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

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Contents

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.[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.

The unambiguous demonstration of atom-transfer reactions[4] was a major advance in the development and understanding of electron transfer between metal complexes.[5] The elucidation of two classes of electron transfer—inner sphere[6] 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.[2] 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.[7] 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).[8] 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.[9] Furthermore, a great deal of effort has centered on using metal–oxo complexes as selective oxidants in industrial processes and laboratory practices.[10] A recent comprehensive review discusses the range of metal complexes and substrates that have been studied.[11]

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In addition to metal oxo complexes, a great deal of research focuses on the chemistry of other metal–ligand multiply-bonded functional groups.[12] Of particular importance are metal–sulfido complexes, $\mathrm{L}_n\mathrm{M}{=}\mathrm{S}$, which are relevant models for intermediates in hydrodesulfurization[13] and metal–nitrido complexes, possible intermediates in hydrodenitrification and nitrogen fixation.[14] 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, $\mathrm{L}_n\mathrm{M}{=}\mathrm{S}$, this may be attributable in part to the lack of terminal sulfide species.[15] On the other hand, a large number of terminal metal nitride compounds are known.[12,16] 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 μ-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.[17]

Analogous sulfur-based chemistry also exists as illustrated by sulfur atom transfer from phosphine sulfides to acceptor complexes to form transition metal terminal sulfide complexes.[18] In related chemistry, sulfur atom abstraction by nucleophiles such as phosphines, cyanide, and sulfite have also been documented.[19] 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.[20] These reactions produced phosphiniminato complexes as shown in eq 1. Such products exemplify the derivatization of nitrogen, as discussed earlier.

$$L_nM\equiv N + PR_3 \rightarrow L_nM{-}N{=}PR_3 \quad (1)$$

II. Definition and Scope

A. Atom-Transfer Reactions

In the manner of Taube,[21] 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.[22] 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 $WCl_2(PMePh_2)_4$ to form an alkane and $S{=}WCl_2(PMePh_2)$[23] 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.[11b] The growing body of literature on imido transfer[12b,24] 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 alkylidene ligands reported by Gibson, will not be discussed.[25] 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.[11b] 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

$$L_nM{-}X + M'L_n \rightleftarrows L_nM + X{-}M'L_n \quad (2)$$

will be defined as reactions which yield a bridged species as the final product (eq 3). Note that the terms

$$L_nM{-}X + M'L_n \rightarrow L_nM{-}X{-}M'L_n \quad (3)$$

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.[11b] 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

$$[(H_2O)_5Cr^*{-}Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightleftarrows [(H_2O)_6Cr^*]^{2+} + [Cl{-}Cr(H_2O)_5]^{2+} \quad (4)$$

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 $[Cp_2M(IV)X]^+$ with Cp_2M (eq 5, M = Ru, Os; X = I, Br), transfer of the univalent halogen atom mediates a formal two-electron redox reaction.[26]

$$[Cp_2M(IV)X]^+ + Cp_2M'(II) \rightleftarrows Cp_2M(II) + [Cp_2M'(IV)X]^+ \quad (5)$$

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.[27] Most redox reactions involving a multielectron step seem to be atom-transfer processes.[21]

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.[28] 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.[29] Furthermore, molecular orbital considerations indicate that strong π-donation from oxygen to metal can lead to metal–oxo triple bond interactions for octahedral d^{0-2} metal complexes[30] and tetrahedral d^4 metal complexes.[31] An increased contribution by the triple bond resonance

$$\mathrm{M{=}\ddot{\underset{\cdot\cdot}{O}}} \longleftrightarrow \mathrm{M^{-}{\equiv}O{:}^{+}}$$

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.[32] For example, treatment of a tetraazo macrocyclic complex $(\mathrm{C_{22}H_{22}N_4})\mathrm{Ti^{IV}{=}O}$ 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.[33] Comparisons with Ti=O (1.613(5) – 1.626(7) Å),[34] Ti–O–Ti (1.838 Å),[35] and Fe–O–Fe[36] bond distances suggest that the μ-oxo interaction consists of a Ti=O double bond and an Fe–O single bond, Ti=O–Fe. 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,[37] 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 hemes by dioxygen. This reaction leads to the formation of a thermodynamic product, μ-oxo ferric porphyrin dimers $[\mathrm{(POR)Fe}]_2\mathrm{O}$ (eq 6).[38] Cohen and Caughey proposed a mechanism

$$2\mathrm{Fe(POR)} + {}^{1}/{}_{2}\mathrm{O_2} \rightarrow \mathrm{(POR)FeOFe(POR)} \qquad (6)$$

for the formation of the μ-oxo product which involved formation of a μ-peroxo diiron intermediate.[38b] Several years later, evidence in support of this intermediate was reported.[39] Using low-temperature ^{1}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

$$\mathrm{(POR)Fe(III)OOFe(III)(POR)} + 2\mathrm{L} \rightarrow 2\mathrm{L(POR)Fe(IV){=}O} \qquad (7)$$

the ferryl species, $\mathrm{Fe^{IV}{=}O}$ with ferrous porphyrin at low temperatures yields the μ-oxo dimer in an incomplete oxygen atom transfer process. Thus a likely mechanism for the oxidation of ferrous hemes is shown in Scheme I.

Scheme I

$$2\,\mathrm{(POR)Fe} + \mathrm{O_2} \longrightarrow \mathrm{(POR)Fe\text{-}O\text{-}O\text{-}Fe(POR)}$$

$$\mathrm{(POR)Fe\text{-}O\text{-}O\text{-}Fe(POR)} \longrightarrow 2\,\mathrm{(POR)Fe{=}O}$$

$$\mathrm{(POR)Fe{=}O} + \mathrm{Fe(POR)} \longrightarrow \mathrm{(POR)Fe\text{-}O\text{-}Fe(POR)}$$

