Metal-Centered Oxygen Atom Transfer Reactions

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I. Introduction

Oxidation/reduction of generalized molecule X/XO by formal gain or loss, respectively, of an oxygen atom as in reaction 1 is a widespread process. In it, the oxygen donor is reduced and the oxygen acceptor is oxidized with the result that the atom transferred is maintained as oxide in reactant and product. Certainly

$$X + AO \rightleftharpoons XO + A \qquad (1)$$

some of the earliest reactions that could be conceived in terms of reaction 1 are those by Hofmann[1] in 1912, who demonstrated that OsO_2 could be oxidized to OsO_4 by aqueous chlorate. Here the metal oxidation state is increased by two units for each oxygen atom added, a defining feature of the stoichiometrically simplest oxygen atom transfer reaction. The advent of ^{18}O isotopic labeling provided the necessary technique to prove that oxygen atom transfer to or from a specific component of a reaction system actually occurs. Thus, the experiments of Taube and co-workers[2–4] in the 1950s marked the beginning of demonstrable atom transfer between inorganic reactants. Among others, reactions 2 and 3 in aqueous solution occur with transfer of the

$$Cl\bullet^- + NO_2^- \xrightarrow{H^+} [HO{-}\ddot{N}(O){-}\bullet Cl]^- \longrightarrow Cl^- + NO_2\bullet^- + H^+ \qquad (2)$$

$$Cl\bullet_3^- + 3SO_3^{2-} \longrightarrow Cl^- + 3SO_3\bullet^{2-} \qquad (3a)$$

$$Cl\bullet_3^- + SO_3^{2-} \longrightarrow Cl\bullet_2^- + SO_3\bullet^{2-} \qquad (3b)$$

$$SO_3^{2-} + Cl\bullet_3^- + 2H^+ \longrightarrow [O_3S{-}Cl\bullet_2]^- + H_2\bullet \;\longrightarrow\; SO_3\bullet^{2-} + Cl\bullet_2^- + 2H^+ \qquad (4a)$$

$$SO_3^{2-} + Cl\bullet_3^- \longrightarrow [O_3S\cdots\bullet\cdots Cl\bullet_2]^{3-} \longrightarrow SO_3\bullet^{2-} + Cl\bullet_2^- \qquad (4b)$$

$$SO_3^{2-} + Cl\bullet_3^- + 2H^+ \longrightarrow [O_2S{-}\bullet{-}Cl\bullet_2]^- + H_2O \;\longrightarrow\; SO_3\bullet^{2-} + Cl\bullet_2^- + 2H^+ \qquad (4c)$$

indicated isotope label. The stoichiometry of reaction 3a is possible because chlorite and hypochlorite, in ad-

dition to chlorate, function as oxygen atom donors. Despite their rather simple appearance, such reactions are not without potential mechanistic ambiguities.[4] A reasonable intermediate is shown for reaction 2, which requires N–O bond-making and Cl–O bond-breaking for product formation. However, reaction 3b might proceed by path 4a, 4b, or 4c. Path 4a is not important because the sulfate does not show the enrichment required by hydrolysis of the S–Cl intermediate. Pathways 4b and 4c cannot be distinguished by isotope labeling, primarily because sulfite oxygen exchange with solvent under the reaction conditions is too fast. Reactions 2–4 should be contrasted to reaction 5, which occurs when anhydrous gaseous sulfur dioxide is dissolved in anhydrous liquid sulfur trioxide, or in the reciprocal system.[5] The lack of ^{35}S isotopic exchange between oxidation states proves that the process is one of *oxide ion*, not *oxygen atom*, exchange. Liquid sulfur dioxide, as water, is an oxide-labile solvent. Reaction 6 is one step in the oxidation of sulfite by nitrite[3] and is somewhat analogous to reaction 4a. Although sulfur is oxidized to sulfate and nitrogen is reduced, this reaction is not what will be referred to subsequently as *primary* oxygen atom transfer inasmuch as the atom ultimately transferred does not derive from a reactant which is oxidized or reduced.

$$S^{\bullet}O_2 + {}^{*}SO_3 \rightleftharpoons SO^{\bullet} + {}^{*}SO_2{}^{\bullet} \quad (5)$$

$$HON(SO_3)_2{}^{2-} + H_2{}^{\bullet} \longrightarrow HONH(SO_3)^{-} + HSO_3{}^{\bullet -} \quad (6)$$

Oxygen atom transfer is a frequent reaction type in inorganic chemistry, particularly with main-group compounds. Yet reactions proceeding in this way are not always recognized, or at least explicitly described, as being of this type. Proof of atom transfer in the preceding reactions required ^{18}O labeling because they were carried out in aqueous solution. When this technique succeeds, it is because atom transfer in the reaction of interest is much faster than oxygen exchange between reactants and bulk solvent. As will be seen, the vast majority of oxygen atom transfer reactions have been carried out in aprotic solvents where this type of exchange is obviated. The purpose of this account is to recognize and classify oxygen atom transfer processes and, insofar as possible, to analyze them in terms of those features that control reactivity. These considerations will extend to a wide variety of inorganic reaction systems and also to enzymes, viz., the molybdenum hydroxylases,[6,7] some of which appear to execute catalytic substrate oxidation and reduction by atom transfer.

II. Definitions and Scope

A. Oxo Transfer Reactions

When used to designate a ligand, the term "oxo" refers to oxide (O^{2-}), the usage being consistent with that of Griffith.[8] For brevity, oxygen atom transfer reactions are signified as *oxo* transfer reactions; the oxidation state of the atom during transfer is moot. *Primary* oxo transfer is defined by reaction 7, under which there are three requirements: (i) reactants XO/X are oxygen *atom* (not oxide) donors/acceptors; (ii) the oxidation/reduction of atom M of (positive) oxidation state $z/z + 2$ results from atom transfer only; (iii) transferable or transferred oxygen ($a = 0$–3) is oxidic and is directly bound in a terminal or bridging mode to M. Ligand number n is not necessarily constant in reactant and product, and XO in the reverse reaction is not always uncoordinated to M. Requirement ii is readily extended to polynuclear cases, in which there must be a net oxidation/reduction of atom set M_m. A frequently encountered situation is one where the final product is a binuclear μ-oxo species in which the oxidation state of M has been increased by one unit. Such species are generally formed by the forward, often irreversible reaction 8 when it is faster than reaction 7. The sum of these is reaction 9, a common stoichiometry in oxo transfer processes. Oxo-bridged metalloporphyrins such as $[Cr(TPP)]_2O$[9] can be formed in this way. A far more complicated case is the reaction of Cp_2V and N_2O to give $Cp_5V_5O_6$[10,11] by an unknown sequence. However, the overall process is one of oxo transfer inasmuch as the vanadium (mean) oxidation state has increased from 2+ to 3.4+ and all oxygen is integrated in a $[V_5(\mu_3\text{-}O)_6]^{5+}$ core.

$$M^{z}O_aL_n + XO \rightleftharpoons M^{z+2}O_{a+1}L_n + X \quad (7)$$

$$M^{z+2}O_{a+1}L_n + M^{z}O_aL_n \rightleftharpoons [L_nM^{z+1}O_a]_2O \quad (8)$$

$$2M^{z}O_aL_n + XO \rightarrow [L_nM^{z+1}O_a]_2O + X \quad (9)$$

Two other oxo transfer processes, termed *secondary* reactions, can be identified. In reaction 10, coordination of ligand L′ causes an internal redox reaction resulting in formation of ligand oxide LO, which may (as shown) or may not dissociate from M. This differs from reverse reaction 7 because L′, unlike X, is not an oxygen atom acceptor. In reaction 11, oxidation of substrate is accompanied by reduction of both metal and ligand.

$$M^{z+}O_aL^{l}_n + L' \rightleftharpoons M^{z}O_{a-1}L^{l}_{n-1}L' + L^{l+2}O \quad (10)$$

$$M^{z+1}(L^{l}O_a)_n + X \rightleftharpoons M^{z}(L^{l}O_a)_{n-1}(L^{l-1}O_{a-1}) + XO \quad (11)$$

These secondary reactions are related in the sense that a second reactant induces an internal electron rearrangement in the first. Reaction 11 differs in that no oxometal group is involved in the oxo transfer process; i.e., the transfer is *ligand-centered*. Both reactions may occur in the forward or reverse directions. Primary and secondary oxo transfers are metal-mediated processes because they cause changes in metal atom oxidation state. Primary reactions are, however, exclusively *metal-centered* by virtue of the foregoing requirements and are differentiated from secondary processes on that basis.

In the considerations that follow, attention is directed toward primary reactions in which M is a transition element. Emphasis is so placed because of the much larger number of, and the currently greater interest and activity in, primary reactions of transition element compounds compared to those of the nonmetals. Secondary reactions are of substantially less frequent occurrence and are only briefly mentioned. As will be found, there are significant limitations on the metals M that can sustain oxo transfer and, for a given M, on ligand features that promote this reaction.

B. Oxo Transfer Reagents

Reaction 7 subsumes the effective changes $XO \rightarrow X + O$ and $O + 2e^{-} \rightarrow O^{2-}$. Obviously, metal oxidation and

TABLE 1. Principal Oxo Transfer Reagents[a]

group			
14	15	16	17[c]
	Donors		
CO_2	N_2O, NO_3^-	O_2, O_3	ClO^-
K_2CO_4	R_3NO, ArNO	H_2O_2	ClO_2^-
$ArCO_3H$	PhN(O)NPh, RNO_2	R_2SO	ClO_3^-, BrO_3^-
ROOH	heterocyclic *N*-oxides, Ph_3AsO, Ph_3SbO		BrO_4^-, H_5IO_6 Cl_2O, PhIO[b]
	Acceptors		
olefins	heterocyclic amines, NO_2^-	CN^-	
CO			
Si_2Cl_6	R_3P, $(RO)_3P$, R_3As	SO_3^{2-}, SeO_3^{2-}	

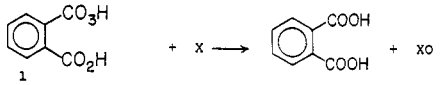
[a] R = alkyl or arene (Ar). [b] And ring-substituted variants. [c] For a useful discussion of oxohalogen species, cf. ref 20.

substrate reduction will be enhanced by a strongly reducing metal center, a strong M–O bond, and an oxygen atom donor with a relatively weak X–O bond, and conversely for the opposite reaction. The first two factors are largely a function of the coordination unit itself. The last is ideally described by bond dissociation energies, but other than for small gaseous molecules, few are available. Listed in Table 1 are the main reagents that have been used in oxo transfer. Reactions of the majority of these will be illustrated subsequently.

In addition to dioxygen and hydrogen peroxide, extensively employed donors include PhIO, *m*-$ClC_6H_4CO_3H$, *t*-BuOOH, pyO, and Me_2SO. Iodosylbenzene, introduced for the purpose in 1979,[12-14] has proved a valuable reagent for formation of oxometalloporphyrins and thus as an oxygen source in catalytic oxygenations of organic substrates. The compound is a polymeric solid with I–O–I bonds and is sparingly soluble in most organic solvents. In methanol it forms $PhI(OMe)_2$, which is readily hydrolyzed to PhIO, thereby providing a convenient route to the ^{18}O-enriched compound.[15] Labeled percarboxylic acids, hydroperoxides, *N*-oxides, and sulfoxides usually are obtained by oxidation of precursors with enriched hydrogen peroxide. Linear logarithmic correlations between increasing rate constants for oxometalloporphyrin formation and increasing leaving group acidities for percarboxylic acids and alkyl hydroperoxides have been described.[16-19] A number of oxohalogen species function as donors.[20] For example, perbromate reacts with a number of two-equivalent reductants, among them sulfite and arsenite, to which is transferred one ^{18}O atom for each sulfate and arsenate formed.[21] From $E°$ values for the two-electron reductions $XO_4^- + 2H^+ + 2e^- \rightleftharpoons XO_3^- + H_2O$ and $H_5IO_6 + 2H^+ + 2e^- \rightleftharpoons HIO_3 + 3H_2O$, the oxidizing power of perhalates decreases in the order BrO_4^- (1.85 V) > H_5IO_6 (1.60 V) > ClO_4^- (1.20 V).[22] No oxo transfer reactions of perchlorate have been reported. Periodic acid, while a thermodynamically poorer oxidant, is more reactive, presumably because of greater oxygen lability. Of the various oxyhalides in Table 1, chlorate and hypochlorite have been the most frequently used. For example, recently developed systems for the catalytic oxidation of olefins via a proposed oxomanganese species employ ClO^- as the oxygen source.[23]

