, Fe(Pc)L_2, on the addition of excess base. It is possible that this occurs through an initial disproportionation of the μ-oxo complex.

Reversible, incomplete oxygen atom transfer reactions are well known in molybdenum chemistry. Much of this chemistry involves ancillary ligands such as dithiocarbamates, dialkylphosphinodithiolates, and related chelates. An early example involves the formation of \([\text{Mo}_2 \text{O}_3 (\text{S}_2 \text{CN} (\text{R})_2)_2] \) on treating \([\text{MoO}_2 (\text{S}_2 \text{CN} (\text{R})_2)_2] \) with half an equivalent of triphenylphosphine (eq 11). The initial step of this process invariably involves the

![Scheme I](attachment:image)
2MoO2(S2CNR2)2 + PPh3 → Mo2O5(S2CNR2)4 + O=PPh3 (11)

complete transfer of an oxygen atom from MoO2-(S2CNR2)2 to phosphine (eq 12). The resulting Mo(VI)
MoO2(S2CNR2)2 + PPh3 → MoO(S2CNR2)2 + O=PPh3 (12)

MoO(S2CNR2)2 + MoO2(S2CNR2)2 → Mo2O5(S2CNR2)4 (13)

oxo complex is subsequently trapped by a second Mo(VI) dioxo species to afford the observed μ-oxo product according to eq 13. The equilibrium reaction in eq 13 was independently established by titrating a solution of the mono-oxo Mo(IV) complex with the dioxo Mo(VI) complex. By spectrophotometrically monitoring this titration past the equivalence point, an equilibrium constant K = 4 × 10−3 M was measured for eq 13, at 41 °C. The reversibility of reactions like that shown in eq 13 have been established by electrochemical,45 spectrophotometric,46 and infrared methods.47 Kinetic and thermodynamic measurements have been made on a number of incomplete oxygen atom transfer reactions between Mo(VI) and Mo(IV) complexes.48

In similar processes, oxygen atom transfer from MoO2(acac)2 or MoO2(oxalate)2 to PPh3 produces the μ-oxo binuclear complexes, Mo2O5L4.49 More recently, tris(pyrazolyl)borate complexes of molybdenum have been shown to undergo incomplete intermetal oxygen atom transfer in toluene, eq 14 (X = Cl, Br, NCS, OPh, SPh).50

2[HB(Me2pz)3]MoO2X + PPh3 → Mo2O5X2[HB(Me2pz)3]2 + O=PPh3 (14)

Vanadium-mediated oxygen atom transfer reactions have been established also. Treatment of VCl4(py)4 in acetonitrile with PhIO produces VOCI2(py)4 (eq 15). However, when only 0.5 equiv of PhIO is used, the V(IV) complex is trapped with a second molecule of VCl4(py)4 to form a μ-oxo complex (eq 16). Because of the slow decomposition of V2OCl4(py)4 in acetonitrile, it was not possible to determine whether or not eq 16 was reversible. Nonetheless, a single-crystal X-ray diffraction study establishes a linear V(III)–O–V(III) bridge for the binuclear product.51 The reaction of Cp*Cr(O)(CH2)3 with Cp*Cr(CN)3py reportedly produces the μ-oxo complex, Cp*Cr(CN)3CrO-Cr(CN)3Cp* (eq 17). However, the μ-oxo product has been characterized only by spectroscopic methods. Thus, this reaction tentatively can be assigned as an example of incomplete oxygen atom transfer.

**B. Complete Oxygen Atom Transfer—One-Electron Processes**

Complete intermetal oxygen atom transfer reactions are much less common in comparison to the incomplete transfer reactions described above. A small subset of complete oxygen atom transfer reactions is known to mediate net one-electron redox processes. Furthermore, all of the reactions in this subset formally involve the pairwise exchange of oxygen and chlorine atoms. A typical example is illustrated in eq 17. In this case the dioxo Mo(VI) complex is reduced to Mo(V) by loss of an oxygen atom and gain of a chlorine atom.53 Two mechanisms are possible for the O/Cl exchange. Initial oxygen atom transfer could produce OMo(acac)2 and OMoCl2(acac)2 as shown in eq 18. A subsequent chlorine atom transfer produces the observed product (eq 19). Support for this mechanism is derived from the observed chlorine atom transfer from OMoCl2-(S2CNR2)2 to OMo(S2CNR2)2 to form OMoCl2(S2CNR2)2.54 However, an equally likely mechanism is a concerted atom transfer involving a doubly bridged intermediate Mo(μ-O)(μ-Cl)Mo. The discussion in section III.C provides additional examples in which a double bridge alternative is likely.