Incomplete oxygen atom transfer between chromium porphyrins has been established definitively by West.[40] When (TTP)Cr(II) is treated with $\mathrm{(TPP)Cr^{IV}{=}O}$ in toluene, a 53% yield of pure (TPP)CrOCr(TPP) can be isolated. The μ-oxo chromium(III) dimer has been characterized by UV–visible spectroscopy, combustion analysis, and magnetic susceptibility measurements. Treatment of (TPP)Cr(II) with a limiting amount of dioxygen also leads to the formation of the μ-oxo dimer $[\mathrm{Cr(TPP)}]_2\mathrm{O}$. The mechanism for this reaction is presumably analogous to that represented in Scheme I for iron porphyrin. When (TPP)Cr(II) is exposed to an excess of $\mathrm{O_2}$, the stable (TPP)Cr=O is formed.

$$\mathrm{(TPP)Cr} + \mathrm{O{=}Cr(TPP)} \rightarrow \mathrm{(TPP)CrOCr(TPP)} \qquad (8)$$

The facility in which (TPP)Cr=O serves as a one-electron oxidant, resulting in the formation of μ-oxo bridged heterobinuclear complexes, has been thoroughly demonstrated. Reduction of (TPP)Cr=O with V(IV), Mn(II), Fe(II), and Mo(IV) complexes produces a variety of mixed metal μ-oxo complexes.[41] For example, reduction of (TPP)Cr=O with Fe(TMeP) produced the μ-oxo complex shown in eq 9. A low accuracy X-ray diffraction study for the CrOFe porphyrin dimer with a pyridine (py) axially ligated to the chromium center, (py)(TTP)CrOFe(TMeP), reveals a linear CrOFe linkage.

$$\mathrm{(TTP)Cr^{IV}{=}O} + \mathrm{Fe^{II}(TMeP)} \rightarrow \mathrm{(TPP)Cr^{III}OFe^{III}(TMeP)} \qquad (9)$$

The equilibria 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 complexes. For example, exposure of solutions of (POR)CrOFe(L) to oxygen results in formation of (L)FeOFe(L) and spectroscopic detection of $\mathrm{(POR)Cr^{IV}{=}O}$.[41] The μ-oxo iron dimer presumably forms from the oxidation of $\mathrm{Fe^{II}(L)}$ (Scheme I) which was produced by the disproportionation of the initial CrOFe complex (eq 10). Also, nitrogenous bases such as pyridine have been shown to convert $[\mathrm{Fe(Pc)}]_2\mathrm{O}$ to bis-ligated monomeric complexes, $\mathrm{Fe(Pc)L_2}$ on the addition of excess base.[42] It is possible that this occurs through an initial disproportionation of the μ-oxo complex.

$$\mathrm{(POR)Cr^{III}OFe^{III}(L)} \rightleftharpoons \mathrm{(POR)Cr{=}O} + \mathrm{Fe^{II}(L)} \qquad (10)$$

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 $\mathrm{Mo_2O_3(S_2CNR_2)_4}$ on treating $\mathrm{MoO_2(S_2CNR_2)_2}$ with half an equivalent of triphenyl phosphine (eq 11).[43] The initial step of this process invariably involves the

$$2MoO_2(S_2CNR_2)_2 + PPh_3 \rightarrow Mo_2O_3(S_2CNR_2)_4 + O{=}PPh_3 \quad (11)$$

complete transfer of an oxygen atom from $MoO_2(S_2CNR_2)_2$ to phosphine (eq 12).[44] The resulting Mo(IV)

$$MoO_2(S_2CNR_2)_2 + PPh_3 \rightarrow MoO(S_2CNR_2)_2 + O{=}PPh_3 \quad (12)$$

$$MoO(S_2CNR_2)_2 + MoO_2(S_2CNR_2)_2 \rightleftarrows Mo_2O_3(S_2CNR_2)_4 \quad (13)$$

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 monooxo Mo(IV) complex with the dioxo Mo(VI) complex. By spectrophotometrically monitoring this titration past the equivalence point, an equilibrium constant $K = 4 \times 10^{-3}$ 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 $Mo^{VI}O_2$ and $Mo^{IV}O$ complexes.[48]

In similar processes, oxygen atom transfer from $MoO_2(acac)_2$ or $MoO_2(oxalate)_2$ to PPh_3 produces the μ-oxo binuclear complexes, $Mo_2O_3L_4$.[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]

$$2[HB(Me_2pz)_3]MoO_2X + PPh_3 \rightarrow Mo_2O_3X_2[HB(Me_2pz)_3]_2 + O{=}PPh_3 \quad (14)$$

Vanadium-mediated oxygen atom transfer reactions have been established also. Treatment of $VCl_2(py)_4$ in acetonitrile with PhIO produces $VOCl_2(py)_4$ (eq 15). However, when only 0.5 equiv of PhIO is used, the $V^{IV}O$ complex is trapped with a second molecule of $VCl_2(py)_4$ to form a μ-oxo complex (eq 16). Because of the slow

$$VCl_2(py)_4 + PhIO \rightarrow VOCl_2(py)_2 + PhI \quad (15)$$

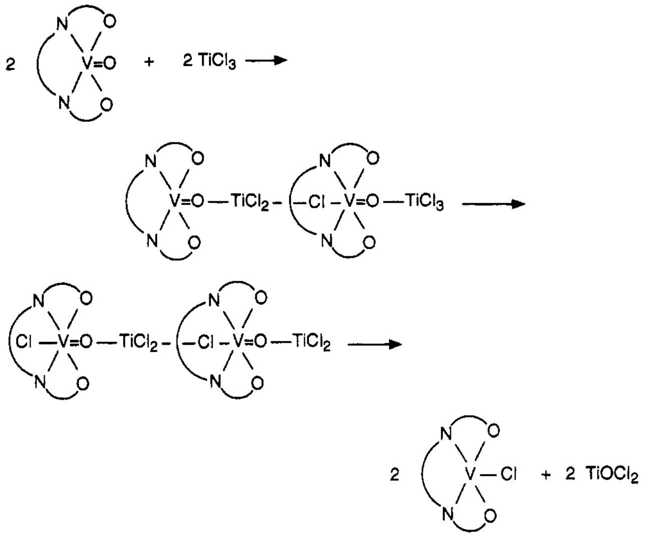
$$VOCl_2(py)_2 + VCl_2(py)_4 \rightarrow V_2OCl_4(py)_6 \quad (16)$$

decomposition of $V_2OCl_4(py)_6$ 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 $Cp^*Cr(O)(CH_3)_2$ with $Cp^*Cr(CH_3)_2py$ reportedly produces the μ-oxo complex, $Cp^*(CH_3)_2CrOCrCp^*(CH_3)_2$ and free pyridine.[52] 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