The most common oxygen atom acceptors are tertiary phosphines, whose basicities or nucleophilicities usually increase with the number of alkyl groups.[24,25] Triphenylphosphine is the most frequently employed acceptor and suffices for a large number of reactions. A kinetics study of the reduction of a $Mo^{VI}O_2$ complex with members of the series $Et_nPh_{3-n}P$ showed that the second-order rate constants increased with increasing nucleophilicity, there being a ca. 7-fold difference between $n = 0$ and $n = 3$.[26] Tertiary arsines are poorer acceptors than phosphines. Thus, Ph_3AsO oxidizes $MoO(S_2CNEt_2)_2$[27] whereas the oxidation product, $MoO_2(S_2CNEt_2)_2$, is reduced by Ph_3P.[26,28,29] The opposite behavior of these compounds must arise largely because the P–O bond strength in Ph_3PO(g) exceeds the As–O bond energy in Ph_3AsO(g) by ca. 27 kcal/mol.[30] Phosphites have been little tested in metal-centered oxo transfers. Use of the remaining, anionic species has been confined to aqueous solution. However, quaternary ammonium salts of all but selenite that are soluble in aprotic solvents are commercially available or have been described.[31]

While there are not generally available thermodynamic criteria of oxygen donor and acceptor relative tendencies of the species in Table 1, Watt et al.[32] have provided an important beginning. By direct calorimetric measurements of 1,2-dichloroethane solutions, they have verified that the thermodynamic order of acceptor ability toward the constant donor monoperoxyphthalic acid (1) is that indicated, assuming small



1

X (ΔH, kcal/mol): Ph_3P (−95.5 ± 3.2) ≈ SO_3^{2-} (−94.0 ± 4.0) > $MoO(S_2CNEt_2)_2$ (−66.4 ± 1.2) > NO_2^- (−62.0 ± 3.0)

$$NO_2^- + {}^1/_2O_2(g) \rightarrow NO_3^- \qquad \Delta H = -32.2 \pm 6.0 \text{ kcal/mol} \qquad (12a)$$

$$SO_3^{2-} + {}^1/_2O_2(g) \rightarrow SO_4^{2-} \qquad \Delta H = -64.0 \pm 7.0 \text{ kcal/mol} \qquad (12b)$$

solvation enthalpies and relatively small and constant $T\Delta S$ contributions. Further, by the derived enthalpy changes of the reactions 12, sulfite is the thermodynamically stronger oxygen acceptor. The experiments with sulfite were performed with a material which is stated to give satisfactory elemental analyses for $(Et_4N)_2(SO_3)$.[32] In this event, reaction solutions presumably were not complicated by the presence of significant amounts of hydrosulfite or pyrosulfite in the equilibrium $2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$.[31] Thermodynamic data for reactions of type 12 are particularly useful, and we shall return to them later.

This account deals with metal-centered oxo transfer systems involving mainly inorganic reactants. Consequently, certain restrictions have been imposed on coverage. The body of reactions of dioxygen and hydrogen peroxide which afford oxometal complexes is far too extensive to be treated efficiently here. However, reaction products are frequently the same as those of the reagents in Table 1, and several such instances are recounted. Systems involving oxidative transformations of organic substrates via oxo- and peroxometal catalysts fall beyond the purview of this treatment, although many of the catalysts themselves are discussed. Leading aspects of these epoxidation and hydroxylation reactions are summarized elsewhere.[33-38]

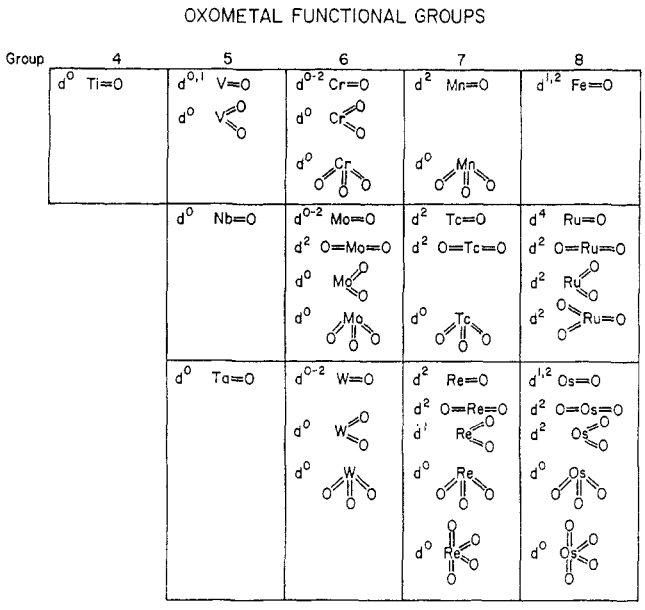


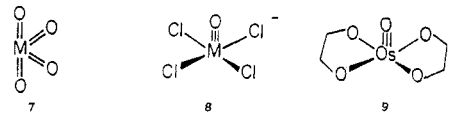
Figure 1. Depiction of known oxometal functional groups by metal and oxidation state. Many compounds in which these groups occur are contained in Tables 2 and 3 and ref 8. Others are given in the text.

C. Oxometal Functional Groups

All oxo transfer reactions involve as reactant, final product, or intermediate an oxometal species containing a terminal oxo ligand. Accordingly, by way of pertinence and general background, known oxometal *groups* are identified and exemplified, whether or not they are known to be implicated in oxo transfer processes. Not included in the following structural tabulations are many of the simpler oxometal compounds such as tetraoxo and oxo halide molecules and molecular ions. These have been described by Griffith,[8] whose 1970 review of the subject remains valuable.

1. Mononuclear

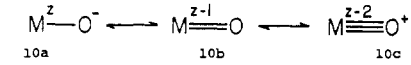
Oxo ligands are stabilized at highly oxidized metal centers. Oxometal groups which have been structurally defined by X-ray diffraction are MO (**2**), linear MO_2 (**3**), bent MO_2 (**4**), and pyramidal MO_3 (**5**). In addition, there is one example of a planar MO_3 group (**6**) and spectroscopic evidence for the cis-octahedral fragment group MO_4 (**7**). These are illustrated in Table 2, which



7 8 9

contains molecular examples with pertinent structural parameters of each group. The occurrence of these groups with different metals is summarized in Figure 1. In general, metal–oxo bonds have lengths of 1.6–1.8 Å and stretching frequencies in the range ca. 850–1100 cm^{-1}, both properties conveying their multiple-bond character. Single bonds to a given metal by neutral and anionic oxygen donors are usually 0.2–0.4 Å longer. The groups MnO, FeO, bent RuO_2, bent OsO_2, ReO_4, and OsO_4 have not been structurally established, but spectroscopic and reactivity properties substantiate their existence. Metal–oxo bonds are usually designated here as M=O, with recognition that bond order may vary depending on the d^n configuration, the presence and nature of trans ligands, and the coordination stereochemistry. The original Ballhausen–Gray MO treatment of VO^{2+} [111] made evident the possibility of a triple bond of electron configuration $...\sigma^2\pi^4$, with the oxo ligand acting as a π-donor to a d^{0-2} metal. The square-pyramidal complexes **8** (M(V) = Nb, Cr, Mo, Tc, Re) and the Os(VI) complex **9**, having relatively short metal–oxo bonds, approach bond order 3 as closely as any species in Table 2. Rappé and Goddard[112] favor the partial triple-bond representation M≡M from the results of ab initio calculations of d^0 molecules. The assembled data reveal several other key features of a M=O group: a strong trans effect on the bond length (and lability) of an opposite ligand; movement of the metal by an amount δM out of the axial ligand plane toward the oxo ligand; a slight increase in the M=O distance and a larger decrease in the δM distance when an axial ligand is present.

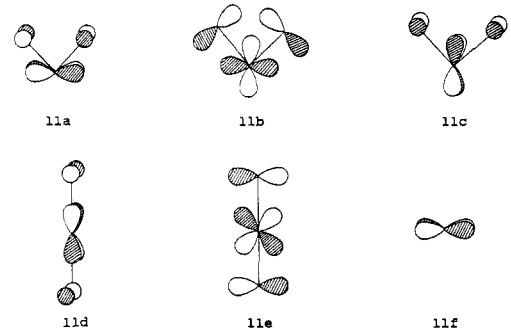
The summary in Figure 1 and other information which follows supply the most important generalization in metal–oxo chemistry: *M=O groups are stabilized at metal centers with an oxidation state of no less than 4+ and no more than four d electrons.* Oxo–metal bonds are describable by the canonical forms **10a–c**,



10a 10b 10c

which show that the metal must be a π-acceptor and adequately electron deficient so as to induce charge distribution as in contribution **10b**. Metal atoms with configurations d^{0-4} have vacant or half-filled π-acceptor orbitals necessary for this interaction. No stable M=O groups are known for any transition metal to the right of group 8. Oxo-element groups are prevalent in the chemistry of groups 15–18, with the same restriction on oxidation state.

The most prevalent dioxometal groups are stabilized under the same conditions as MO groups, and with the regularity that d^0 and d^2 metals sustain the bent (**4**) and linear (**3**) geometries, respectively. The dominant cause of this behavior lies in the relative strengths of M=O bonds and has been recognized on symmetry grounds for some time.[113] In type **4** one pπ orbital of each oxygen atom interacts with a separate dπ orbital, and the third dπ orbital mixes with the remaining two pπ orbitals. The situation is illustrated in **11a–c**. The im-

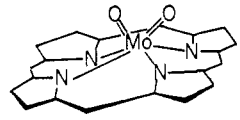


11a 11b 11c 11d 11e 11f

portant π-interactions in linear group **3** are **11d,e**, with the electron pair in nonbonding orbital **11f**. In the d^0 case π-bonding involves three d orbitals in the bent and two in the linear arrangement and thus leads to a higher π-bond order when bent. If the d^2 case were bent, one of the dπ orbitals would be destabilized by π-bonding, whereas two are stabilized and one is unaffected in the

linear configuration. These considerations follow from the analysis of Tatsumi and Hoffmann.[114] The pyramidal MO_3 (5) and MO_4 (7) groups are known only for d^0 metals with oxidation states of 6+ to 8+; the latter occurs only in the cis-octahedral configurations. Alternative arrangements containing one (5) and two (7) linear fragments are disfavored by competing oxo–metal π-interactions.

The simplicity of the preceding rationalizations of oxometal group structures is justified by the near absence of exceptions to the predicted structures. Several apparent exceptions are noted subsequently. There is no better example of the tendency of a d^0 MO_2 group to bend than MoO_2(TTP) (12). The bent configuration



12

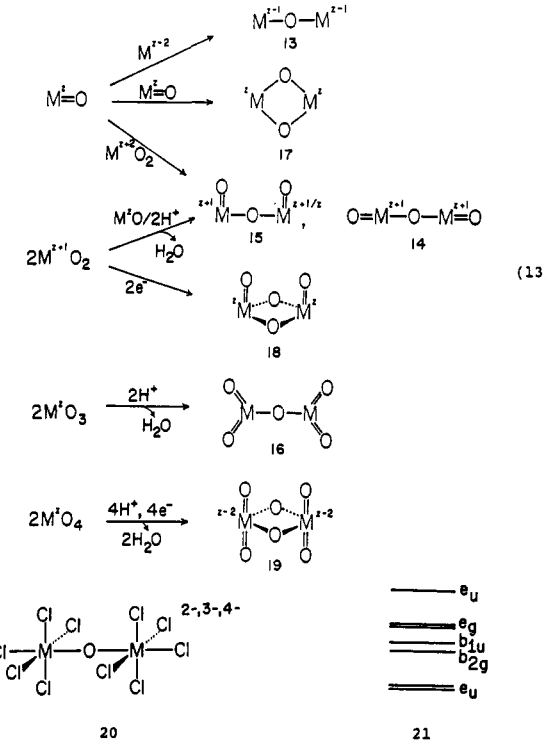
is maintained at the expense of a severe distortion of the porphyrin to a saddle-shaped configuration with attendant placement of the Mo atom 0.97 Å above the N_4 plane and formation of a distorted trigonal-prismatic MoO_2N_4 coordination unit.[92] Calculations at the extended-Hückel level for the MoO_2^{2+} group indicate an energy minimum at a bond angle of ~110°,[114] in good agreement with the large majority of observed structures.