Heterometallic O/Cl exchange has also been used as a preparative method. When VO(acac)2 is treated with TiCl3(THF)3 in refluxing THF, good yields of VCl(acac)2 can be obtained as shown in eq 20.55 This reaction formally involves a reductive deoxygenation of O=V(IV). When the reaction is carried out at lower temperatures, a μ-oxo bridged complex, Cl(acac)-V(IV)OTi(IV)Cl3(THF)3 could be isolated in 23% yield and was structurally characterized by single-crystal X-ray diffraction. On the basis of the isolation of the μ-oxo species, Scheme II was suggested as a plausible mechanism for the O/Cl exchange in reaction 20.
Table I. Half-Wave Reduction Potentials for Chromium Porphyrin Complexes

<table>
<thead>
<tr>
<th>couple</th>
<th>( E^\circ ) (V)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr}^{III} \text{(TPP)}]^{+}/\text{Cr}^{III} \text{(TPP)}^b )</td>
<td>-1.06</td>
<td>60</td>
</tr>
<tr>
<td>([\text{K(TPP)} \text{Cr}^{IV} \text{Cl}]^{+}/\text{K(TPP)} \text{Cr}^{IV} \text{Cl}^b )</td>
<td>0.80</td>
<td>61</td>
</tr>
<tr>
<td>((\text{TPP}) \text{Cr}^{IV} \text{O}/(\text{TPP}) \text{Cr}^{III} \text{O})^b )</td>
<td>-1.12</td>
<td>61</td>
</tr>
</tbody>
</table>

* a Versus SCE. b Metal oxidation states are listed for electron counting purposes only. These redox processes may not be metal centered.

Intermetal O/Cl exchange also has been demonstrated for V(III)/V(V) complexes. The reaction between \([\text{VO}_2\text{Cl}]^2^- \) and \([\text{VCl}_4(\text{MeCN})_2]^2^- \) proceeds immediately to yield a V(IV) product (eq 21). The reaction is presumed to involve formation of a \( \mu\)-oxo bridged intermediate, \([\text{Cl}_2\text{V}(\text{O})\text{VCl}_4]^2^- \) which dissociates on electron transfer.

Metalloporphyrin complexes have been well-known to undergo intermetal halogen atom transfer reactions. \( ^{56} \) However, their use in intermetal oxygen atom transfer was not reported until recently. \( ^{57} \) Although isolable metalloporphyrin oxo complexes are known for a variety of metals, only titanium and chromium species have been examined (eqs 22 and 23). These reactions formally involve a net one-electron transfer mediated by O/Cl exchange. However, unlike the previous O/Cl exchange processes discussed in this section, eqs 22 and 23 are reversible. The equilibrium constants for the titanium reaction is 2.4 \( \pm \) 0.5 and that for the chromium reaction is 3.1 \( \pm \) 0.1. Thus the differences between the porphyrin ligands are sufficiently small such that eqs 22 and 23 can be considered as pseudoself-exchange processes. Consequently, rates for these processes serve as a measure of the intrinsic tendency to undergo reaction without complications arising from a thermodynamic driving force.

The chromium O/Cl exchange has been thoroughly studied. \( ^{58} \) The thermodynamic parameters for eq 23 are \( \Delta H^\circ = -2.0 \pm 0.4 \text{ kcal/mol} \) and \( \Delta S^\circ = -4.6 \pm 1.2 \text{ cal/(mol K)} \). The rate constant for oxygen atom transfer from \((\text{TPP})\text{Cr}=\text{O} \) to \((\text{OEP})\text{Cr}=\text{O} \) is 0.14 \( \pm \) 0.01 M\(^{-1}\) s\(^{-1}\) at 30 °C with activation parameters of \( \Delta H^\ddagger = 15.4 \pm 0.7 \text{ kcal/mol} \) and \( \Delta S^\ddagger = -12 \pm 2 \text{ cal/(mol K)} \).

The electrochemical data listed in Table I indicate that chlorochromium(III) porphyrin is not capable thermodynamically of reducing the oxochromium(IV) complex in an outer-sphere pathway. Thus, eq 23 must proceed by an inner-sphere process. An atom-transfer pathway in this system is complicated mechanistically by the presence of two good bridging ligands, chloride and oxide. However, mechanistic studies using a pyrromellitoyl capped porphyrin, \( ^{59} \) or a bulky univalent axis ligand, pivalate, in place of chloride rule out \( \mu\)-Cl bridged intermediates such as A and B. Furthermore, when chlorochromium(III) porphyrins are used as the reductant, the O/Cl exchange is inhibited by excess chloride ion. This strongly supports a mechanism which involves a pre-equilibrium chloride dissociation step (Scheme III). Oxygen atom transfer subsequently occurs between \((\text{POR})\text{Cr}=\text{O} \) and \((\text{POR})\text{Cr(III)}^\ddagger \), presumably through a \( \mu\)-oxo-bridged intermediate. Thus, in this particular type of reaction, the oxo ligand is preferred over chloride as the bridging species.