Scheme II



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

$$MoO_2(acac)_2 + MoCl_2(acac)_2 \rightarrow 2MoOCl(acac)_2 \quad (17)$$

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 $OMoCl_2(acac)_2$ as shown in eq 18. A subsequent chlorine atom transfer produces the observed product (eq 19). Support for this mechanism is derived from

$$MoO_2(acac)_2 + MoCl_2(acac)_2 \rightarrow OMo(acac)_2 + OMoCl_2(acac)_2 \quad (18)$$

$$OMo(acac)_2 + OMoCl_2(acac)_2 \rightarrow 2OMoCl(acac)_2 \quad (19)$$

the observed chlorine atom transfer from $OMoCl_2(S_2CNR_2)_2$ to $OMo(S_2CNR_2)_2$ to form $OMoCl(S_2CNR_2)_2$.[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(acacen) is treated with $TiCl_3(THF)_3$ in refluxing THF, good yields of VCl(acacen) can be obtained as shown in eq 20.[55] This

$$VO(acacen) + TiCl_3(THF)_3 \rightarrow VCl(acacen) + \text{“}TiOCl_2\text{”} \quad (20)$$

reaction formally involves a reductive deoxygenation of O=V(IV). When the reaction is carried out at lower temperatures, a μ-oxo bridged complex, $Cl(acacen)V(IV)OTi(IV)Cl_3(THF)_2$ 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

couple	$E°$ (V)[a]	ref
$[Cr^{III}(TPP)]^+/Cr^{II}(TPP)^b$	-1.06	60
$[(TTP)Cr^{IV}Cl]^+/(TTP)Cr^{III}Cl^b$	0.80	61
$(TTP)Cr^{IV}{=}O/[(TTP)Cr^{III}{=}O]^{-\ b}$	-1.12	61

[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 $[VO_2Cl_2]^-$ and $[VCl_4(MeCN)_2]^-$ proceeds immediately to yield a V(IV) product (eq 21).[51] The reaction is

$$[VO_2Cl_2]^- + [VCl_4(MeCN)_2]^- + 2Cl^- \rightarrow 2[VOCl_4]^{2-} + 2MeCN \quad (21)$$

presumed to involve formation of a μ-oxo bridged intermediate, $[Cl_2V(O)OVCl_4]^{2-}$ 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

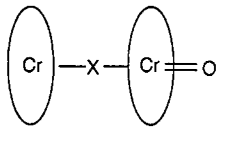
$$(TTP)Ti{=}O + (OEP)TiCl \rightleftharpoons (TTP)TiCl + (OEP)Ti{=}O \quad (22)$$

$$(TTP)Cr{=}O + (OEP)CrCl \rightleftharpoons (TTP)CrCl + (OEP)Cr{=}O \quad (23)$$

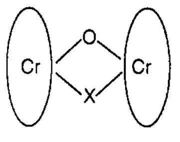
formally involve a net one-electron transfer mediated by O/Cl exchange. However, unlike the previous O/Cl exchange processes discussed in this section, eqs 22 and 23 are reversible. The equilibrium constants for the titanium reaction is 2.4 ± 0.5 and that for the chromium reaction is 3.1 ± 0.1. Thus the differences between the porphyrin ligands are sufficiently small such that eqs 22 and 23 can be considered as pseudo-self-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 $\Delta H° = -2.0 \pm 0.4$ kcal/mol and $\Delta S° = -4.6 \pm 1.2$ cal/(mol K). The rate constant for oxygen atom transfer from (TTP)Cr=O to (OEP)CrCl is 0.14 ± 0.01 M^{-1} s^{-1} at 30 °C with activation parameters of $\Delta H^{\ddagger} = 15.4 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -12 \pm 2$ 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 μ-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 preequilibrium chloride dissociation step (Scheme III). Oxygen atom transfer subsequently occurs between (POR)Cr=O and $[(POR)Cr(III)]^+$, presumably through a μ-oxo-bridged intermediate. Thus, in this particular type of reaction, the oxo ligand is preferred over chloride as the bridging species.



A



B

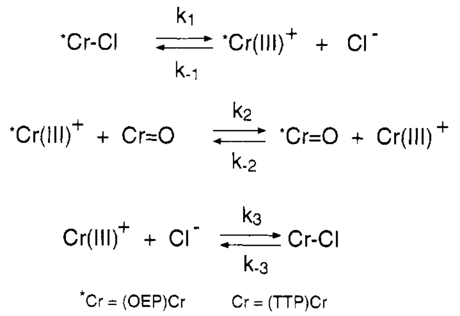
The contrast in reactions 8 and 23 is important to note. Clearly, the reduction products of oxochromium porphyrins are strongly dependent on the reducing agent. When a Cr(II) porphyrin is the reductant, incomplete oxygen atom transfer occurs, yielding a μ-oxo product. However, chromium(III) porphyrins result in reversible oxygen atom transfer. Because the μ-oxo complex, (TPP)Cr–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, (TPP)Cr, is a much stronger one-electron reducing agent than (TPP)Cr–Cl by more than 1 V. Thus in the inner-sphere precursor complex, $[Cr^{IV}{-}O{-}Cr^{II}]^{4+}$, a strong driving force exists for single electron transfer to occur to form the μ-oxo Cr(III) dimer. In order for complete oxygen atom transfer to occur, a second electron must transfer to form the successor complex, $[Cr^{II}{-}O{-}Cr^{IV}]^{4+}$. However this second electron transfer is thermodynamically uphill. Consequently, the μ-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 μ-oxo intermediate, $[Cr^{IV}OCr^{III}]^{5+}$. Single electron transfer within the activated μ-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 two μ-oxo species, $[Cr^{III}OCr^{III}]^{4+}$ and $[Cr^{IV}OCr^{III}]^{5+}$, 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 μ-oxo metalloporphyrin dimers. One such d-orbital energy level scheme for $[Fe(TPP)]_2O$ has been calculated by Tatsumi and Hoffmann using extended Hückel methods (Figure 1).[62] To a first approximation, this MO diagram should apply to μ-oxo chromium complexes. The magnetic moment of 1.61 μ_B per Cr atom in $[Cr(TPP)]_2O$[40] is consistent with an S = 2 electronic state arising from an $(e_2)^4(e_3)^2$ configuration. However in the d^5 μ-oxo intermediate, $[Cr^{IV}OCr^{III}]^{5+}$, formed in the Cr(III) reduction of (POR)Cr=O, the electronic configuration can be either $(e_2)^4(e_3)^1$ (low spin) or