The oxo group is formally a four- or six-electron donor. As such, it is isoelectronic with η^2-O_2^{2-},[115] η^2-S_2^{2-},[116] η^2-RNO^{2-}, S^{2-} and Se^{2-},[117] RN^{2-},[118] N^{3-},[119] and RCH^{2-}[120] when a four-electron donor and with all but the η^2 ligands and RCH^{2-} when a six-electron donor. Consequently, there are a number of species with the same or mixed ligands that are effectively isoelectronic with one another and with well-known oxo complexes. These ligands form short, multiple bonds to metals with the same stabilization restrictions as for M=O bonds. All such bonds are polarized as in $M^{\delta+}=O^{\delta-}$, the terminal atom being nucleophilic. Other than a few reactions of the M=S group and several instances of metal-mediated transfer of nitrene and carbene equivalents, a reaction chemistry analogous to oxo transfer has not been developed for the remaining ligands.

Species such as $[VO_4]^{3-}$, $[MnO_4]^{2-,3-}$, and RuO_4, which depart from the stability rules of 7, are tetrahedral molecular ions or molecules rather than functional groups. The anions are stabilized in the solid by electrostatic interactions and in aqueous solution by hydrogen bonding. However, neither manganate nor hypomanganate ion is particularly stable. Both are readily oxidized to permanganate, and manganate disproportionates to $[MnO_4]^-$ and MnO_2 except in very strongly alkaline solution.

2. Binuclear

Collected in Table 3 are molecular examples of binuclear oxometal groups $M_2(\mu\text{-O})$ (13), linear $M_2O_2(\mu\text{-O})$ (14), *syn-* or *anti*-$M_2O_2(\mu\text{-O})$ (15), $M_2O_4(\mu\text{-O})$ (16), $M_2(\mu\text{-O})_2$ (17), *cis-* or *trans*-$M_2O_2(\mu\text{-O})_2$ (18), and $M_2O_4(\mu\text{-O})_2$ (19). Also included for comparison are $[M_2O_7]^{0,2-,4-}$, the most familiar oxometal species with a single μ-O bridge. Some of the ways in which these groups may be formed from mononuclear groups 2–7 are summarized in reaction set 13. Formation of 13–15 is anticipated by reaction 8. The familiar triangular $M_3(\mu_3\text{-O})$ group is excluded because it is not known to be formed by means similar to those in scheme 13 and no molecule containing it has been implicated in an oxo transfer reaction.



(13)

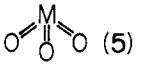
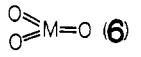
20 21

Unsupported bridge group 13 is stabilized by metals in oxidation state 3+ or higher. The most familiar examples are encountered with Fe(III) and in the series $[M_2OCl_{10}]^{4-}$ (20). At least in the solid state, bond angles in ferric complexes, all of which are antiferromagnetically coupled, range over 140–180°. The linearity, bond lengths indicative of some double-bond character, and diamagnetism of the 4– complexes 20 are accountable by the original Dunitz–Orgel model of bridge bonding.[195] Under D_{4h} symmetry with the z axis coincident with the M–O bond, metal $d_{xz,yz}$ and oxygen $p_{x,y}$ orbitals combine to give bridge orbitals $e_u + e_g + e_u^*$. The remaining, nonbonding orbitals $b_{1u} + b_{2g}$ are combinations of d_{xy}. For d^4 metals all bonding and nonbonding orbitals are filled. The mixed-valence complex $[Re_2OCl_{10}]^{3-}$ is paramagnetic. The newest complex 20 is $[Ta_2OCl_{10}]^{2-}$,[127] in which only the bonding e_u orbitals are filled. The only other characterized Ta_2O group is in $Ta_2O(NHMe)_2(NMe_2)_4Cl_4$. The group is nearly linear; its longer bond distances are likely due to π-bonding of the d^0 metal with the dimethylamido groups cis to the oxo ligand. This interaction competes with Ta–O π-bonding and otherwise diminishes electron deficiency at the Ta atom. The planar dioxo bridge unit 17 is an uncommon structural element and has been encountered thus far in species with the 4+ metal oxidation state and, in one case, $[Mn_2O_2(bpy)_4]^{3+}$, with 3+ and 4+ metals. The presence of highly oxidized metals here and to a lesser extent in 13 presumably diminishes the basicity of the oxo bridges to the point where they are not subject to protonation and cleavage under roughly neutral protic conditions. The sharp decrease in bridge angle upon passing from Ti(IV) to Tc(IV) and

TABLE 2. Structural Features of MO, MO_2, and MO_3 Groups in Selected Complexes

ox. state	complex	M=O, Å	δM^a (Å), O=M=O (deg)	ref
		M=O (2)		
Ti(IV)	TiO(OEP) (30)	1.613 (5)[b]	0.56	39
	$TiO(OEPMe_2)$	1.619 (4)	0.58	40
V(IV)	VO(acen)	1.585 (7)	0.58	41
	$VO(ox)_2$(O-*i*-Pr)	1.600 (2)	0.28	42
	VO(OEP)	1.620 (2)	0.54	43
	VO(DPEP)	1.63 (2)	0.48	44
V(V)	$VO(S_2CNEt_2)_3$	1.65 (2)		45
Nb(V)	$[NbOCl_4]^-$ (8)	1.70 (2)	*d*	46
	$[NbO(CN)_5]^{2-}$	1.70 (4)	*d*	47
	$NbO(bpy)(OEt)Cl_2$	1.71 (4)		47
	NbO(TPP)(OAc) (51)	1.720 (6)	1.00	48
	$NbO(S_2CNEt_2)_3$	1.74 (1)		45
Cr(IV)	CrO(TPP) (39)	1.62 (2)	0.49	49
	CrO(TTP) (39)	1.572 (6)	0.47	50
Cr(V)	$[CrOCl_4]^-$ (7)	1.519 (12)	0.56	51
	$[CrO(salen)]^+$ (43)	1.49 (4)	0.5	52
	$[CrO(saltmen)]^+$	1.545 (2)	0.53[c]	53
	$[CrO(saltmen)(pyO)]^+$	1.554 (2)	0.26	53
	$[CrO(OCMe_2CO_2)_2]^-$	1.554 (14)	*d*	54
Cr(VI)	$CrO(O_2)_2(py)$	1.576 (18)	*d*	55
Mo(IV)	$MoO(S_2CN(n\text{-}Pr)_2)_2$ (60)	1.664 (8)	0.83	56
	MoO(TPP)	1.656 (6)	0.64	57
Mo(V)	$[MoOCl_4(DMF)]^-$	1.653 (5)	*d*	106
	$[MoOCl_4]^-$ (8)	1.610 (10)	0.61	58
	$[MoOCl_4(OH_2)]^-$	1.66 (1)	*d*	59, 60
	$[MoOBr_4(OH_2)]^-$	1.62 (2)	*d*	61
	$[MoOI_4(OH_2)]^-$	1.65 (1)	*d*	61
	$[MoO(edt)_2]^-$	1.678 (5)	0.76	62
Mo(VI)	$[MoO(O_2)F_4]^{2-}$	1.64 (3)		63
W(IV)	$WOCl_2(C_2H_4)(PMePh_2)_2$	1.716 (4)		64
	$WOCl_2(CO)(PMePh_2)_2$	1.689 (6)		65
W(V)	$[WO(edt)_2]^-$	1.641 (10)	0.74	62
W(VI)	$WOCl_4(PhN(O)NPh)$	1.669 (18)	*d*	66
	$[WO(O_2)F_4]^{2-}$	1.74 (3)		67
	$WO(CHCMe_3)(PMe_3)_2Cl_2$	1.675 (15)		68
Tc(V)	$[TcOCl_4]^-$ (8)	1.610 (4)	*d*	69
	TcO(salen)Cl	1.626 (11)	*d*	70
	$[TcO(edt)_2]^-$	1.64 (1)	0.76	71
Re(V)	$[ReOBr_4(OH_2)]^-$	1.71 (4)	0.32	72
	$[ReO(edt)_2]^-$	1.742 (16)	*d*	73
	$ReOCl_3(PPh_3)_2$ (trans)	1.60		74
	$ReOCl_2(PPh_3)$(abh)	1.685 (8)		75
Ru(IV)	$[RuO(tmc)Cl]^+$	1.765 (7)		415
Os(VI)	$OsO(O_2C_2H_4)_2$ (9)	1.670 (12)	0.64	76
		O=M=O (3)		
Mo(IV)	$[MoO_2(CN)_4]^{4-}$	1.834 (9)	180	77
Tc(V)	$[TcO_2(en)_2]^+$	1.747 (8)	178.6 (3)	78
	$[TcO_2(cyclam)]^+$	1.751 (4)	180	79
Re(V)	$[ReO_2(py)_4]^+$	1.76 (3)	174.5 (4)	80, 81
	$[ReO_2(en)_2]^+$	1.765 (6)	179.3 (3)	81
	$[ReO_2(CN)_4]^{3-}$	1.78 (1)	180	82, 83
Ru(VI)	$[RuO_2(tmc)]^{2+}$	1.705 (7)	180	413
	$RuO_2(py)_2(OAc)_2$	1.726 (1)	180	414
Os(VI)	$[OsO_2Cl_4]^{2-}$	1.75 (2)	180	84
	$[OsO_2(OH)_4]^{2-}$	1.77	180	85
	$[OsO_2(en)_2]^{2+}$	1.74 (1)	180	86
		 (4)		
V(V)	$[VO_2(C_2O_4)_2]^{3-}$	1.642 (9)	103.8 (1)	87
	$[VO_2(ox)_2]^-$	1.62 (1)	106.1 (5)	88
	$[VO_2(EDTA)]^{3-}$	1.65 (1)	107.0 (1)	89
	$[VO_2((S)\text{-peida})]^-$	1.63 (2)	105.7 (1)	90
Mo(VI)	$[MoO_2F_4]^{2-}$	1.71 (2)	95 (1)	91
	$MoO_2(TTP)$ (12)	1.73 (2)	0.97, 95.1 (4)	92
	$MoO_2((R)\text{-salpn})$	1.709 (1)	103.2 (1)	93
	$MoO_2(S_2CN(n\text{-}Pr)_2)_2$ (61)	1.696 (1)	105.7 (1)	56
	$MoO_2(S_2CNEt_2)_2$ (61)	1.703 (2)	105.8 (1)	94
	$MoO_2(tox)_2$	1.705 (16)	106.3 (3)	95
	$MoO_2(H_2NCMe_2CH_2S)_2$	1.705 (3)	106.7 (2)	96
	$MoO_2((S)\text{-pen·OMe})_2$ (A)	1.716 (5)	107.0 (2)	97
	MoO_2(L-Cys·OMe)$_2$	1.714 (4)	108.1 (3)	98

TABLE 2 (Continued)

ox. state	complex	M=O, Å	δM[a] (Å), O=M=O (deg)	ref
	MoO_2(L-NS_2) (68)	1.705 (3)	110.5 (3)	99
	MoO_2(dttd)	1.72 (2)	111.1 (1)	100
	$MoO_2(Me_2NCH_2CMe_2S)_2$[e]	1.720 (3)	122.0 (3)	101
	$MoO_2(MeNHCH_2CMe_2S)_2$[e]	1.716 (5)	122.2 (8)	101
W(VI)	$[WO_2Cl_2(acac)]^-$	1.729 (7)	d	102
	$[WO_2(O_2C_2Me_4)(CH_2CMe_3)]^-$	1.716 (6)	110.4 (3)	103
	$CpWO_2(CH_2SiMe_3)$	1.720 (5)	107.8 (3)	104
Re(VI)	$ReO_2(mes)_2$	1.688 (5)	121.5 (4)	105
Os(VI)	$OsO_2(mes)_2$	1.695 (7)	136.1 (3)	105
	 (5)			
Mo(VI)	MoO_3(dien)	1.736 (2)	105.8 (9)	107
	$[(MoO_3)_2(EDTA)]^{4-}$	1.74 (1)	106 (2)	108
Re(VII)	$[ReO_3(tacn)]^+$	1.756 (5)	102.7 (4)	109
	 (6)			
Ru(VI)	$[RuO_3(OH)_2]^{2-}$ (97)	1.754 (5)	119.2 (14)	110

[a] Distance of metal atom from coordination mean plane. [b] Number in parentheses is the esd of a single value or the esd of the mean of two or more values. [c] Disordered structure. [d] Not reported. [e] Skew-trapezoidal structure.