In reactions 8 and 23 is important to note. Clearly, the reduction products of oxochromium porphyrins are strongly dependent on the reducing agent. When a Cr(II) porphyrin is the reductant, incomplete oxygen atom transfer occurs, yielding a \( \mu\)-oxo product. However, chromium(III) porphyrins result in reversible oxygen atom transfer. Because the \( \mu\)-oxo complex, \((\text{TPP})\text{Cr}=\text{O} \)–Cr(TPP) can be isolated, this difference cannot be due to steric effects.

A significant factor appears to involve the reduction potentials of the two reducing agents (Table I). The chromium(II) complex, \((\text{TPP})\text{Cr} \) is a much stronger one-electron reducing agent than \((\text{TPP})\text{Cr}=\text{Cl} \) by more than 1 V. Thus in the inner-sphere precursor complex, \([\text{Cr}^{IV}-\text{O} \cdot \text{Cr}^{II}]^\ddagger \) is a strong driving force exists for single electron transfer to occur to form the \( \mu\)-oxo Cr(III) dimer. In order for complete oxygen atom transfer to occur, a second electron must transfer to form the successor complex, \([\text{Cr}^{II} \cdot \text{O} \cdot \text{Cr}^{IV}]^\ddagger \). However this second electron transfer is thermodynamically uphill. Consequently, the \( \mu\)-oxo Cr(III) dimer is stable with respect to disproportionation to the O=Cr(IV) and Cr(II) complexes.

In the O=Cr(IV)/ClCr(III) reaction (eq 23), kinetic and mechanistic evidence are consistent with a pathway which involves a \( \mu\)-oxo intermediate, \([\text{Cr}^{IV} \cdot \text{OCr}^{II}]^\ddagger \). Single electron transfer within the activated \( \mu\)-oxo complex always produces one metal in a +IV oxidation state. The instability of this intermediate with respect to formation of mononuclear chromium species may reflect an inherent tendency for the Cr(IV) center \( (d^2) \) and the oxo ligand to form a strong metal–oxygen double bond rather than for the oxo ligand to form two M–O single bonds. A key difference between the stability of the \( \mu\)-oxo species, \([\text{Cr}^{III} \cdot \text{OCr}^{II}]^\ddagger \) and \([\text{Cr}^{IV} \cdot \text{OCr}^{II}]^\ddagger \), solely may be a matter of oxidation state. In order to form O=Cr(IV), the III–III complex must disproportionate while the IV–III complex simply dissociates.

An alternative explanation for the variation in the oxygen atom transfer chemistry of chromium porphyrins involves an examination of the electronic structure of \( \mu\)-oxo metalloporphyrin dimers. Such d-orbital energy level scheme for \([\text{Fe(TPP)}]_2 \text{O}\) has been calculated by Tatsami and Hoffmann using extended Hückel methods (Figure 1). \( ^{62} \) To a first approximation, this MO diagram should apply to \( \mu\)-oxo chromium complexes. The magnetic moment of 1.61 \( \mu_B \) for Cr atom in \([\text{Cr(TPP)}]_2 \text{O}]^\ddagger \) is consistent with an \( S = 2 \) electronic state arising from an \( (e_g)^4(e_g)^1 \) configuration. However in the \( d^1 \)-\( \mu\)-oxo intermediate, \([\text{Cr}^{IV} \cdot \text{OCr}^{II}]^\ddagger \), formed in the Cr(III) reduction of \((\text{POR})\text{Cr}=\text{O} \), the electronic configuration can be either \( (e_g)^4(e_g)^1 \) (low spin) or
C. Complete Oxygen Atom Transfer—Two-Electron Processes

It was not until 1976 that the first documented case of intermetal oxygen atom transfer was reported. This involved the complete transfer of oxygen between Mo(VI) and Mo(II) complexes (eq 24).64 This formally

\[
\text{MoO}_2\text{(S}_2\text{CNR}_2)_2 + \text{Mo}(\text{CO})_2\text{(S}_2\text{CNR}_2)_2 \rightarrow 2\text{O} = \text{Mo}(\text{S}_2\text{CNR}_2)_2 + 2\text{CO} \quad (24)
\]

represents a two-electron redox reaction between M(VI) and M(II) mediated by oxygen atom transfer as schematically represented by eq 25. This type of

\[
\text{M}^{\text{VI}}\text{O}_2 + \text{M}^{\text{II}} \rightarrow 2\text{M}^{\text{IV}}\text{O} \quad (25)
\]

reaction has been utilized in a synthetically useful manner to prepare the first examples of oxotungsten(VI)—acycylene complexes (eq 26).55 The acetylene

\[
\text{W(CO)}(\text{R'}\equiv\text{CR'}\equiv\text{CR'}\equiv\text{S}_2\text{CNR}_2)_2 + \\
\text{Mo}_2\text{O}_3[\text{S}_2\text{P(OEt)}_2]_4 \rightarrow \text{OW(CR'\equiv\text{CR'}\equiv\text{CR'}\equiv\text{S}_2\text{CNR}_2)_2} + \\
2\text{MO}[\text{S}_2\text{P(OEt)}_2]_2 + \text{CO} \quad (26)
\]