Scheme III



$(e_2)^2(e_3)^2(e_1)^1$ (high spin). Both of these configurations are electronically degenerate and Jahn–Teller destabilized. Thus the O=Cr(IV)/ClCr(III) reaction is electronically disposed toward complete oxygen atom transfer whereas the O=Cr(IV)/Cr(II) reaction produces an electronically stable μ-oxo complex.

This electronic rationale also appears to correctly explain the stability of μ-oxo titanium porphyrin dimers. For example, the O=Ti(IV)/ClTi(III) reaction (eq 22) results in complete oxygen atom transfer. The presumed μ-oxo intermediate in this process, $[\mathrm{TiOTi}]^{5+}$ should have an electronically degenerate $(e_2)^1$ configuration. However, the neutral μ-oxo dimer, (TTP)Ti-OTi(TTP), is a stable d^1–d^1 complex which should have a nondegenerate $(e_2)^2$ ground-state configuration. This complex has been isolated and structurally characterized by single-crystal X-ray diffraction.[63]

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

$$\mathrm{MoO_2(S_2CNR_2)_2 + Mo(CO)_2(S_2CNR_2)_2 \rightarrow 2O{=}Mo(S_2CNR_2)_2 + 2CO} \tag{24}$$

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

$$\mathrm{M^{VI}O_2 + M^{II} \rightarrow 2M^{IV}O} \tag{25}$$

reaction has been utilized in a synthetically useful manner to prepare the first examples of oxotungsten(IV)–acetylene complexes (eq 26).[65] The acetylene

$$\mathrm{W(CO)(R'C{\equiv}CR^2)(S_2CNR_2)_2 + Mo_2O_3[S_2P(OEt)_2]_4 \rightarrow OW(R'C{\equiv}CR^2)(S_2CNR_2)_2 + 2OMo[S_2P(OEt)_2]_2 + CO} \tag{26}$$

ligands used in this reaction were HC≡CH, PhC≡CH, and $\mathrm{MeC_6H_4C(O)C{\equiv}CC(O)C_6H_4Me}$. Presumably, the actual oxygen donor source is the putative Mo(VI) complex, $\mathrm{MoO_2[S_2P(OEt)_2]_2}$, which forms from the dissociation of $\mathrm{Mo_2O_3[S_2P(OEt)_2]_4}$ illustrated in eq 27.[66]

$$\mathrm{Mo_2O_3[S_2P(OEt)_2]_4 \rightleftharpoons O{=}Mo[S_2P(OEt)_2]_2 + MoO_2[S_2P(OEt)_2]_2} \tag{27}$$

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

$$\mathrm{Mo(CO)_3(S_2PPh_2)_2 + MoO_2(S_2PPh_2)_2 \rightarrow 2MoO(S_2PPh_2)_2 + 3CO} \tag{28}$$

In contrast to the above reactions, oxygen atom transfer to $\mathrm{W(CO)_2(PPh_3)(S_2CNR_2)_2}$ does not produce a W(IV) complex but instead results in complete oxidation to W(VI). When 2 equiv of $\mathrm{Mo_2O_3[S_2P(OEt)_2]_4}$ are used to oxidize $\mathrm{W(CO)_2(PPh_3)(S_2CNR_2)_2}$, formation of a dioxotungsten complex occurs according to eq 29. When an equimolar amount of

$$\mathrm{W(CO)_2(PPh_3)(S_2CNR_2)_2 + 2Mo_2O_3[S_2P(OEt)_2]_4 \rightarrow WO_2(S_2CNR_2)_2 + 2MoO[S_2P(OEt)_2]_2 + 2CO + PPh_3} \tag{29}$$

$\mathrm{Mo_2O_3[S_2P(OEt)_2]_4}$ is used, the reaction produced only half an equivalent of $\mathrm{WO_2(S_2CNR_2)_2}$ and the remaining W(II) starting material was unchanged. Thus, if reaction 29 proceeds through $\mathrm{WO(S_2CNR_2)_2}$, this W(IV) intermediate must undergo a second oxygen atom transfer step faster than does the 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 $\mathrm{Mo^{VI}O_2}$ and $\mathrm{Mo^{IV}O}$ complexes is the formation of a μ-oxo–Mo(V) dimer product (eq 30) when the ligand environment involves dithio-

$$\mathrm{MoO_2L_\mathit{n} + MoOL_\mathit{n} \rightleftharpoons Mo_2O_3L_{2\mathit{n}}} \tag{30}$$

carbamate 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

$$\mathrm{Mo^{VI}O_2 + {*}Mo^{IV}O \rightleftharpoons Mo^{IV}O + {*}Mo^{VI}O_2} \tag{31}$$

of ligands used in these reactions were dithiocarbamates and the tridentate chelates, 2,3-bis(2,2-diphenyl-2-sulfidoethyl)pyridinate ($\mathrm{L\text{-}NS_2^{2-}}$), 2-(salicylideneamino)phenolate ($\mathrm{sap^{2-}}$), and 2-(salicylideneamino)benzenethiolate ($\mathrm{ssp^{2-}}$) shown in Figure 2. Representative reactions are illustrated by eqs 32–35. These reactions

$$\mathrm{(L\text{-}NS_2)MoO + MoO_2(S_2CNR_2)_2 \rightarrow (L\text{-}NS_2)MoO_2 + MoO(S_2CNR_2)_2} \tag{32}$$

$$\mathrm{(sap)MoO + (ssp)MoO_2 \rightarrow sapMoO_2 + (ssp)MoO} \tag{33}$$

$$\mathrm{(sap)MoO + MoO_2(S_2CNR_2)_2 \rightarrow (sap)MoO_2 + MoO(S_2CNR_2)_2} \tag{34}$$

$$\mathrm{(ssp)MoO + (L\text{-}NS_2)MoO_2 \rightleftharpoons (ssp)MoO_2 + (L\text{-}NS_2)MoO} \tag{35}$$

are spontaneous and allow the development of a relative thermodynamic scale for oxygen atom transfer. Reactions 32–34 proceed quantitatively while reaction 35