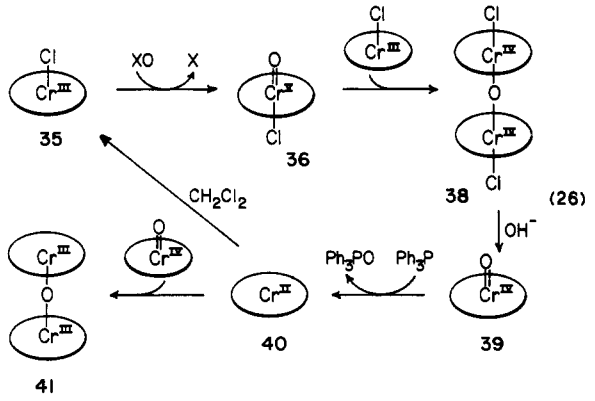


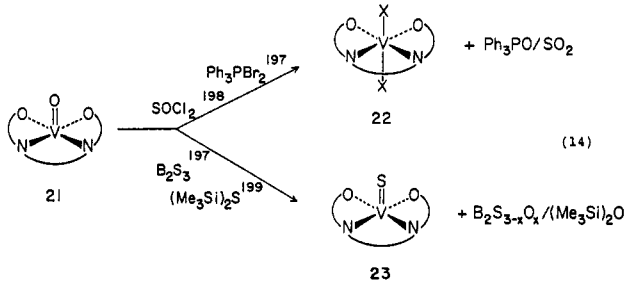
Figure 2. Reaction scheme of chromium porphyrins, including primary and intermetal oxo transfer reactions.

Re(IV) occurs because of metal–metal bonding. The diamagnetic d^3–d^3 complexes $Tc_2O_2(H_2EDTA)\cdot 5H_2O$[184] (2.33 Å) and $[Re_2O_2(C_2O_4)_4]^{4-}$[185] (2.36 Å) have the indicated metal–metal distances. Extended-Hückel calculations on the former support a bond order near 2.

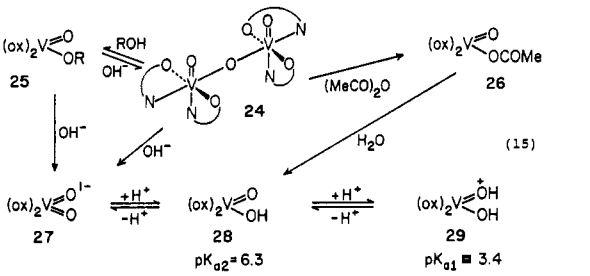
The remaining bridging groups are usually stabilized by metal oxidation states the same as or one unit less than those of the mononuclear groups from which they are derivable by the reactions 13. As noted above, several of these groups have alternative geometries. The linear form **14** of M_2O_3 is consistently observed with Re(V) (d^2) but is doubtless sterically forced in paramagnetic $Mo_2O_3(TPP)_2$.[154] All other d^1–d^1 M_2O_3 groups are diamagnetic and bent at the metal atoms (**15**), permitting syn and anti conformations. $W_2O_3(CH_2CMe_3)_6$ provides the only case of a d^0–d^0 M_2O_3 group.[155] Its linearity may be partially stabilized by the steric demands of the neopentyl groups. As will be seen, certain of these binuclear groups appear in the products of oxo transfer reactions. Numerous other examples of terminal and bridging M–O interactions are found in the isopoly- and heteropolyoxometalates.[196]

3. Functional Group Concept

In contrast to a conventional circumstance in organic chemistry, regiospecific reactions of inorganic compounds are less readily accomplished in the main, owing to the presence of competing reaction sites offered by highly polar and relatively weak bonds. The situation is improved if the putative functional group is supported by a less reactive ligand system, as is sometimes the case with oxometal complexes. Consider the localized reactivity of oxovanadium(IV,V) groups as established by Floriani and co-workers, who have drawn analogies between these groups and organic functionalities. Complexes such as VO(salen) (**21**) are efficiently transformed in the reactions 14 with oxophilic reagents to **22** (X = Cl^-, Br^-) and **23**. Reaction product V-



(acen)Cl(THF), from **21** and $TiCl_3(THF)_3$,[198b] is a useful precursor, affording $[RV(acen)]_2$ in reactions with RMgX.[200] Reactions 15 based on $V_2O_3(ox)_4$ (**24**) better emphasize the organic functional group analogy. Thus,



"anhydride" **24** can be esterified (**25**), acylated (**26**), and base-hydrolyzed to a product (**27**) which can be protonated (**28**, **29**).[88] Complexes **25** and **28** evidently have reactivity characteristics of esters and carboxylic acids, respectively. Transformations 13 and the metal-centered oxo transfer reactions that follow are examples of regiospecific processes. These further support the concept of oxometal units as functional groups, a be-

TABLE 3. Structural Features of Selected Binuclear μ-Oxo Complexes

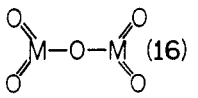
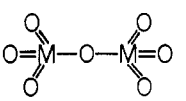
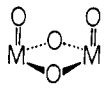
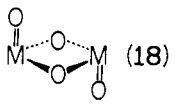
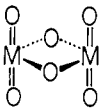
ox. state	complex	M–O, Å	M=O, Å	M–O–M, deg	ref
		M–O–M (13)			
Ti(III)	Cp_4Ti_2O	1.838 (1)[a]		170.9 (4)	121
Ti(IV)	$[Ti_2O(O_2)_2(NTA)_2]^{4-}$	1.819 (2)		167.6 (2)	122
	$Ti_2O(acac)_4Cl_2$	1.80 (1)		168 (1)	123
	$Cp_4Ti_2OCl_2$	1.837 (2)		173.8	124
V(III)	$V_2O(THF)_6Cl_4$	1.769 (5)		180	125
Nb(V)	$[Cp_4Nb_2OCl_2]^{2+}$	1.88 (1)		169.3 (8)	126
Ta(V)	$[Ta_2OCl_{10}]^{2-}$ (**20**)	1.880 (1)		180	127
	$Ta_2O(NHMe_2)_2(NMe_2)_4Cl_4$	1.923 (8)		174.3 (3)	128
Cr(III)	$[Cr_2O(NH_3)_{10}]^{4+}$	1.821 (3)		180	129, 130
	$[Cr_2O(NCS)_2(TPyEA)_2]^{2+}$	1.82 (1)		176.5	131
	(TPP)(py)CrOFe(TMeP)	*b*		178 (2)	132
Mo(IV)	$[Mo(TPP)Cl]_2O$	1.851 (6)		177.5 (3)	133
Mo(IV,V)	$[Mo_2O(S_2CNEt_2)_6]^+$	1.848 (2)		175.6 (2)	134
W(IV)	$[W_2OCl_{10}]^{4-}$ (**20**)	1.87 (1)		180	135
Mn(III)	$[Mn_2O(CN)_{10}]^{6-}$	1.723 (4)		180	136
	$Mn_2O(Pc)_2(py)_2$	1.71 (1)		180	137
	$Mn_2O(TPP)_2(N_3)_2$	1.743 (4)		180	138
		1.794 (4)			
Re(IV)	$[Re_2OCl_{10}]^{4-}$ (**20**)	1.86 (1)		180	140
Re(IV,V)	$[Re_2OCl_{10}]^{3-}$ (**20**)	1.832 (3)		180	139
Fe(III)	$Fe_2O(salen)_2{\cdot}2py$	1.80 (3)		139.1 (9)	141
	$Fe_2O(FFP){\cdot}H_2O{\cdot}2PhMe$	1.787 (18)		161.4 (1)	142
	$[Fe_2O(HEDTA)_2]^{2-}$	1.80 (1)		165.0 (8)	143
	$[Fe(3\text{-}t\text{-}Busaltmen)]_2O$	1.779 (5)		173.4 (3)	144
	$Fe_2O(TPP)_2$ (**54**)	1.763 (1)		174.5	145
	$Fe_2O(cpdc)_2(OH_2)_2$	1.773 (1)		180	146
Ru(III)	$[Ru_2O(bpy)_4(NO_2)_2]^{2+}$	1.883 (10)		157.2 (3)	147
Ru(IV)	$[Ru_2OCl_{10}]^{4-}$ (**20**)	1.80 (2)		180	148, 149
	$Ru_2O(TPP)_2(p\text{-}tolO)_2$ (**99**)	1.789 (11)		177.8 (7)	150
	$Ru_2O(OEP)_2(OH)_2$[c] (**99**)	1.847 (13)		180	151
Os(IV)	$[Os_2OCl_{10}]^{4-}$ (**20**)	1.778 (2)		180	152
	$[Os_2O(chba\text{-}Et)_2(OPPh_3)_2]^{2-}$	1.795		175	153
		O=M–O–M=O (14)			
Mo(V)	$Mo_2O_3(TPP)_2$	1.936 (3)	1.707 (3)	178.6 (1)	154
W(VI)	$W_2O_3(CH_2CMe_3)_6$	1.977 (10)	1.726 (10)	180	155
		1.923 (10)	1.689 (13)		
Re(V)	$Re_2O_3(py)_4Cl_4$	1.903 (16)	1.764 (16)	174.5 (9)	156
		1.943 (16)	1.715 (16)		
	$Re_2O_3(en)_2Cl_4$	1.912 (5)	1.65 (5)	180	157
	$[Re_2O_3(CN)_8]^{4-}$	1.915 (1)	1.698 (7)	180	158
	$Re_2O_3(S_2CNEt_2)_4$	1.920 (7)	1.722 (1)	180	159
		 (15)			
V(IV,V)	$[V_2O_3(pmida)_2]^-$	1.81 (2)	1.606 (19)	175.3 (7)	160
	$[V_2O_3((S)\text{-}peida)_2]^-$	1.875 (4)	1.618 (6)	179.5 (3)	161
	$[V_2O_3(NTA)_2]^{3-}$	1.810 (1)	1.607 (6)	180	162
V(V)	$V_2O_3(ox)_4$ (**24**)	1.779 (2)	1.587 (6)	173.4 (4)	161
Mo(V)	$Mo_2O_3(S_2CS\text{-}i\text{-}Pr)_4$	1.84 (1)	1.69 (1)	170.3 (8)	163
	$Mo_2O_3(S_2COEt)_4$	1.86 (1)	1.65 (1)	178 (4)	164
	$Mo_2O_3(S_2CN(n\text{-}Pr)_2)_4$ (**76**)	1.87 (1)	1.68 (1)	178.1 (7)	56
	$Mo_2O_3(S_2P(OEt)_2)_4$	1.86 (1)	1.65 (1)	180	165
	$[Mo_2O_3(NCS)_8]^{4-}$	1.849 (1)	1.661 (5)	180	166
	$Mo_2O_3Cl_4(py)_4$	1.858 (1)	1.675 (8)	180	167
W(VI)	$[W_2O_3(O_2)_4(OH_2)_2]^{2-}$	1.93 (2)	1.66	139	168
		 (16)			
Mo(VI)	$Mo_2O_5(mtd)_2$	1.923 (8)	1.713 (3)	143.8 (2)	169
	$[Mo_2O_5(HNTA)_2]^{2-}$	1.876 (8)	1.693 (7)	167.0 (2)	170
	$[Mo_2O_5(Me_4tacn)_2]^{2+}$	1.898 (1)	1.695 (1)	180	171
	$[Mo_2O_5(xanthopterinate)_2]^{2-}$	1.884 (1)	1.696 (16)	*b*	194
					
V(V)	$Cd_2[V_2O_7]$	1.76 (1)	1.69 (3)	180	172
Cr(VI)	$K_2[Cr_2O_7]$	1.786 (4)	1.629 (11)	106	173
Mo(V)	$[Mo_2O_7]^{2-}$[g]	1.876 (2)	1.716 (4)	153.6 (5)	174
	$Mg[Mo_2O_7]$	1.869 (17)	1.734 (26)	160.7 (3)	175

TABLE 3 (Continued)

ox. state	complex	M–O, Å	M=O, Å	M–O–M, deg	ref
	$K_2[Mo_2O_7]\cdot KBr$	1.87	1.72	180	176
Mn(VII)	Mn_2O_7	1.770 (3)	1.595 (8)	120.7	177
Tc(VII)	Tc_2O_7 (87)	1.840 (1)	1.672 (23)	180	178
Re(VII)	$Re_2O_7(OH_2)_2$ (86)	1.80 (2) 2.10 (2)	1.76 (3)	179.3	179
	 (17)				
Ti(IV)	$Ti_2O_2(acac)_4$	1.828 (5)		96.6 (2)	180
	$(Cp^*Ti)_2O_2(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)$ (32)	1.961 (3) 1.787 (3)		93.1 (1)	181
Mn(III,IV)	$[Mn_2O_2(bpy)_4]^{3+}$	1.855 (2)[e] 1.784[f]		90.3 (1.4)	182
	$[Mn_2O_2(phen)_4]^{3+}$	1.814 (7)		96.0 (1)	183
Mn(IV)	$[Mn_2O_2(phen)_4]^{4+}$	1.800 (4)		99.5 (2)	183
Tc(IV)	$Tc_2O_2(H_2EDTA)_2$	1.913 (8)		75.2 (3)	184
Re(IV)	$[Re_2O_2(C_2O_4)_4]^{4-}$	1.937 (19)		75.2 (8)	185
	  (18)				
Mo(V)[d]	$[Mo_2O_4Cl_4]^{2-}$	1.92 (2)	1.69 (1)	85 (1)	186
	$Mo_2O_4(L\text{-}Cys\text{-}OEt)_2$	1.93 (2)	1.66 (1)	83.0 (4)	187
	$[Mo_2O_4(L\text{-}Cys)_2]^{2-}$	1.93 (2)	1.71 (1)	83.4 (2)	188
	$Mo_2O_4(S_2CNEt_2)_2$	1.941 (2)	1.679 (2)	83.4 (1)	56
	$Mo_2O_4(bpy)_2Cl_2$	1.94	1.63 (3)	83.4 (6)	189
	$[Mo_2O_4(tacn)_2]^{2+}$ (67)	1.945 (14)	1.695 (6)	82.1 (9)	190
	$[Mo_2O_4(tacn)_2]^{2+}$ (66, trans)	1.942 (1)	1.696 (5)	82.6 (2)	190
	$[Mo_2O_4(tacd)_2]^{2+}$ (66, trans)	1.951 (5)	1.695 (6)	83.0 (1)	191
Os(VI)	$Os_2O_4(O_2C_2Me_4)_2$ (trans)	1.92 (3)	1.675 (7)	103.9 (4)	192
	 (19)				
Os(VI)	$[Os_2O_6(NO_2)_4]^{4-}$	1.99 (2)	1.79 (1)	102	193

[a] Cf. footnote *b*, Table I. [b] Not reported. [c] Formulation questioned.[150] [d] Cis configuration unless otherwise noted. [e] Mn(III). [f] Mn(IV). [g] *n*-Bu_4N^+ salt.