ligands used in this reaction were HC\equiv\text{CH}, \text{PhC} \equiv \text{CH}, and \text{MeC}_2\text{H}_2\text{C(O)C} \equiv \text{CC(O)C}_2\text{H}_4\text{Me}. Presumably, the actual oxygen donor source is the putative Mo(VI) complex, \text{MoO}[\text{S}_2\text{P(OEt)}_2]_2, which forms from the dissociation of \text{MoO}[\text{S}_2\text{P(OEt)}_2]_2, illustrated in eq 27.66

\[
\text{Mo}_2\text{O}_3[\text{S}_2\text{P(OEt)}_2]_4 \rightarrow \\
\text{O} = \text{Mo}[\text{S}_2\text{P(OEt)}_2]_2 + \text{MoO}[\text{S}_2\text{P(OEt)}_2]_2 \quad (27)
\]

Most recently, the oxygen atom transfer, reaction 25, was used to prepare bis(diphenylthiophosphinato)molybdenum complexes.67

\[
\text{Mo}(\text{CO})_5[\text{S}_2\text{P(Ph)}_2]_2 + \text{MoO}_2[\text{S}_2\text{P(Ph)}_2]_2 \rightarrow \\
2\text{MoO}[\text{S}_2\text{P(Ph)}_2]_2 + 3\text{CO} \quad (28)
\]

In contrast to the above reactions, oxygen atom transfer to \text{W(CO)}_2(\text{PPh}_3)_2(\text{S}_2\text{CNR}_2)_2 does not produce a \text{W(IV)} complex but instead results in complete oxidation to \text{W(VI)}. When 2 equiv of \text{MoO}_3[\text{S}_2\text{P(OEt)}_2]_4 are used to oxidize \text{W(CO)}_2(\text{PPh}_3)_2(\text{S}_2\text{CNR}_2)_2, formation of a dioxotungsten complex occurs according to eq 29. When an equimolar amount of

\[
\text{W(CO)}_2(\text{PPh}_3)_2(\text{S}_2\text{CNR}_2)_2 + 2\text{MoO}_3[\text{S}_2\text{P(OEt)}_2]_4 \rightarrow \\
\text{WO}_2(\text{S}_2\text{CNR}_2)_2 + 2\text{MoO}[\text{S}_2\text{P(OEt)}_2]_3 + \\
2\text{CO} + \text{PPh}_3 \quad (29)
\]

\[
\text{MoO}_3[\text{S}_2\text{P(OEt)}_2]_4 \text{ is used, the reaction produced only half an equivalent of \text{WO}_2(\text{S}_2\text{CNR}_2)_2 and the remaining \text{W(II)} starting material was unchanged. Thus, if reaction 29 proceeds through \text{WO}_2(\text{S}_2\text{CNR}_2)_2, this \text{W(IV)} intermediate must undergo a second oxygen atom transfer step faster than does the \text{W(II)} starting material.}
\]

A comprehensive examination of complete intermetal oxygen atom transfer chemistry has been reported by Holm for Mo(IV) and Mo(VI) complexes.68 The most common reaction between Mo(VI) and Mo(IV) complexes is the formation of a \mu-oxy-Mo(V) dimer product (eq 30) when the ligand environment involves dithiocarbamate and related chelate systems (see section III.A). However, when the molybdenum center is encumbered by a sterically demanding ligand coordination sphere, complete oxygen atom transfer between Mo(VI) and Mo(IV) (eq 31) can be observed. The types

\[
\text{Mo}_n\text{O}_2 + *\text{Mo}^{\text{IV}}\text{O} \rightarrow \text{Mo}_n\text{O}_2 + *\text{Mo}^{\text{V}}\text{O}_2 \quad (31)
\]

of ligands used in these reactions were dithiocarbamates and the tridentate chelates, 2,3-bis(2,2-diphenyl-2-sulfidoethyl)pyridinate (L-\text{NS}_2)\text{S}_2, 2-(\text{salicylideneamino})phenolate (\text{sap})\text{S}_2, and 2-(\text{salicylideneamino})benzenethiolate (\text{ssp})\text{S}_2 shown in Figure 2. Representative reactions are illustrated by eqs 32–35. These reactions

\[
\text{L}_n\text{MoO} + \text{Mo}_n\text{O}_2(\text{S}_2\text{CNR}_2)_2 \rightarrow \\
\text{L}_n\text{MoO}_2 + \text{MO}(\text{S}_2\text{CNR}_2)_2 \quad (32)
\]

\[
\text{sapM}_n\text{O} + (\text{sap})\text{MoO}_2 \rightarrow \\
\text{sapM}_n\text{O} + (\text{ssp})\text{MoO} \quad (33)
\]