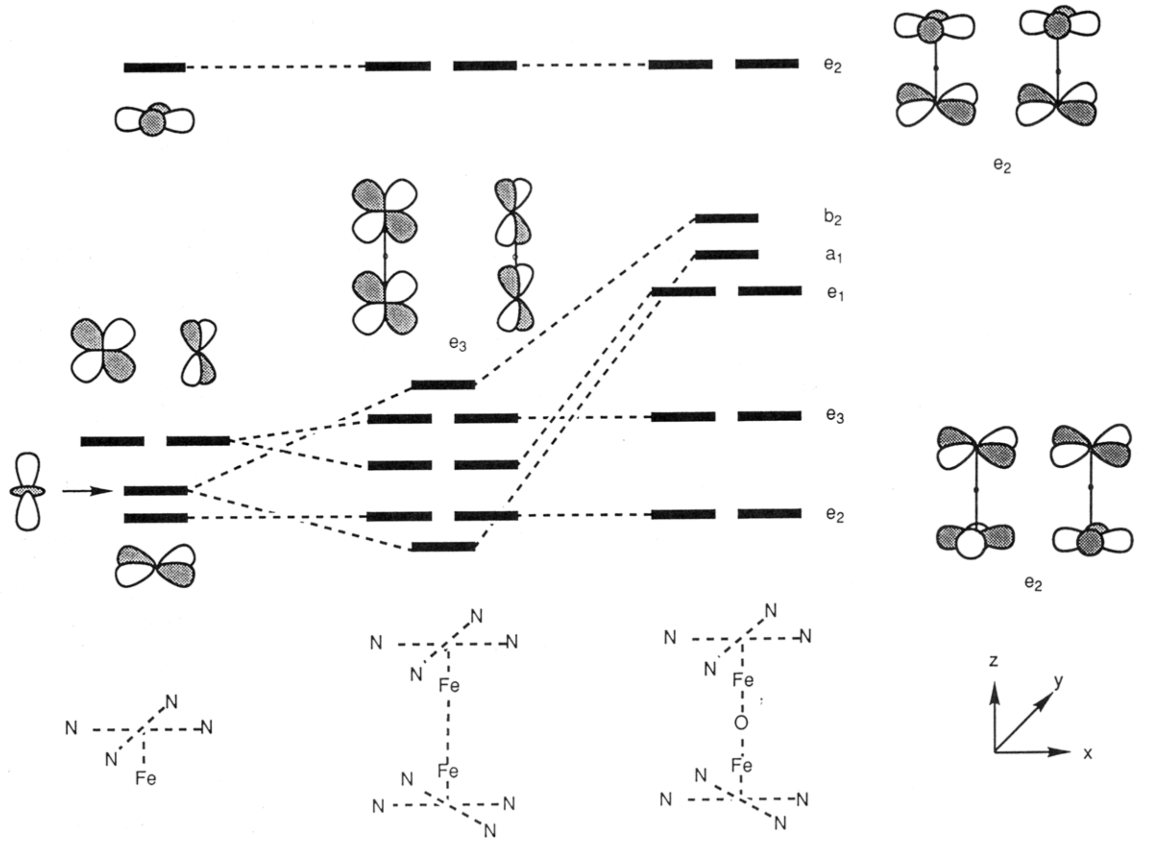


Figure 1. The building up of the orbitals of $[(NH_2^-)_4Fe{-}O{-}Fe(NH_2^-)_4]^{4-}$: (from left to right) the orbitals of the pyramidal N_4Fe unit with Fe 0.5 Å out of the N_4 plane; two N_4Fe fragments with a 3.526-Å Fe–Fe separation; orbitals of the composite μ-oxo complex (from ref 62).

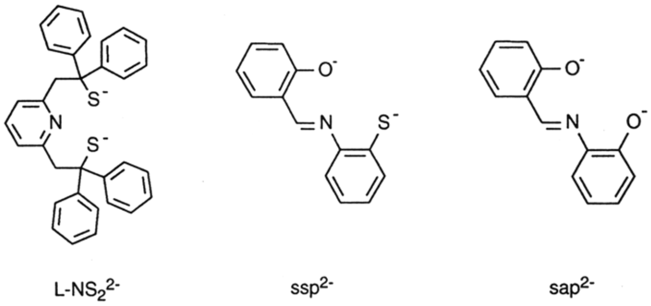


Figure 2. Ligand systems used for Mo(VI)/Mo(IV) intermetal oxygen atom transfer reactions.

is a reversible process with an equilibrium constant of approximately 30. Thus the reducing power or oxygen atom acceptor ability of the molybdenum(IV) complexes decrease in the order MoO(sap) > MoO(ssp) > MoO(L-NS$_2$) > MoO(S_2CNR_2)$_2$. Conversely, the oxidizing strength or oxygen atom donor capability of the Mo(VI) complexes falls in the order $MoO_2(S_2CNR_2)_2$ > MoO_2(L-NS$_2$) > MoO_2(ssp) > MoO_2(sap). These thermodynamic trends parallel the activation enthalpies for the ligand environments $S_4 > N_2S_2 >$ ONS $\gg O_2N$ in the reduction of $Mo^{VI}O_2$ 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 (d^2) 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 = $PMePh_2$).

$$Re(O)Cl_3L_2 + WCl_2L_4 \rightarrow ReCl_3L_3 + W(O)Cl_2L_3 + WCl_3L_3 + W(O)Cl_3L_2 \quad (36)$$

$$Re(O)Cl_3L_2 + MoCl_2L_4 \rightarrow ReCl_3L_3 + Mo(O)Cl_2L_2 + MoCl_3L_3 \quad (37)$$

$$Mo(O)Cl_2L_3 + WCl_2L_4 \rightarrow W(O)Cl_2L_3 + WCl_3L_3 + W(O)Cl_3L_2 \quad (38)$$