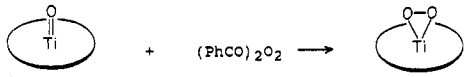
havior that relies much on structural constancy and stability and on $M^{\delta+}{=}O^{\delta-}$ bond polarity. Differences in behavior of a given group type appear to have less to do with variations in these factors than with the relative stabilities of oxidation states.

III. Primary Oxo Transfer Reactions

Before proceeding to an examination of the primary reaction 7, it is useful for classification purposes to cite examples of oxygen atom transfer reactions that are *not* of this type. While these reactions can be identified by their failure to meet one or more of the requirements i–iii on reaction 7, a closer look will help facilitate such identification. In reactions 16[201] and 17,[202] oxo is sub-

$$ReO(PPh_3)_2Cl_3 + PhNCO \longrightarrow Re(NPh)(PPh_3)_2Cl_3 + CO_2 \quad (16)$$

$$MoO_2(S_2CNEt_2)_2 + p\text{-tolNHOH} \longrightarrow MoO(p\text{-tolNO})(S_2CNEt_2)_2 + H_2O \quad (17)$$

 (18)

TiO(OEP) (30) $\qquad$ Ti(O_2)(OEP) (31)

$$Ni(PR_3)_2(N{\bullet})_2 + CO \longrightarrow Ni(PR_3)_2(N{\bullet})(N{\bullet}_2) + CO{\bullet} \quad (19)$$

$$Co(saloph)(NO_2)(py) + Ph_3P \longrightarrow Co(saloph)(NO)(py) + Ph_3PO \quad (20)$$

$$Ni(O_2)(RNC)_2 + 4RNC \longrightarrow Ni(RNC)_4 + 2RNCO \quad (21)$$

$$Ir(PPh_3)_2(N_2)Cl + 4NO \longrightarrow Ir(PPh_3)_2(NO)(NO_2) + N_2 + N_2O \quad (22)$$

stituted by an isoelectronic ligand with no change in metal oxidation state. In reaction 18,[39] an oxygen atom is transferred to the titanyl group of **30**, whose oxo ligand is oxidized to peroxide; the metal remains Ti(IV). The η^2-bonding mode in **31** has been proven by X-ray diffraction.[39] Reactions 19[203] and 20[204] are examples from a large set in which coordinated nitrite acts as an oxygen atom donor to a variety of substrates.[205] These are ligand-based, secondary oxo transfers. The metals do undergo redox changes in reactions 20, 21,[206] and 22,[207] but no oxo functional groups are in the products or are otherwise implicated in the reactions. Lastly, a particularly common process is the generalized version of reaction 17: $M^zO_aL_n + 2HL' \rightarrow M^zO_{a-1}L_nL'_{1,2} + H_2O$ (a = 1, 2). This is merely elimination of an oxo ligand with no change in oxidation state and possible retention of ligand L′ in the coordination sphere. Reaction types exemplified by (16)–(22) are not considered further.

In the sections which follow, primary oxo transfer reactions are organized in terms of individual metals. For each metal, oxygen atom addition (oxidative) and removal (reductive) reactions are tabulated. Specified products are final products of oxo transfer processes; many of these have been isolated. In a few instances these products are not the ultimate products of the reaction systems, there being further degradative or other reactions. When the product of reactant X/XO is simply XO/X, as in reaction 7, it is not listed. Only those reactions are included for which there is at least some modicum of identification of the metal-containing product. While not exhaustive, coverage is sufficiently extensive to expose all leading reaction variations, in-

TABLE 4. Oxo Transfer Reactions of Titanium and Vanadium Compounds

species	reactant	product	ref
		Ti(II) → Ti(IV)	
Cp^*_2Ti	N_2O	$(Cp^*Ti)_2O_2(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)$ (**32**)	181
		V(II) → V(III–V)	
Cp_2V	N_2O	$Cp_5V_5O_6$ (**33**)	10, 11
Cp_2V	Me_3NO (PhMe)	$Cp_{11}V_{13}O_{18}(NMe_3)_2$	215
		$Cp_5V_6O_{17}$	216
Cp_2V	Me_3NO (THF)	$Cp_{14}V_{16}O_{24}$	215
Cp_2V	pyO (PhMe)	$Cp_4V_4O_4 + Cp_6V_6O_8$	216
$[V(OH_2)_6]^{2+}$	pyrO	$[V(OH_2)_6]^{3+}$ [a]	217
$[V(OH_2)_6]^{2+}$	$[Ru(NH_3)_5(pyrO)]^{2+}$	$[V(OH_2)_6]^{3+}$ [a] + $[Ru(NH_3)_5(pyr)]^{2+}$	217
$[V(OH_2)_6]^{2+}$	$[Ru(NH_3)_5(N_2O)]^{2+}$	$[V(OH_2)_6]^{3+}$ [a] + $[Ru(NH_3)_5N_2]^{2+}$	219
		V(IV) → V(V)	
$VO(ox)_2(py)$	ArNO	$V_2O_3(ox)_4$ (**24**)	218
$Cp^*_2VCl_2$	NO	Cp^*VCl_2O	220

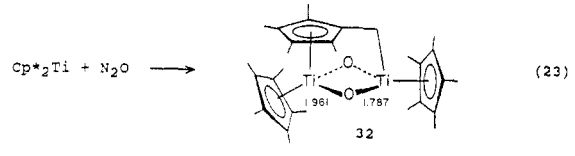
[a] Formation not directly established.

cluding oxygen atom donors and acceptors, metal oxidation state changes, ligand influences, and product stereochemistry. Most structures referred to are in Tables 2 and 3. Reactions of peroxometal complexes, even if they contain oxo ligands or are converted to oxo species, are omitted inasmuch as the overwhelming number of them result in the oxidation of organic compounds. Other reactivity aspects of oxometal complexes not already mentioned—non-oxo ligand substitution[208] and ^{18}O aqueous exchange[209,210]—have recently been treated.

A. Titanium

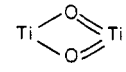
Discrete $Ti^{IV}{=}O$ species are few and usually do not exist in the solid state in favor of polymerization by –Ti–O–Ti–O– chains. The individual Ti^{IV}–O–Ti^{IV} unit is well characterized in a number of compounds.[121-124] $TiO(acac)_2$ is not monomeric but is a dimer with a Ti_2O_2 bridge **17**. In $(Et_4N)_2[TiOCl_4]$[211] the anion is square pyramidal and contains a Ti=O group, but its bond length (1.79 Å), from a preliminary structure determination,[212] is suggestive of Ti=O···Ti stacking. The use of this complex in the synthesis of oxotitanium compounds has not been explored. The nature of Ti(IV) in aqueous acid is complicated; both the mononuclear TiO^{2+} ion and oligomers not containing the titanyl group are present.[213] In three acid media a reaction described as $TiO^{2+} + H_2O_2 \rightarrow Ti(O_2)^{2+} + H_2O$ occurs.[214] If the species are correctly formulated, it is analogous to reaction 18, whose reactant and product structures are known. The only structurally authenticated discrete Ti=O groups are in two porphyrin complexes where bond lengths are 1.61–1.62 Å. The TiO_2 group, bent or linear, is unknown.

Reaction 23, listed in Table 4, is the only oxo transfer reaction of a titanium compound (excluding here and subsequently, as noted earlier, reactions of dioxygen and hydrogen peroxide). Titanium(II) is oxidized to Ti(IV),



32 (23)

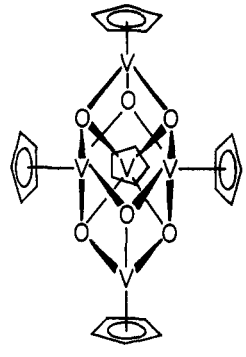
with dinitrogen oxide being the only source of oxygen in the product **32**. This compound contains only the second example of a Ti_2O_2 unit. Unlike that in $Ti_2O_2(acac)_4$, the bridge unit is not planar and the Ti–O distances are markedly unequal.[181] The short distance involves the 12-electron Ti(IV) center and is normal for a Ti–O bond to such an electron-deficient site; the other bond is longer than usual to 16-electron Ti(IV).[121] It has been supposed that the demands of the 12-electron center reduce the basicity of the oxo ligands to the point where a normal bond length cannot be sustained.[181] The situation approaches the limiting description



The oxidative sensitivity of Ti(II,III) complexes presages a substantial body of oxo transfer chemistry, particularly if sources of these oxidation states can be broadened beyond cyclopentadienyl-type compounds.

B. Vanadium

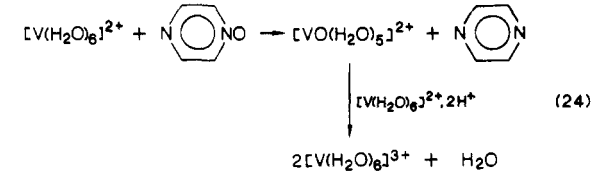
The $V^{IV}O$ and $V^{V}O_2$ groups are common structural elements. Reductive oxo transfer from these groups would afford V(II,III) species, which with π-donor ligands are expected to be readily oxidized and thus somewhat unstable reaction products. Not surprisingly, the known oxo transfer reactions, listed in Table 4, are oxidative in nature. The preparation of $Cp_5V_5O_6$ (**33**)



33

from Cp_2V is a second example of the use of N_2O as an oxygen atom donor. With Me_3NO and pyO as donors, at least five other polynuclear clusters have been obtained. Several of these have been structurally characterized as derivatives of $Cp_6V_6O_8$, in which a Cp group is substituted by a μ-O atom that is part of a smaller Cp–V–O unit.[215]

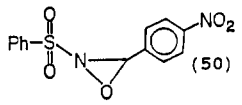
The formation of $[V(H_2O)_6]^{3+}$ from excess $[V(H_2O)_6]^{2+}$ and pyrazine *N*-oxide is most simply expressed by the coupled reactions 24. Analogous



(24)

schemes may apply to the reduction of coordinated ligands in $[Ru(NH_3)_5L]^{2+}$ (L = pyrO, N_2O) and of 2,2′-bipyridine-4,4′-disulfonic acid *N*,*N*′-dioxide,[221] all in acid solution with excess V(II). The second step is well documented.[222] These reactions are considered as probable oxo transfers and are included in Table 4 on