\[
\text{sapM}_n\text{O} + \text{Mo}_n\text{O}_2(\text{S}_2\text{CNR}_2)_2 \rightarrow \\
(\text{ssp})\text{MoO}_2 + \text{MO}(\text{S}_2\text{CNR}_2)_2 \quad (34)
\]

\[
(\text{ssp})\text{MoO} + (\text{L}_n)\text{MoO}_2 = \\
(\text{ssp})\text{MoO}_2 + (\text{L}_n)\text{MoO} \quad (35)
\]

are spontaneous and allow the development of a relative thermodynamic scale for oxygen atom transfer. Reactions 32–35 proceed quantitatively while reaction 35
Intermetal Atom Transfer Reactions

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Figure 1. The building up of the orbitals of [(NH2-)4Fe-O-Fe(NH2-)4],4-: (from left to right) the orbitals of the pyramidal N4Fe unit with Fe 0.5 Å out of the N4 plane; two N4Fe fragments with a 3.526 Å Fe-Fe separation; orbitals of the composite μ-oxo complex (from ref 62).

Figure 2. Ligand systems used for Mo(VI)/Mo(IV) intermetal oxygen atom transfer reactions.

is a reversible process with an equilibrium constant of approximately 30. Thus the reducing power or oxygen atom acceptor capability of the molybdenum(IV) complexes decrease in the order MoO(sap) > MoO(ssp) > MoO(L-NS2) > MoO(S2CNR2). Conversely, the oxidizing strength or oxygen atom donor capability of the Mo(VI) complexes falls in the order MoO2(S2CNR2) > MoO2(L-NS2) > MoO2(ssp) > MoO2(sap). These thermodynamic trends parallel the activation enthalpies for the ligand environments S4 > N2S2 > ONS ≫ O,N in the reduction of Mo(VI) complexes by phosphines.69 This indicates that the activation barrier for oxygen atom transfer by molybdenum complexes is dictated to a large degree by factors which stabilize or destabilize the IV and VI oxidation states.

Complete oxygen atom transfer reactions have been reported recently for an isoelectronic (d2) series of octahedral metal oxo complexes of Re(V), W(IV), and Mo(IV).70 When dichloro metal phosphine complexes are used as reducing agents, a variety of atom transfer products are observed (reactions 36–38, L = PMePh2).

Re(O)Cl3L2 + WC12L4 → ReCl3L3 + W(O)Cl2L3 + WCl3L2 + W(O)Cl3L2 (36)
Re(O)Cl3L2 + MoCl2L4 → ReCl3L3 + Mo(O)Cl2L2 + MoCl3L3 (37)
Mo(O)Cl2L3 + WC12L4 → W(O)Cl2L3 + WCl3L2 + W(O)Cl3L2 (38)

In all cases, the products of complete two-electron oxygen atom transfer are observed. This is evident in the conversion of the d4 MoCl2L3 reductants to the d2 M(O)Cl2L3 complexes. Moreover, reactions 39–41, W(O)Cl3L3 + ReCl3L3 → NR (39)
Mo(O)Cl2L3 + ReCl3L3 → NR (40)
W(O)Cl2L3 + MoCl3L3 → NR (41)

which are formally the reverse oxygen atom transfer processes of reactions 36–38, do not proceed to any measurable extent. Thus, reactions 36–38 are irreversible processes.71

In addition to complete oxygen atom transfer, chlorine atom transfer occurs to produce secondary products. For example, in reaction 36 involving Re(O)Cl3L2 and WC12L4, WCl3L3 is produced by chlorine atom transfer and W(O)Cl3L2 is formed by both oxygen and chlorine atom transfer. The latter represents a net three-electron oxidation of WC12L4.
MCl₃L₃ complexes that appear as secondary products also act as oxygen or chlorine atom acceptors as was demonstrated by reactions 42–45. As in the
\[
\text{Re(O)Cl₃L₂ + WCl₃L₃ → ReCl₅L₃ + W(O)Cl₃L₂ + WCl₄L₂ + W(O)Cl₂L₃}
\]
above reaction using M(II) reductants, reactions 42–45 show the same relative thermodynamic trend in the direction of oxygen atom transfer: Re → Mo → W. This indicates that the M═O bond strengths for these chlorophosphine complexes decrease in the order W > Mo > Re.

Reactions 36–38 and 42–45 illustrate that oxygen atom transfer and chlorine atom transfer are competitive pathways. In addition, O/Cl exchange also occur in reactions 42–45. The complexity and the product distributions observed in these atom transfer reactions can be explained by a mechanism involving doubly bridged intermediates (Scheme IV).