In all cases, the products of complete two-electron oxygen atom transfer are observed. This is evident in the conversion of the d^4 MCl_2L_4 reductants to the d^2 $M(O)Cl_2L_3$ complexes. Moreover, reactions 39–41,

$$W(O)Cl_2L_3 + ReCl_3L_3 \rightarrow NR \quad (39)$$

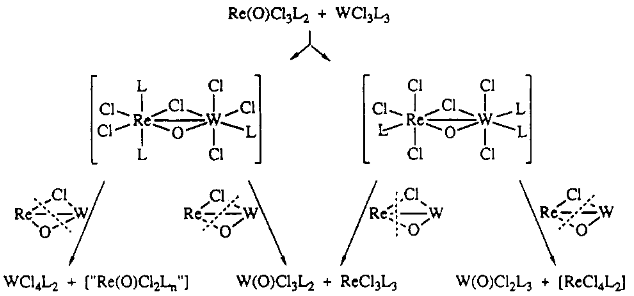
$$Mo(O)Cl_2L_3 + ReCl_3L_3 \rightarrow NR \quad (40)$$

$$W(O)Cl_2L_3 + MoCl_2L_4 \rightarrow NR \quad (41)$$

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 $Re(O)Cl_3L_2$ and WCl_2L_4, WCl_3L_3 is produced by chlorine atom transfer and $W(O)Cl_3L_2$ is formed by both oxygen and chlorine atom transfer. The latter represents a net three-electron oxidation of WCl_2L_4.

Scheme IV



The MCl_3L_3 complexes that appear as secondary products also act as oxygen or chlorine atom acceptors as was demonstrated by reactions 42–45. As in the

$$Re(O)Cl_3L_2 + WCl_3L_3 \rightarrow ReCl_3L_3 + W(O)Cl_3L_2 + WCl_4L_2 + W(O)Cl_2L_3 \quad (42)$$

$$W(O)Cl_3L_2 + WCl_3L_3 \rightarrow W(O)Cl_2L_3 + WCl_4L_2 \quad (43)$$

$$Re(O)Cl_3L_2 + MoCl_3L_3 \rightarrow ReCl_3L_3 + Mo(O)Cl_3L_2 + Mo(O)Cl_2L_3 + MoCl_4L_2 \quad (44)$$

$$Mo(O)Cl_2L_3 + WCl_3L_3 \rightarrow W(O)Cl_3L_2 + W(O)Cl_2L_3 + WCl_4L_2 \quad (45)$$

above reaction using M(II) reductants, reactions 42–45 show the same relative thermodynamic trend in the direction of oxygen atom transfer: Re → Mo, Re → W, 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 lead 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 $Mo_2(\mu\text{-}Cl)(\mu\text{-}S)$ derivative has been characterized structurally by single-crystal X-ray diffraction.[72]

$$2MoCl_2(PMe_3)_4 + SPMe_3 \rightarrow Mo_2(\mu\text{-}Cl)(\mu\text{-}S)Cl_3(PMe_3)_5 + 4PMe_3 \quad (46)$$

An unusual example of oxygen atom transfer is shown in eq 47.[73] In this case, a formal net four-electron redox

$$[(5\text{-}Cl\text{-}salen)Mn^{IV}(\mu\text{-}O)]_2 + 4(salen)Fe^{II} \rightarrow 2(5\text{-}Cl\text{-}salen)Mn^{II} + 2[(salen)Fe^{III}(\mu\text{-}O)]_2 \quad (47)$$

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 $[(5\text{-}Cl\text{-}salen)Mn^{IV}(\mu\text{-}O)]_2$ into monomeric terminal oxo complexes. This suggests that the oxo transfer in reaction 47 may proceed through a triple bridging oxo ligand, μ_3-O, such as in a $Mn_2Fe_2(\mu_3\text{-}O)_2$ core. Analogous tetranuclear $Mn_4(\mu_3\text{-}O)_2$ 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, $(TTP)Ti(\eta^2\text{-}PhC{\equiv}CPh)$[75] is a powerful atom transfer acceptor. Thus, when $(OEP)Ti(\eta^2\text{-}O_2)$[76] is treated with $(TTP)Ti(\eta^2\text{-}PhC{\equiv}CPh)$ quantitative formation of (OEP)Ti=O and (TTP)Ti=O results as illustrated in eq 48.[77] This reaction formally

$$(OEP)Ti(O_2) + (TTP)Ti(PhC{\equiv}CPh) \rightarrow (OEP)Ti{=}O + (TTP)Ti{=}O + PhC{\equiv}CPh \quad (48)$$

involves a two-electron reduction of peroxide (O_2^{2-}) to $2O^{2-}$ by Ti(II). Since ligand reduction has occurred, eq 48 is formally a secondary oxygen atom transfer process. Reaction 48 supports a mechanism proposed by Marchon and Guilard to explain the formation of (TPP)Ti=O from the photolysis of $(TPP)Ti(\eta^2\text{-}O_2)$ shown in eq 49.

$$2(TPP)Ti(\eta^2\text{-}O_2) \xrightarrow{h\nu} 2(TPP)Ti{=}O + O_2 \quad (49)$$

In a similar manner, the persulfido and perselenido complexes, $(OEP)Ti(S_2)$ and $(OEP)Ti(Se_2)$ undergo atom transfer processes (eqs 50 and 51). These reactions

$$(OEP)Ti(S_2) + (TTP)Ti(PhC{\equiv}CPh) \rightarrow (OEP)Ti{=}S + (TTP)Ti{=}S + PhC{\equiv}CPh \quad (50)$$

$$(OEP)Ti(Se_2) + (TTP)Ti(PhC{\equiv}CPh) \rightarrow (OEP)Ti{=}Se + (TTP)Ti{=}Se + PhC{\equiv}CPh \quad (51)$$