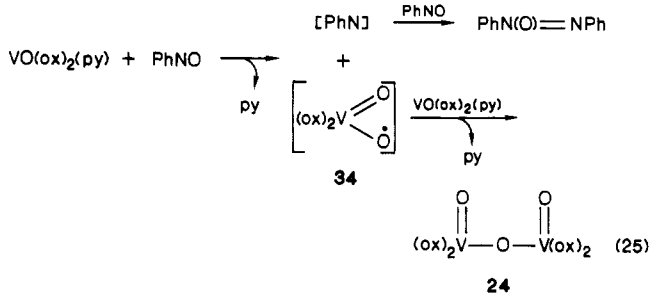
TABLE 5. Oxo Transfer Reactions of Chromium Compounds

species	reactant	product	ref
	Cr(II) → Cr(III)		
Cp_2Cr	N_2O	$Cp_4Cr_4O_4$	10, 224
Cp_2Cr	Me_3NO	$Cp_4Cr_4O_4$ + $Cp_4(\eta^2\text{-}C_5H_4)Cr_4O_3$	225
$[Cr(OH_2)_6]^{2+}$	HOCl	$[Cr_2O(OH_2)_{10}]^{4+}$	234
$[Cr(OH_2)_6]^{2+}$	ClO_3^-	$[Cr_2O(OH_2)_{10}]^{4+}$	234
	Cr(III) → Cr(IV)		
Cr(TPP)Cl (**35**)	PhIO	CrO(TPP) (**39**)	14, 16, 50, 226
Cr(P)Cl	PhIO	CrO(P)[a]	50
$Cr(TPP)(OH)\cdot 2H_2O$	PhIO	CrO(TPP)	227
Cr(TPP)Cl	NaOCl	CrO(TPP)	50
$Cr(TPP)(OH)\cdot 2H_2O$	NaOCl	CrO(TPP)	227
$Cr(OEP)(OH)\cdot {}^1/_2H_2O$	NaOCl	CrO(OEP)	227
Cr(P)Cl	*t*-BuOOH	CrO(P)[a]	50
Cr(TPP)Cl	*m*-$ClC_6H_4CO_3H$	CrO(TPP)	50, 228
	Cr(III) → Cr(V)		
Cr(TPP)Cl	PhIO (excess)	CrO(TPP)Cl (**36**)	16, 228, 229
$[SiMo_{11}O_{39}Cr(OH_2)]^{5-}$	PhIO (excess)	$[SiMo_{11}O_{39}CrO]^{5-}$	233
$[SiW_{11}O_{39}Cr(OH)]^{6-}$	PhIO (excess)	$[SiW_{11}O_{39}CrO]^{5-}$	233
Cr(TPP)Cl	ROOH[f]	CrO(TPP)Cl	16
Cr(TPP)Cl	RCO_3H[b]	CrO(TPP)Cl	16
Cr(TPP)Cl	*p*-$NCC_6H_4NMe_2O$ (*hν*) (**49**)	CrO(TPP)Cl	16, 231
Cr(TPP)Cl	 (**50**)	CrO(TPP)Cl	16
$[Cr(salen)(OH_2)_2]^+$ (**42**)	PhIO	$[CrO(salen)]^+$[c] (**43**)	52, 53, 232
$[Cr(saltmen)(OH_2)_2]^+$	PhIO	$[CrO(saltmen)]^+$[d]	53, 232
	Cr(IV) → Cr(III)		
CrO(TPP)	Ph_3P (PhH)	$[Cr(TPP)]_2O$ (**41**)	9
CrO(P)	Ph_3P (CH_2Cl_2)	Cr(P)Cl[a]	9
	Cr(V) → Cr(III)		
$[CrOCl_4]^-$ (**8**)	Ph_3P, Cl^-	$[Cr_2Cl_9]^{3-}$	230
$[CrO(salen)]^+$	Et_3P	$[Cr(salen)(OPEt_3)]^+$[e]	53

[a] P = TMP, TPP, TTP. [b] R = *m*-C_6H_4Cl, $C_{11}H_{23}$. [c] Also 5,5′-Cl_2, 7,7′-Cl_2, 7,7′-Me_2, and 7,7′-Ph_2 derivatives. [d] Also 5,5′-Cl_2 derivative. [e] Similar reactions reported with *n*-Bu_3P[52] and pyO[53]. [f] R = *t*-Bu, $Ph_2C(CN)$, $Ph_2C(CO_2Me)$, Ph_3C.

this basis. Vanadium product studies were not performed and mechanisms were not proposed. In the reduction of $[Ru(NH_3)_5(N_2O)]^{2+}$ the characteristic brown color of the VOV^{4+} aquo ion,[222] the expected intermediate in the second step, was not observed, leading to the conclusion that the mechanism does not involve a vanadium oxidation state below 3+.[219] The examination was apparently made visually and perhaps failed to detect the ion, whose decay is competitive with its rate of formation in strong acid solution.

Vanadium(IV) deoxygenates nitrosobenzene in reaction 25 with a nearly quantitative yield of azoxybenzene.



The reaction likely proceeds by the indicated scheme whose key point is the concerted development of the paramagnetic *cis*-dioxo (**34**) and nitrene intermediates which would form products by coupling to a V(IV) center and nitrosobenzene, respectively.

No reductive primary oxo transfers of VO and VO_2 groups have been described. These groups are of course reducible by electron transfer with deoxygenation to V(II,III) in aqueous acid solution. A number of chelated V(IV) complexes $VO(L\text{–}L)_2$ have been deoxygenated without change in oxidation state to $VCl_2(L\text{–}L)_2$ as in reaction 14. Recent developments in the oxygen-based chemistry of titanium and vanadium porphyrins have been reviewed.[223]

C. Chromium

Of the groups $Cr^{IV\text{-}VI}O$, $Cr^{VI}O_2$, and $Cr^{VI}O_3$ found in stable compounds, only the first has been involved in oxo transfer reactions. The latter two groups are usually encountered only in oxyhalides such as CrO_2Cl_2 and $[CrO_3Cl]^-$[8] and in $[Cr_2O_7]^{2-}$.[173] Reactions are summarized in Table 5.

Chromium(II) in Cp_2Cr is oxidized to the blue cubane cluster $Cp_4Cr_4(\mu_3\text{-}O)_4$ and a green, structurally related product in which an oxo ligand is formally replaced by dianionic $\eta^2\text{-}C_5H_4$. The reactions are complicated by the appearance of two products and because these products contain Cr(III). Any oxochromium(IV) intermediate must have been reduced, probably by unreacted Cp_2Cr. The yield of $Cp_4Cr_4O_4$ was only 21% based on Cp_2Cr consumed.[10] Nothing is known of the course of the reaction. $Cp_4Cr_4O_4$ was initially prepared from the reaction of Cp_2Cr and dioxygen.[235]

In aqueous solution the product of the oxidation of $[Cr(H_2O)_6]^{2+}$ is dependent on the oxidant. In the perchloric acid media used by Ardon and Plane,[234] one-electron reagents (e.g., Fe^{3+}, Cu^{2+}) gave only [Cr-

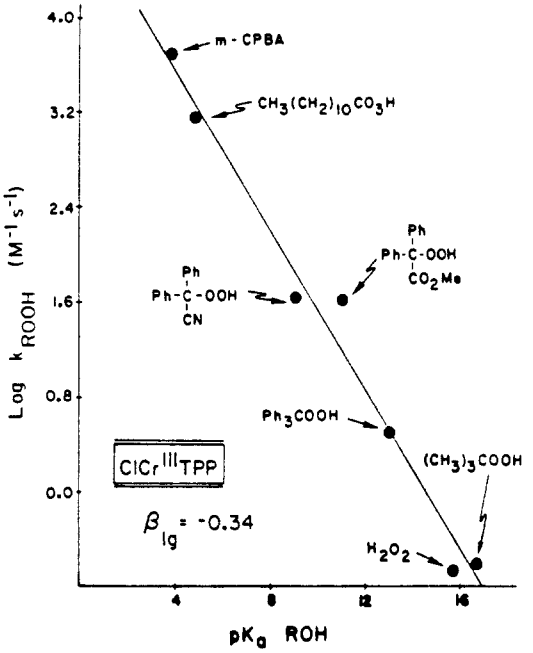


Figure 3. Dependence of the log of rate constant $k = k_{ROOH}$ for reaction 26a with Cr(TPP)Cl and XO = RCO_3H and ROOH (CH_2Cl_2, 25 °C) on the pK_a of the carboxylic acid and alcohol leaving groups (from ref 16).

$(H_2O)_6]^{3+}$, but two-electron oxidants such as dioxygen, HOCl, and chlorate afforded a mixture of this ion and $[Cr_2O(H_2O)_{10}]^{4+}$ (and/or a protonated form thereof). The linear Cr–O–Cr bridge **13** is a characterized structural unit. In their interpretation of the origin of the binuclear species, Ardon and Plane in 1959 postulated a Cr(IV) intermediate formed by atom transfer; reaction with $[Cr(H_2O)_6]^{2+}$ would afford the final binuclear product. The likely Cr(IV) intermediate is $[CrO(H_2O)_5]^{2+}$, which has not been separately detected. A more complicated system with a possibly dominant reaction pathway involving one-electron steps is indicated by subsequent work.[236,237] Reactions in aprotic solvents below show that under some circumstances Cr(II) can participate in oxo transfer. Inclusion of aquo Cr(II) as an oxo transfer reactant in Table 5 is speculative.

Nearly all other chromium oxo transfer reactions have been executed with porphyrin and tetradentate Schiff base complexes. Reactions in the porphyrin system are summarized in scheme 26 of Figure 2. Treatment of Cr(P)Cl (**35**) with a variety of donors XO, usually in excess, in reaction 26a generates initially the oxochromium(V) complex CrO(P)Cl (**36**), for which rate = k[Cr(P)Cl][XO]. At sufficiently large [XO] the conversion of **35** to **36** is complete. All are thermal reactions except that with *p*-cyano-*N*,*N*-dimethylaniline *N*-oxide, which is photocatalyzed. The d^1 complexes **36** are readily detected by their EPR spectra, which exhibit ^{53}Cr and ^{17}O hyperfine splittings.[229] These species are olefin epoxidation catalysts. Rate constants for the oxidation of Cr(TPP)Cl to CrO(TPP)Cl by percarboxylic acids and alkyl hydroperoxides vary from ca. 0.2 (*t*-BuOOH) to 5000 M^{-1} s^{-1} (*m*-$ClC_6H_4CO_3H$) in dichloromethane at 25 °C.[16] The linear dependence of log k on the pK_a of the leaving group, from the analysis of Yuan and Bruice[16] as shown in Figure 3, indicates a consistent mechanism with both reactant types. Formation of $PhCH_2CO_2H$ (recovered in high yield as the methyl ester by reaction with diazomethane) when XO = $PhCH_2CO_3H$ is the expected consequence of *hetero*lytic O–O bond fission. A similar linearity has been found in the oxidation of non-metal species,[238] where the reactions presumably proceed via S_N2 displacement by substrate lone pair operating on the terminal oxygen atom. The pathway represented by **37** is similar. Upon coordination of the oxidant, the indicated charge bias is developed, which leads to separation of anion $R'O^-$ and address of the electron deficiency at the α oxygen atom by formation of a Cr=O bond involving two metal $d\pi$ electrons. The linear correlation suggests that the ability of the R'O group to support a negative charge is a major component of the driving force of the reaction and that proton transfer to this group is not.

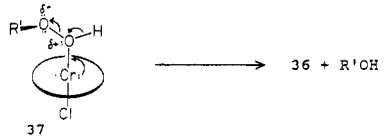
TABLE 6. Kinetics of the Oxidation of Ph_3P by Oxochromium(IV) Porphyrins (CH_2Cl_2, 25 °C)[a]

complex	k,[b] M^{-1} s^{-1}
CrO(TPP) (**39**)	0.47
CrO(TTP)	0.37
CrO(TMP)	0.054
$\Delta H^{\ddagger}$ = 6.96 kcal/mol[a]	$\Delta S^{\ddagger}$ = -39 eu[c]

[a] Data from ref 9. [b] Reaction 26c. [c] CrO(TMP).