The manner in which the bridging interactions form and cleave to complete oxygen atom transfer, O/Cl exchange, or chlorine atom transfer. Stable analogs of the proposed doubly bridged intermediate have been isolated with trimethylphosphine ligands (eq 46). The Mo₂(Cl)₂(S) derivative has been characterized structurally by single-crystal X-ray diffraction. 72

\[
2\text{MoCl₃(PMe₃)₄ + SPMe₃ → Mo₂(Cl)(S)(PMe₃)₄ + 4PMMe₃}
\]

An unusual example of oxygen atom transfer is shown in eq 47. 73 In this case, a formal net four-electron reduct
\[
[(5-Cl-salen)MnIV(μ-O)]²⁺ + 4(salen)FeIII⁺ → 2(5-Cl-salen)MnIVII + 2(salen)FeIII(μ-O)]²⁺
\]
process mediated by the transfer of two oxygen atoms has occurred. This reaction has an estimated half-life of less than 5 s. Cyclic voltammetric monitoring of reaction 47 provided no evidence for the dissociation of [(5-Cl-salen)MnIV(μ-O)]²⁺ into monomeric terminal oxo complexes. This suggests that the oxo transfer in reaction 47 may proceed through a triple bridging oxo ligand, μ₂-O, such as in a Mn₃Fe₂(μ₂-O)₂ core. Analogous tetranuclear Mn₄(μ₂-O)₂ complexes have been prepared. 74

IV. Secondary O, S, or Se Atom Transfer Reactions

The preparation of new Ti(II) porphyrin complexes has led to additional developments in atom transfer chemistry. For example, [(TPP)Ti(η²-PhC=CP)]⁷⁵ is a powerful atom transfer acceptor. Thus, when (OEP)Ti(η²-0₂)⁷⁶ is treated with [(TPP)Ti(η²-PhC=CP)] quantitatively formation of (OEP)Ti═O and (TPP)Ti═O results as illustrated in eq 48. ⁷⁷ This reaction formally

\[
(OEP)Ti(η²-0₂) + (TPP)Ti(PhC=CP) → (OEP)Ti═O + (TPP)Ti═O + PhC=CP
\]

In a similar manner, the persulfido and perselenido complexes, (OEP)Ti(S₂) and (OEP)Ti(Se₂) undergo atom transfer processes (eqs 50 and 51). These reactions

\[
(OEP)Ti(S₂) + (TPP)Ti(PhC=CP) → (OEP)Ti═S + (TPP)Ti═S + PhC=CP
\]

\[
(OEP)Ti(Se₂) + (TPP)Ti(PhC=CP) → (OEP)Ti═Se + (TPP)Ti═Se + PhC=CP
\]

represent some of the few known intermetal atom transfer reactions of the heavier group 16 elements. Moreover, reactions 48, 50, and 51 should allow a systematic comparison of group 16 atom transfer processes.

Other known intermetal sulfur or selenium transfer reactions involve the use of Cp₂TiS₅ and Cp₂TiSe₅ as transfer reagents. In general, these deliver S₂ or Se₂ fragments as shown in eqs 52–55. ⁷⁸ The exception is reaction 56 in which a single selenium atom is transferred from Cp₂TiSe₅ to a vanadium(II) complex. ⁷⁹

\[
[\text{Ir(dppe)}₂Cl + \text{Cp₂TiSe₅} → [\text{Ir(dppe)}₂Se₂]Cl²⁻ + \text{Cp₂TiSe₅}
\]

\[
[\text{Ir(dppe)}₂Cl + \text{Cp₂TiSe₅} → [\text{Ir(dppe)}₂Se₂]Cl²⁻ + \text{Cp₂TiSe₅}
\]

(V. Nitrogen Atom Transfer Reactions

A. Three-Electron Processes

Although the bonding in terminal metal nitrides (M≡N) is formally analogous to the triple bond
resonance form in metal oxo complexes (M=O), the related intermetal nitrogen atom transfer reaction was not discovered until 1985. The first example of this reaction, reported by Takahashi, involved the reduction of N=Mn(V)(TTP) with Cr(III)(TTP) in THF. The resulting reaction quantitatively formed nitridochromium(V) as represented in eq 57. The nitridomanganese(V) complex is formally reduced to manganese(II) upon transfer of the nitrogen ligand to chromium. Thus, complete nitrogen atom transfer formally mediates a three-electron redox process. This was clearly a new advance in the area of inner-sphere electron transfer.

Reversible, three-electron nitrogen atom transfer reactions have also been reported for manganese porphyrin complexes (eq 58). The equilibrium constant for this reaction in toluene is 

\[(\text{TTP})\text{Mn} \rightleftharpoons \text{N} + \text{Cr}(\text{TTP}) \]

and the bond lengths listed for manganese porphyrins indicate that the inner sphere reorganization energies are likely to be small for reaction 58. The Mn-\text{pyrrole} distances differ only by 0.07 Å in the +V and +II oxidation states. The largest change is a decrease in the displacement of the manganese ion out of the porphyrin plane by 0.11 Å on loss of the axial nitrogen. Thus, nitrogen atom transfer between manganese porphyrins involves an economy of motion as the nitrogen ligand migrates from Mn(V) to Mn(II) without involving any other significant nuclear motions. Consequently, porphyrin macrocycles seem to be ideal ancillary ligands for promoting facile multielectron atom transfer processes.