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 Cp_2TiS_5 and Cp_2TiSe_5 as transfer reagents. In general, these deliver S_2 or Se_2 fragments as shown in eqs 52–55.[78,79] The exception is reaction 56 in which a single selenium atom is transferred from Cp_2TiSe_5 to a vanadium(II) complex.[80]

$$[Ir(dppe)_2]Cl + Cp_2TiS_5 \rightarrow [Ir(dppe)_2S_2]Cl \quad (52)$$

$$[Ir(dppe)_2]Cl + Cp_2TiSe_5 \rightarrow [Ir(dppe)_2Se_2]Cl \quad (53)$$

$$(TTP)TiF_2 + Cp_2TiS_5 \rightarrow (TTP)Ti(S_2) \quad (54)$$

$$(TTP)TiF_2 + Cp_2TiSe_5 \rightarrow (TTP)Ti(Se_2) \quad (55)$$

$$(OEP)V(THF)_2 + Cp_2TiSe_5 \rightarrow (OEP)V{=}Se \quad (56)$$

V. Nitrogen Atom Transfer Reactions

A. Three-Electron Processes

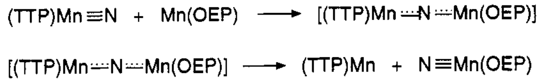
Although the bonding in terminal metal nitrides (M≡N:) is formally analogous to the triple bond

Table II. Reduction Potentials for Manganese Porphyrins

	$E°$ (V)[a]	ref
$[Mn^{III}(TTP)]^+/Mn^{II}(TTP)$	–0.33	83
$Mn^{III}(OEP)/Mn^{II}(OEP)$	–0.45	84
$N{\equiv}Mn^V(TTP)/N{\equiv}Mn^V(TTP^{\bullet -})$	–1.14	85
$N{\equiv}Mn^V(OEP)/N{\equiv}Mn^V(OEP^{\bullet -})$	–1.30	85
$ClMn^{III}(TPP^{\bullet +})/ClMn^{III}(TPP)$	1.18	86

[a] Versus SCE.

Scheme V



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,[81] involved the reduction of $N{\equiv}Mn^V(TTP)$ with $Cr^{II}(TTP)$ 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.

$$(TTP)Mn{\equiv}N + Cr(TTP) \rightarrow (TTP)Mn + N{\equiv}Cr(TTP) \quad (57)$$

Reversible, three-electron nitrogen atom transfer reactions have also been reported for manganese porphyrin complexes (eq 58).[82] The equilibrium constant for this reaction in toluene is $K = 1.2 \pm 0.5$ at 20 °C [$\Delta H° = 2.0 \pm 0.2$ kcal/mol and $\Delta S° = 7.1 \pm 0.6$ cal/(mol K)]. The rate constant for the forward direction of reaction 58 in toluene is $k_1 = (5.6 \pm 1.2) \times 10^{-3}\ M^{-1}\ s^{-1}$ at 20 °C, with $\Delta H^{\ddagger} = 9.4 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -10 \pm 2$ cal/(mol K). Since $\Delta G° \approx 0$, these activation parameters for reaction 58 reflect the intrinsic properties of the reactants toward nitrogen atom transfer.

$$(TTP)Mn{\equiv}N + Mn(OEP) \rightleftharpoons (TTP)Mn + N{\equiv}Mn(OEP) \quad (58)$$

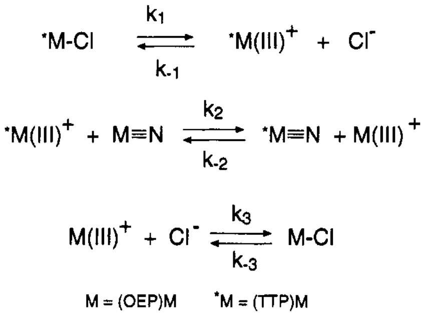
The reduction potentials listed in Table II indicate that the Mn(II) complexes are not capable of reducing the nitridomanganese(V) complexes by an outer-sphere process. Thus, reaction 58 must proceed by an atom transfer mechanism (Scheme V). The μ-nitrido intermediate shown in Scheme V is supported further by kinetic studies and solvent effects. For example, when reaction 58 is run in the more coordinating solvent THF, the rate is 3 orders of magnitude slower than when toluene is the solvent. In this case, THF presumably coordinates to the Mn(II) complex and inhibits formation of the bridged intermediate. Furthermore, the small $\Delta H^{\ddagger}$ (9.4 kcal/mol) and the negative $\Delta S^{\ddagger}$ (–10 eu) are consistent with an associative process.

Table III. Metrical Parameters (Å) of Manganese Porphyrins

	$Mn–N_{pyrrole}$[a]	Mn–Ct[b]	Mn–X	ref
Mn(TPP)	2.090(9)	0.28		87
ClMn(TPP)	2.008(7)	0.27	2.363(3)	88
$N{\equiv}Mn(TMeP)$	2.021(2)	0.388	1.512(2)	89

[a] Average $Mn–N_{pyrrole}$ distance. [b] Displacement out of the N_4-porphyrin plane.

Scheme VI



The facility in which nitrogen atom transfer occurs between metalloporphyrins appears remarkable when factors such as the breaking and remaking of a metal–nitrogen triple bond, spin state changes from low spin Mn(V) to high spin Mn(II), and the transfer of three electrons are involved. However, the metrical parameters 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 $Mn–N_{pyrrole}$ 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 $(OEP)Mn{\equiv}N$ 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.[90] The chromium analog has also been reported by Bottomley (eq 60).[91] In addition, the irreversible transfer of nitrogen from $(OEP)Mn{\equiv}N$ to (TPP)CrCl is also known (eq 61).[92] For all three reactions (59–61), the kinetic analysis, solvent dependencies, M(III) axial ligand effects, steric factors, and Cl^- inhibition studies support the mechanism shown in Scheme VI. The N/Cl exchange pathway for metalloporphyrins involves a preequilibrium dissociation of the monoanionic axial

$$(OEP)Mn{\equiv}N + (TTP)MnCl \rightleftharpoons (OEP)MnCl + (TTP)Mn{\equiv}N \quad (59)$$

$$(OEP)Cr{\equiv}N + (TPP)CrCl \rightleftharpoons (OEP)CrCl + (TPP)Cr{\equiv}N \quad (60)$$

$$(OEP)Mn{\equiv}N + (TPP)CrCl \rightarrow (OEP)MnCl + (TPP)Cr{\equiv}N \quad (61)$$