At lower concentrations of XO, **36** competes with the oxidant for **35**, yielding in reaction 26b diamagnetic, square-pyramidal CrO(P) (**39**). The μ-oxo dimer **38** is a probable intermediate and may partially dissociate to **35** and **36**.[226] It is cleaved in a subsequent base addition step to **39**, which is the isolated product of synthesis.[50,227] Atom transfer has been demonstrated by the synthesis of $Cr^{18}O$(TPP) from $PhI^{18}O$,[50] as well as by the EPR detection of ^{17}O splittings.[229] This isotope was also transferred from PhIO. In dichloromethane complex **39** is reduced by Ph_3P in reaction 26c to Cr(P)

$$Cr(P)Cl + XO \xrightarrow{k} CrO(P)Cl + X \qquad (26a)$$



37

$$CrO(P)Cl + Cr(P)Cl + 2NaOH \rightarrow 2CrO(P) + 2NaCl + H_2O \qquad (26b)$$

$$CrO(P) + Ph_3P \xrightarrow{k} Cr(P) + Ph_3PO \qquad (26c)$$

(**40**). Typical of Cr(II) with halocarbons, **40** reacts immediately with solvent to produce **35**. However, in benzene the final product is the μ-oxo complex $[Cr(P)]_2O$ (**41**), formed by inner-sphere electron transfer between **39** and **40**. This has been confirmed by the reaction of prepared Cr(TPP) and CrO(TPP) in toluene.[49,239] Reactions of this type are examined in section IV. For now, it is observed that the sequence affording $[Cr(TPP)_2]O$[9,50] is an example of coupled reactions 7 and 8. This compound has been additionally obtained by base hydrolysis of **35**.[50] CrO(P) complexes are most simply prepared by aerial oxidation of Cr(P)Cl in HCl/chloroform mixtures.[239] Rate data for reaction 26c are summarized in Table 6. The phosphine nucleophile likely interacts with the π^*-orbital of the Cr=O group, leading to a possible Ph_3P–O–Cr^{III}(P) radical intermediate before collapsing to product. The lower rate

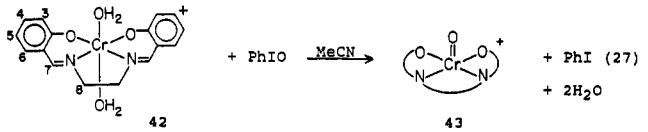
TABLE 7. Oxo Transfer Reactions of Manganese Compounds

species	reactant	product	ref
	Mn(III) → Mn(IV)		
Mn(TMP)Cl	*m*-$ClC_6H_4CO_3H$ (0 °C)	MnO(TMP)(OH_2)	250
Mn(TMP)Cl	*m*-$ClC_6H_4CO_3H$ (−78 °C)	MnO(TMP)Cl	250
Mn(TPP)L[a] (**44**)	PhIO	[Mn(TPP)L(PhIO)]$_2$O	242, 247
Mn(TPP)L[b]	PhIO	[Mn(TPP)L]$_2$O (**46**)	138
Mn(TCPP)[c]	ClO^-, BrO_3^-	[Mn(TCPP)]$_2$O[c]	246
	Mn(III) → Mn(V)		
Mn-P-450	PhIO	MnO-P-450[d]	248
Mn(TMP)Cl	NaOCl	MnO(TMP)Cl (**45**)	243, 251
Mn(TCPP)[c]	NaOCl	MnO(TCPP)[c]	247
Mn(TPP)Cl	RCO_3H[e]	MnO(TPP)Cl	17, 244[f]
Mn(TPP)L[g]	*p*-$NCC_6H_4NMe_2O$ (**49**)	MnO(TPP)L	245
Mn(TPP)Cl	ROOH[h]	MnO(TPP)Cl	244[f]
	Mn(IV,V) → Mn(III)		
[Mn(TPP)Cl(PhIO)]$_2$O	Ph_3P	Mn(TPP)Cl + Ph_3PO + PhI	242
[Mn(TPP)(N_3)]$_2$O	Ph_3P	Mn(TPP)N_3	242
MnO(TMP)Cl	Ph_3P	Mn(TMP)Cl	243
	Mn(IV) → Mn(II)		
MnO(P)[i]	Ph_3P, py	Mn(P)(py)$_2$	249

[a] L = Cl^-, Br^-. [b] L = N_3^-, OCN^-. [c] Aqueous solution: axial ligands unspecified; charge pH-dependent. [d] Axial ligand unidentified. [e] R = *m*-C_6H_4Cl, $PhCH_2$, $(CH_2)_4Cl$, $C_{11}H_{23}$. [f] Reactants and products (not isolated) in this reference contain Im or py ligands. [g] L = F^-, Cl^-, Br^-, I^-, N_3^-, OCN^-. [h] R = *t*-Bu, $Ph_2C(CN)$, $Ph_2C(CO_2Me)$, $PhCMe_2$. [i] P = TPP, TPFPP, TpivP.

constant for CrO(TMP) is a steric manifestation of the *o*-methyl groups. The large negative activation entropy indicates an associative pathway, particularly since solvation differences in dichloromethane are not likely to be a dominant factor. Much of our present knowledge of the oxo transfer reactions of chromium porphyrins derives from the investigations of Bruice,[16,231] Groves,[9,14,50,228,229] and their co-workers.

In a related approach to oxochromium(V) species, Kochi and co-workers[52,53,232] have employed the Cr(III)–salen complexes **42** in reaction 27. The spin-



42 **43**

doublet products **43** are readily isolated as triflate salts. Two representative complexes have been shown to have essentially square-pyramidal structures. Adduct formation occurs with Ph_3PO, pyO, and chloride.[53] In $[CrO(saltmen)(pyO)]^+$ the adducted and oxo ligands are mutually trans. The usual effects of a smaller δM and a trans effect of the oxo ligand on the opposite bond length are observed. The complexes **43** are reducible to the Cr(IV) state at potentials of ca. 0.4–0.7 V vs SCE.[53] Reaction of **43** with Et_3P is reported to occur with atom transfer to give the Cr(III) product "[Cr(salen)($OPEt_3$)]$^+$". The solvent was unspecified but presumably occupies the sixth coordination position. The oxochromium(V) complexes are catalysts for the epoxidation of olefins with PhIO.[232] As with the porphyrins, the

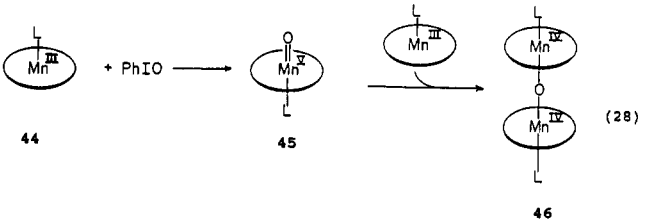
$$Cr^{V}O \underset{PhIO}{\overset{olefin}{\rightleftharpoons}} Cr^{III}$$

conversions are the critical metal-mediated steps. The oxidative reaction has also been reported for two substituted Keggin anions containing Cr(III) in an octahedral environment. EPR spectra of the products are consistent with the presence of an oxochromium(V) group.

D. Manganese

The only oxomanganese group of fully documented structure is $Mn^{VII}O_3$. From microwave spectroscopy, MnO_3F is tetrahedral with Mn–O = 1.586 (5) Å.[240] This group also occurs in Mn_2O_7, which forms molecular crystals below 6 °C with Mn–O = 1.595 (8) Å. The MnO_2 group is unknown. As will be seen, evidence for the Mn=O group is based mainly on reactivity, beginning with the findings that addition of NaOCl or PhIO to Mn(III) porphyrins produced species capable of oxidizing organic substrates including alkanes.[241] Other oxo transfer reactions of manganese compounds are set out in Table 7.

In the reactions of Mn(III) porphyrins **44** with PhIO, the final product is dependent on the axial ligand L. When L = N_3^- or OCN^- in reaction 28, the recoverable product is the Mn(IV) μ-oxo dimer **46**. It is probable



44 **45** **46**

$$[Mn(TPP)(N_3)]_2O + Ph_3P \rightarrow 2Mn(TPP)N_3 + Ph_3PO \quad (29a)$$

$$[Mn(TPP)Cl(PhIO)]_2O + 3Ph_3P \rightarrow 2Mn(TPP)Cl + 2PhI + 3Ph_3PO \quad (29b)$$

that the initial product is the oxomanganese(V) complex **45**, which reacts analogously to CrO(P)Cl in forming **46**. When L = Cl^- or Br^- the final product has the composition [Mn(TPP)L(PhIO)]$_2$O. The manner in which PhIO and/or labile halide is bound to the metal and the nature of the interaction, if any, between them are not known. Both types of products have low magnetic moments (~1.5 μ_B/Mn), suggestive of antiferromagnetic coupling. On this basis, it is probable that all products have or closely approach the linear bridge

established crystallographically for $[Mn(TPP)(N_3)]_2O$. Both products are reduced to the Mn(III) state by Ph_3P in reactions 29a and 29b.

Either type of μ-oxo complex is capable of oxidizing alkanes at ambient temperature.[252] Porphyrin[23c,d,245,253] and Schiff base[254] manganese systems have been developed which catalytically oxygenate organic substrates via the agency of species generated by the reaction of, usually, PhIO or NaOCl with Mn(III) complexes. The prevailing mechanistic view is that an oxomanganese(V) complex resembling **45** is the catalytic oxidant. It is also possible that this species is the actual oxidant of Ph_3P in reactions 29a and 29b, requiring a slight amount in equilibrium with **44** and the μ-oxo dimer. Oxidation of $(n\text{-}Bu_4N)_4H[PW_{11}O_{39}Mn]$ with PhIO affords an olefin epoxidation catalyst which is suggested to contain, prior to substrate interaction, an oxomanganese(V) group.[255] An analogous Cr^VO complex has already been noted (Table 5). Because of its low magnetic moment, the oxidation product of water-soluble Mn(TCPP) with hypochlorite or bromate in alkaline solution has been formulated as a μ-oxo Mn(IV) dimer. With excess hypochlorite at pH 14 a different species is produced whose absorption spectrum and magnetic moment of 2.7 μ_B are consistent with an oxomanganese(V) (d^2) complex.[246] This species could be converted to the Mn(III) state by various reductants but was otherwise fairly stable at pH 14 ($t_{1/2} > 8$ h).

In more recent work, strong evidence has been obtained for the formation of mononuclear oxomanganese(IV) porphyrins. One approach is summarized by the reactions 30 (P = TPP, TPFPP, TpivPP), which start with Mn(II) superoxide complexes.[249] The

$$[Mn^{II}(O_2)(P)]^- + CO_2 \xrightarrow[-70\ °C]{THF/DMF} [Mn^{III}(OOCO_2)(P)]^- \quad (30)$$

$$[Mn^{III}(OOCO_2)(P)]^- \xrightarrow{-70\ °C,\ THF} [Mn^{IV}O(P)] + CO^{\bullet-}$$

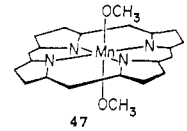
$$[Mn^{III}(OOCO_2)(P)]^- \xrightarrow{-35\ °C,\ PhMe} [Mn^{V}O(P)]^+ + CO_3^{2-}$$

overall stoichiometries resemble that of primary oxo transfer. However, the reactions proceed through detectable peroxycarbonate Mn(III) intermediates that decay to the indicated oxomanganese(IV,V) products. In the presence of pyridine, MnO(P) is reduced to $Mn(P)(py)_2$ with Ph_3P. Reactions 31 of Mn(TMP)Cl with the percarboxylic acid in dichloromethane in the presence of 2 equiv of methanolic $(Me_4N)OH$ affords the $Mn^{IV}O$ product at 0 °C and the Mn^VO product at −78 °C.[250] Presumably, in the latter reactions Mn^VO

$$Mn^{III}(TMP)Cl + m\text{-}ClC_6H_4CO_3H \underset{-78\ °C}{\overset{0\ °C}{\rightleftharpoons}} \begin{matrix} Mn^{IV}O(TMP)(OH_2) \\ [Mn^VO(TMP)]^+ \end{matrix} \quad (31)$$

is first formed by atom transfer but is reduced to the Mn(IV) state, perhaps by hydroxide. The mesityl substituents provide steric hindrance to the formation of **46**. Both oxo complexes epoxidize *cis*-β-methylstyrene but with different product stereospecificities.[250]

Preliminary X-ray absorption spectroscopic results at low temperature indicate for the species formulated as MnO(TPFPP) in reaction 30 the presence of Mn(IV) from edge shifts and, from EXAFS, the existence of a Mn=O group with a bond length of 1.67 (3) Å.[249] This distance is about 0.1 Å longer than that in MnO_3F, but the oxidation state is three units lower. It is also 0.15 Å shorter than the Mn–O distance (1.84 (2) Å) from EXAFS of the products of reaction of Mn(TMP)Cl with NaOCl and NaOBr.[251] While these products are included in Table 7 as oxo complexes, they may actually be complexes containing the intact hypohalite ion. The compound isolated from the reaction of Mn(TPP)(OAc), $NaBH_4$, and PhIO in methanol and formulated as MnO(TPP)[256] is actually $Mn(TPP)(OMe)_2$. The magnetic moment of 3.9 μ_B, bond distance Mn–O = 1.839 (2) Å, and the absence of an IR band characteristic of a porphyrin π-radical identify this as the Mn(IV) complex **47**.[257] This complex has also been obtained from