### B. Two-Electron Processes

In addition to formal three-electron redox processes, nitrogen atom transfer can also mediate net two electron redox reactions. This is readily accomplished by using a trivalent metalloporphyrin reductant in place of the M(II) reducing agent. For example, when (OEP)Mn=\text{N} is treated with (TTP)MnCl, a formal two-electron transfer occurs which is attended by a reversible, double exchange of axial ligands as shown in eq 59.

\[(\text{OEP})\text{Mn} \rightleftharpoons \text{N} + \text{Mn}(\text{OEP}) \]


deters in Table III provide a rationale for this phenomenon. The bond lengths listed for manganese porphyrins indicate that the inner sphere reorganization energies are likely to be small for reaction 58. The Mn-\text{pyrrole} distances differ only by 0.07 Å in the +V and +II oxidation states. The largest change is a decrease in the displacement of the manganese ion out of the porphyrin plane by 0.11 Å on loss of the axial nitrogen. Thus, nitrogen atom transfer between manganese porphyrins involves an economy of motion as the nitrogen ligand migrates from Mn(V) to Mn(II) without involving any other significant nuclear motions. Consequently, porphyrin macrocycles seem to be ideal ancillary ligands for promoting facile multielectron atom transfer processes.
ligand on the M(III) reductant. The cationic square planar M(III) species undergoes nitrogen atom transfer with the nitrido oxidant via a \( \mu \)-nitrido bridged intermediate. This mechanism is analogous to that for the O/Cl exchange shown in Scheme III. A comparison of thermodynamic and kinetic parameters for the two-electron nitrogen atom transfer reactions is given in Table IV.

Bottomley and Neely have examined the effect of porphyrin substituents on the rate of nitrogen atom transfer from manganese to chromium (reaction 61). Electronic factors were studied by changing substituents at the para position of meso-tetraphenylporphyrins, T-2,6-(MeO)PP

The generality of nitrogen atom transfer has also been extended to other macrocyclic complexes. For example, treatment of \( \text{N}==\text{Mn} \text{(OEP)} \) with ClM(salen), where M = Cr or Mn, results in the formation of the Cr(V) or Mn(V) nitrido complexes with the salen ligand. Formation of a nitridomanganese tetraazamacrocycle

<table>
<thead>
<tr>
<th>reaction</th>
<th>solvent</th>
<th>dielectric constant</th>
<th>( T (°C) )</th>
<th>( K_{eq} )</th>
<th>( k_f ) (M(^{-1}) s(^{-1}))</th>
<th>ref</th>
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<tr>
<td>59</td>
<td>CDCl(_3)</td>
<td>4.79</td>
<td>22</td>
<td>23.5 ± 3.6</td>
<td>0.010 ± 0.007</td>
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<td>30</td>
<td>17.5</td>
<td>0.025 ± 0.001</td>
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<td></td>
<td></td>
<td></td>
<td>40</td>
<td>12.2 ± 1.5</td>
<td>0.061 ± 0.006</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>8.7 ± 1.5</td>
<td>0.150 ± 0.012</td>
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</tr>
<tr>
<td>THF</td>
<td></td>
<td>7.3</td>
<td>50</td>
<td>0.98</td>
<td>0.10 ± 0.02</td>
<td>90</td>
</tr>
<tr>
<td>CH(_2)NHC(O)H</td>
<td>182</td>
<td></td>
<td>50</td>
<td>20 ± 2</td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>60</td>
<td>benzene</td>
<td>2.27</td>
<td>23</td>
<td>1.4 ± 0.2</td>
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<td>91</td>
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<td></td>
<td></td>
<td></td>
<td>23</td>
<td>1.1 ± 1</td>
<td>440</td>
<td></td>
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<tr>
<td>61</td>
<td>benzene</td>
<td>2.27</td>
<td>25</td>
<td>irreversible</td>
<td>48 ± 5</td>
<td>92</td>
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<td>25</td>
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<td>86 ± 5</td>
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<td>irreversible</td>
<td>200 ± 17</td>
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<td>25</td>
<td>irreversible</td>
<td>350 ± 20</td>
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<td>25</td>
<td>irreversible</td>
<td>1170 ± 140</td>
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Table IV. Thermodynamic and Kinetic Comparison of N/Cl Exchange Reactions