Table IV. Thermodynamic and Kinetic Comparison of N/Cl Exchange Reactions

reaction	solvent	dielectric constant	T (°C)	K_{eq}	k_f (M^{-1} s^{-1})	ref
59	$CDCl_3$	4.79	22	23.5 ± 3.6	0.010 ± 0.007	90
			30	17.5	0.025 ± 0.001	90
			40	12.2 ± 1.5	0.051 ± 0.005	90
			50	8.7 ± 1.5	0.150 ± 0.012	90
	THF	7.3	50	0.98	0.10 ± 0.02	90
	$CH_3NHC(O)H$	182	50		20 ± 2	90
60	benzene	2.27	23	1.4 ± 0.2	94 ± 9	91
	CH_2ClCH_2Cl	10.35	23	1.1 ± 1	440	91
61	benzene	2.27	25	irreversible	48 ± 5	92
	$CHCl_3$	4.79	25	irreversible	66 ± 5	92
	C_6H_5Cl	5.70	25	irreversible	200 ± 17	92
	CH_2Cl_2	9.08	25	irreversible	350 ± 20	92
	CH_2ClCH_2Cl	10.35	25	irreversible	1170 ± 140	92

ligand on the M(III) reductant. The cationic square planar M(III) species undergoes nitrogen atom transfer with the nitrido oxidant via a μ-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-*p*-XPP. Strongly electron-donating substituents compared with electron-withdrawing groups on N≡Mn(T-*p*-XPP) increase the rate of nitrogen atom transfer to ClCr(OEP) by a factor of 50 (ρ = −0.40). Conversely, electron-withdrawing groups increase the rate of nitrogen atom transfer from N≡Mn(OEP) to ClCr(T-*p*-XPP) with a linear free energy ρ-value of 0.17. These observations are consistent with Scheme VI in which the rate of reaction is increased by greater nucleophilic character of the nitrido complex and enhanced electrophilicity of the chromium acceptor complex.

Steric factors were evident when ortho substituents were used with either N≡Mn(V) or ClCr(III). For example, the reaction rate of N≡Mn(OEP) with ClCr(T-2-MeOPP) decreased by 70% relative to the control reaction between N≡Mn(OEP) and ClCr(T-4-MeOPP). Furthermore, the bis-pocket porphyrins, T-2,6-$(MeO)_2$PP or T-2,4,6-$(MeO)_3$PP completely inhibited nitrogen atom transfer. These sterically encumbered metalloporphyrin complexes indicate the importance of forming a μ-nitrido intermediate on the pathway to complete nitrogen atom transfer.

Reactions 59 and 60 can be considered as pseudo-self-exchange reactions, since their equilibrium constants are near unity. Correspondingly, reaction 61 represents the associated cross reaction. Unfortunately, a comprehensive kinetic study of these reactions under the same conditions has not yet been done. Thus, it is not clear whether or not a Marcus-type relationship applies to these N/Cl exchange reactions.

The generality of nitrogen atom transfer has also been extended to other macrocyclic complexes.[93] For example, treatment of N≡Mn(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 can be accomplished in a similar manner. Thus, nitrogen atom transfer can be used in a preparative manner.

Table V. Thermodynamic Limits for the Reaction $L_nM + {}^1/_2O_2 \rightarrow L_nM{=}O$ in Nonaqueous Media

half reaction	ΔH (kcal/mol)
$Cr(POR)Cl/O{=}Cr(POR)Cl$, $Mn(POR)Cl/O{=}Mn(POR)Cl$, $[Cr(Salen)(H_2O)_2]^+/[O{=}Cr(Salen)]^+$	$\lesssim +15$
$Fe(POR)Cl/O{=}Fe(POR^{\bullet})Cl$	$\gtrsim -27$
$Mn(O)(S_2CNR_2)_2/MnO_2(S_2CNR_2)_2$	−35
$MoO(L{-}NS_2)(DMF)/MoO_2(L{-}NS_2) >$ $MoO(ssp)(DMF)/MoO_2(ssp)(DMF)$	$\lesssim -35$
$Cr(POR)/O{=}Cr(POR)$, $Mn(POR)L_2/O{=}Mn(POR)$, $Fe(POR)L_n/O{=}Fe(POR)L$, $MoO(POR)/MoO_2(POR)$	≥ -67
$MO(sap)(DMF)/MO_2(sap)(DMF)$ ($M{=}Mo, W$)	$\lesssim -67$

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, M=S, M=Se, or M≡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 M=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.[11b] In this approach, a thermodynamic oxygen atom transfer "half-reaction" is used (eq 62). Representative enthalpies

$$ {}^1/_2O_2 + X \rightarrow XO \qquad (62) $$

for selected half-reactions are listed in Table V. The ΔH limits shown in this table were established by the reaction or lack of reaction of metal complexes with oxygen atom donor–acceptor reagents with known enthalpies for half-reaction 62. Unfortunately, only a limited thermodynamic data set has been developed 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.

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Abbreviations

acac	acetylacetonato(1–)
acacen	*N,N'*-ethylenebis(acetylacetone iminate)(2–)
5-Cl-salen	1,2-bis[(5-chlorosalicylidene)amino]ethane(2–)
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
DMF	dimethylformamide
$HB(Me_2pz)_3$	tris (3,5-dimethylpyrazolyl)borate(1–)
L	general ligand, monodentate or chelating
$L\text{-}NS_2$	2,6-bis(2,2-diphenyl-2-sulfidoethyl)pyridinate(2–)
OEP	octaethylporphyrinato(2–)
POR	general porphyrinato dianion
py	pyridine
salen	1,2-bis(salicylideneamino)ethane(2–)
sap	2-(salicylideneamino)phenolate(2–)
SCE	saturated calomel electrode
S_2CNR_2	dithiocarbamate(1–); R generally is an alkyl group
ssp	2-(salicylideneamino)benzenethiolate(2–)
THF	tetrahydrofuran
TMeP	*meso*-tetrakis(4-methoxyphenyl)porphyrinato(2–)
TPP	*meso*-tetraphenylporphyrinato(2–)
TTP	*meso*-tetrakis(4-tolyl)porphyrinato(2–)

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