Table V. Thermodynamic Limits for the Reaction \( \text{L}_2\text{M} + \frac{1}{2}\text{O}_2 \rightarrow \text{L}_2\text{M}=\text{O} \) in Nonaqueous Media

\[
\Delta H (\text{kcal/mol})
\]

\[
\begin{array}{llll}
\text{Cr(POR)Cl/O} & \text{Cr(POR)Cl} & \pm 15 \\
\text{Mn(POR)Cl/O} & \text{Mn(POR)Cl} & \pm 25 \\
\text{[Cr(Salen)](H}_2\text{O)} & [\text{Cr(Salen)](\text{H}_2\text{O)} & \pm 15 \\
\text{Fe(POR)Cl/O} & \text{Fe(POR)Cl} & \pm 25 \\
\text{Mn(O)(S}_2\text{CR}_2\text{N)} & \text{Mn(O)(S}_2\text{CR}_2\text{N)} & \pm 35 \\
\text{MoO(L=NS}_2\text{)(DFM)/MoO}_2\text{(L=NS}_2)(\text{DFM)} & \pm 35 \\
\text{Cr(POR)O} & \text{Cr(POR)} & \pm 67 \\
\text{Mn(POR)O} & \text{Mn(POR)} & \pm 35 \\
\text{Fe(POR)O} & \text{Fe(POR)} & \pm 35 \\
\text{MoO(POR)/MoO}_2(\text{POR)} & \pm 35 \\
\text{MoO}_2(\text{DFM)/MoO}_2(\text{DFM)} & \pm 35 \\
\end{array}
\]

can be accomplished in a similar manner. Thus, nitrogen atom transfer can be used in a preparative manner.

**VI. Summary**

Although atom transfer reactions have been known for over 40 years, an understanding of intermetal oxygen atom transfer processes still remains underdeveloped. Furthermore, atom transfer reactions involving other multiply bonded elements, \( \text{M}==\text{S}, \text{M}==\text{Se}, \text{or M}==\text{N} \) have been reported only recently. Nonetheless, important aspects of these fundamental reactions are emerging. The oxygen atom transfer processes shown in reactions 32-45 allow metal complexes to be ranked in order of their reactivity toward atom transfer. It is apparent that these reactions are driven in part by \( \text{M}=\text{O} \) bond strengths. The metalloporphyrin-based reactions also indicate that electronic factors such as oxidation state and d-electron configurations have a significant role in the type of atom transfer reactions that take place. A more systematic approach in terms of developing a thermodynamic scale for oxygen atom transfer reactions has been summarized by Holm. In this approach, a thermodynamic oxygen atom transfer "half-reaction" is used (eq 62). Representative enthalpies

\[
\frac{1}{2}\text{O}_2 + \text{X} \rightarrow \text{XO}
\]
and much more work remains to be done. A similar thermodynamic scale for nitrogen atom transfer has not been developed yet. At this point, a severe limitation is the lack of complete nitrogen atom transfer examples. Furthermore, the only known cases involve transfer between two metal complexes.

Reactions 36–45 illustrate another significant consideration. In these examples, the chloro and oxo functional groups, which are present in the metal complexes, are both capable of serving as reaction sites and in fact do result in competitive chlorine atom and oxygen atom transfer. This demonstrates the complications in transition metal chemistry arising from relatively polar, weak metal-ligand bonds. However, when a less reactive supporting ligand system is used, such as porphyrins or other macrocycles, regioselective reactions of functional groups can be achieved in transition metal complexes. Furthermore, these types of ligands have allowed the extension of inner-sphere redox processes to intermetal sulfur and selenium atom transfer reactions.

VII. Acknowledgment

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Abbreviations

acac acetylacetonato(1–)
acacen N,N′-ethylenbis(acetylacetonate iminate)(2–)
5-Cl-salen 1,2-bis[(5-chlorosalicylidene)aminato]ethane(2–)
Cp cyclopentadienyl
Cp* pentamethylcyclopentadienyl
DMF dimethylformamide
HB(Me$_2$P)$_3$ tris(3,5-dimethylpyrazolyl)borate(1–)
L general ligand, monodentate or chelating
2,6-bis(2,2-diphenyl-2-sulfdioethyl)-pyridinate(2–)
OEP octaethylporphyrinato(2–)
POR general porphyrinato dianion
py pyridine
salen 1,2-bis(salicilideneamino)ethane(2–)
sap 2-(salicylideneamino)phenolate(2–)
SCE saturated calomel electrode
S$_2$CN$_2$ dithiocarbamate(1–); R generally is an alkyl group
ssp 2-(salicylideneamino)benzenethiolato(2–)
THF tetrahydrofuran
TMeP meso-tetrakis(4-methoxyphenyl)-porphyrinato(2–)
TPP meso-tetrathiaporphyrinato(2–)
TTP meso-tetrakis(4-tolyl)porphyrinato(2–)

VIII. References


(6) The terms inner sphere and atom transfer will be used interchangeably.


(9) (a) The terms intermetal and atom transfer will be used interchangeably.