47

the reaction of PhIO and Mn(TPP) made in situ and from the oxidation of Mn(TPP)(OAc) in basic methanol using PhIO or NaOCl. In the case of iodosylbenzene, solvolysis to $PhI(OMe)_2$[15] apparently precludes oxo transfer. Details of the oxidation reactions and of the facile reduction of **47** to Mn(III) under acidic conditions have not been elucidated. Products from the oxidations of Mn(TPP)Cl[241c] and Mn(TMP)Cl[243] with excess PhIO and NaOCl, respectively, have been isolated but not characterized in detail. One of these has been described as MnO(TMP)Cl, containing $Mn^{IV}O$ and an oxidized porphyrin or oxo ligand. While no oxomanganese(V) complex has been proven, it is the probable first product in the reaction of Mn(III) with oxidant XO under conditions of X–O heterolytic bond cleavage. Such complexes are listed in Table 7 on this basis. The Mn(V) state is accessible and stable in isoelectronic complexes. Thus the nitrido complexes **48** are readily obtained by reaction 32 with L = Cl^-, Br^-, and OAc^- and

$$Mn(P)L + XO \xrightarrow[CH_2Cl_2]{xs\ NH_3} \underset{\textbf{48}}{\overset{N}{\underset{Mn}{\bigcirc}}} \quad (32)$$

XO = PhIO[258] and L = MeO^- and XO = ClO^-[259] and by photoirradiation of $Mn(P)N_3$.[260] These results are analogous to those for CrN(P), which is accessible from NaOCl oxidation of Cr(III) porphyrins[261] or by photolysis of $Cr(P)N_3$.[262] CrN(salen) has also been photolytically prepared.[263] Both the Cr(V) and Mn(V) nitrides have square-pyramidal structures with M–N interactions that are best interpreted in terms of triple bonds. Indeed, the Mn–N distance of 1.515 (3) Å in MnN(TMeP)[258] is one of the shortest metal–ligand multiple bonds known. In reactions such as 32, it has not been established whether there is a M=O intermediate from which the nitride is formed or if XO acts as an oxidant of a $M\text{–}NH_3$ intermediate. The current state of characterization of manganese porphyrins owes much to the endeavors of Hill and co-workers.[138,242,257,258,264]

The mechanism of oxo transfer to Mn(III) porphyrins has been examined by Bruice and co-workers.[17,244,245] An effective transfer agent to a number of such porphyrins is *p*-cyanodimethylaniline *N*-oxide (**49**). Oxo

$$Mn(TPP)L + NC\text{–}C_6H_4\text{–}N^+(Me)(Me)O^- \rightleftharpoons Mn(TPP)L\cdot\textbf{49} \longrightarrow$$

49

$$MnO(TPP)L + p\text{-}NCC_6H_4NMe_2 \quad (33)$$

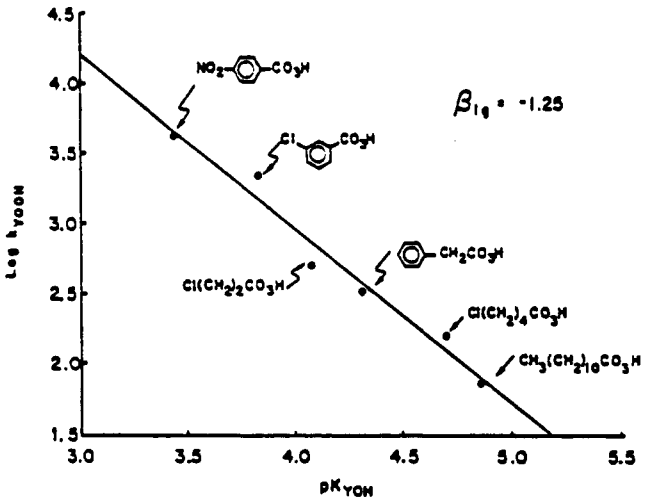
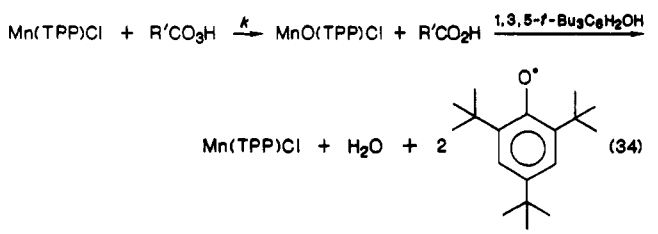


Figure 4. Dependence of the log of rate constant $k = k_{YOOH}$ for reaction 34 (PhCN, 30 °C) on the $pK_a = pK_{YOH}$ of the carboxylic acid leaving group (from ref 17).

transfer takes the course of the reactions 33 in which reversible adduct formation is followed by irreversible capture of oxygen by the metal center. Rate constants are dependent on axial ligand and follow the order L = OCN^- (0.071 s^{-1}) ≳ N_3^- > I^- > Br^- ≳ Cl^- ≫ F^- (5.6 × 10^{-5} s^{-1}) in benzonitrile solution.[245] When a capped Mn(III) porphyrin chloride is employed, the reaction is much slower. The cap encumbers the face opposite the axial chloride ligand. The probable cause for reduced reactivity is the necessity to dissociate chloride upon binding **49**, thereby generating two ions in a low dielectric medium. One difficulty with **49** as an atom donor is that its adduct also decomposes unproductively to *p*-NCC_6H_4NHMe, formaldehyde, and Mn(TPP)L. Nonetheless, it does act as an oxygen source for the catalytic epoxidation of cyclohexene.[245]

Through examination of organic substrate oxidations it has been found that Cr(TPP)Cl, Mn(TPP)Cl, and Fe(TPP)Cl are competent catalysts with oxygen donors such as PhIO and percarboxylic acids. An independent examination of the kinetics of reaction 34 yields the behavior in Figure 4 for the second-order rate constant *k*. Reactions were monitored by the absorbance of the



2,4,6-*tert*-butylphenoxy radical, which is formed in a trapping reaction of MnO(TPP)Cl by the parent phenol that is faster than oxo transfer.[17] As for reaction 26a, the rate behavior is indicative of heterolytic O–O bond cleavage. It further suggests some generality to the relation between rate constants and leaving group acidities. Mn(TPP)Cl, in contrast to Cr(TPP)Cl and Fe(TPP)Cl, does not react with alkyl hydroperoxides, including one of the otherwise most reactive, Ph_2C-(CN)OOH. On the basis of the correlation in Figure 4, the nil reaction rate can be traced to the low acidity of the potential product $Ph_2C(CN)OH$ ($pK_a \approx 9$). However, in the presence of a nitrogenous base such as imidazole, oxo transfer proceeds to the monoadduct complex, and to the mono- and dibase adducts when the base is imidazole itself. This ligand also increases second-order rate constants for transfer from percarboxylic acids by a factor of ≳200. A mechanism to account for these observations has been proposed.[244] For all donors whose leaving groups have $pK_a \lesssim 10$, O–O bond heterolysis applies. Homolytic bond cleavage is apparently dominant for donors whose leaving groups are less acidic ($pK_a > 11$).

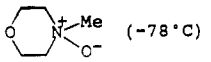
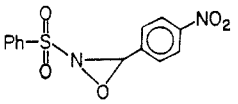
E. Iron

The only oxoiron species containing a terminal Fe=O bond to have been definitively characterized is the ferrate(VI) ion, $[FeO_4]^{2-}$, an extremely powerful oxidant. Alkali metal and alkaline earth salts of this ion, obtained by the oxidation of Fe(III) with hypochlorite in strongly basic solution, have been isolated. Variations of an early procedure[265] have led to compounds of improved purity.[266] As its potassium salt, $[FeO_4]^{2-}$ is tetrahedral with a mean Fe–O bond length of 1.650 (2) Å, within ca. 0.02 Å of the distances in the isomorphous potassium salts of $[CrO_4]^{2-}$ and $[MnO_4]^{2-}$.[267]

Much of the oxo transfer chemistry of chromium and manganese porphyrins has been directed toward the development of model systems for the enzyme cytochrome P-450, which oxygenates a wide spectrum of xenobiotics through a presumed oxoheme catalytic intermediate. Bacterial cytochrome P-450 induced by camphor can be reconstituted with Mn(III) protoporphyrin IX. Upon treatment with PhIO, the Mn-substituted protein develops an absorption spectrum similar to that of oxomanganese(V) porphyrins and shows some catalytic epoxidation activity.[268] Clearly, iron porphyrin systems are more relevant, and much of the work in this area has been summarized.[34,37] Of particular interest is the ability of several P-450 enzymes[37,269] and Fe(III) bleomycin[270] to effect atom transfer to organic substrates from donors such as the *N*-oxide **49**, alkyl hydroperoxides, and PhIO. In such cases and in purely synthetic systems, substrate oxygenation—usually olefin epoxidation—is taken as evidence of (highly reactive) oxoiron species, which has been identified as the Fe(IV) porphyrin π-radical complex $[FeO(P^{\bullet})]^+$. With one apparent exception (vide infra), no such oxoiron species has been isolated, but several have been spectroscopically detected in situ. As one example, laser irradiation of $Fe(TPP)O_2$ in a dioxygen matrix at ~15 K affords a strong band at 852 cm^{-1} in its resonance Raman spectrum. This feature undergoes ^{18}O and ^{54}Fe isotopic shifts in a manner consistent with the vibrations of a FeO unit.[271] This unit is almost certainly Fe^{IV}=O, but the metal oxidation state cannot be established by this method. Oxo transfer reactions are collected in Table 8. Nearly all reactions have been carried out with porphyrin complexes, and, in contrast to the reactions of Mn(III) and Cr(III) porphyrins affording M(V) products, no oxoiron(V) species have been identified.

As with Cr(III) and Mn(III) porphyrins, reactions of Fe(III) porphyrins with oxo donors are first order in each reactant, and under the pseudo-first-order conditions [XO] ≫ [Fe(P)L] the transfer of the oxygen atom to the metal is rate determining. Kinetics and

TABLE 8. Oxo Transfer Reactions of Iron Compounds

species	reactant	product	ref
	Fe(II) → Fe(III)		
$[Fe(OH_2)_6]^{2+}$	HOCl; O_3	$[Fe(OH_2)_6]^{3+}$ + $[Fe_2O]_{aq}^{4+}$	275
Fe(salen)	RNO_2;[a] RNO[b]	$[Fe(salen)]_2O$	276
Fe(TPP)	$R_1R_2R_3NO$;[d] R′NO[e]	$[Fe(TPP)]_2O$	277
	Fe(II) → Fe(IV)		
Fe(TPP)	 (−78 °C)	FeO(TPP)	278
	Fe(III) → Fe(IV)		
Fe(TMP)Cl (**55**)	PhIO	FeO(TMP)Cl (**56**)	279
Fe(TMP)(OH)	PhIO	FeO(TMP) (**53**)	280
Fe(TMP)(OH)	$PhCH_2CO_3H$	FeO(TMP)	281
Fe(TMP)(OH)	p-$O_2NC_6H_4CO_3H$	FeO(TMP)	282
Fe(OEP)Cl	2,4-$Me_2C_6H_3IO$	FeO(OEP)Cl	13
Fe(TMP)Cl	m-$ClC_6H_4CO_3H$	FeO(TMP)Cl	279, 283, 284
Fe(TMP)(ClO_4)	m-$ClC_6H_4CO_3H$	FeO(TMP)(ClO_4)	284
Fe(TPP)Cl	p-$NCC_6H_4NMe_2O$ (**49**)	FeO(TPP)Cl	18, 272, 285, 286
Fe(Cl_8TPP)Cl	p-$NCC_6H_4NMe_2O$	FeO(Cl_8TPP)Cl	273
Fe(Me_8TPP)Cl	p-$NCC_6H_4NMe_2O$	FeO(Me_8TPP)Cl	287
Fe(TPP)Cl	 (**50**)	FeO(TPP)Cl	18
Fe(TpivPP)Cl	K_2CO_4 (THF)	FeO(TpivPP)(THF)	288
	Fe(IV) → Fe(II,III)		
FeO(TPP)	Ph_3P	$[Fe(TPP)]_2O$ (**54**)	277, 278, 289
FeO(TMP)	Ph_3P	Fe(TMP)	290
FeO(TmTP)L	Ph_3P, L[c]	Fe(TmTP)L_2	289, 290
FeO(TmTP)(*N*-MeIm)	Ph_3As	Fe(TmTP)(*N*-MeIm)$_2$	290
	Fe(III) → Fe(II)		
$[Fe(TPP)]_2O$	Et_3P, py ($h\nu$)	Fe(TPP)$(py)_2$	291

[a] R = Me, Et, Ph. [b] R = Ph, 2-C_6H_4Ph, p-$C_6H_4NMe_2$. [c] L = *N*-MeIm, pip, py. [d] $R_1R_2R_3$ = Ph/Me/Me, Ph/Et/Et, Me/Me/CH_2Ph. [e] R′N = quinoline, isoquinoline, 5,6-benzoquinoline, 7,8-benzoquinoline.

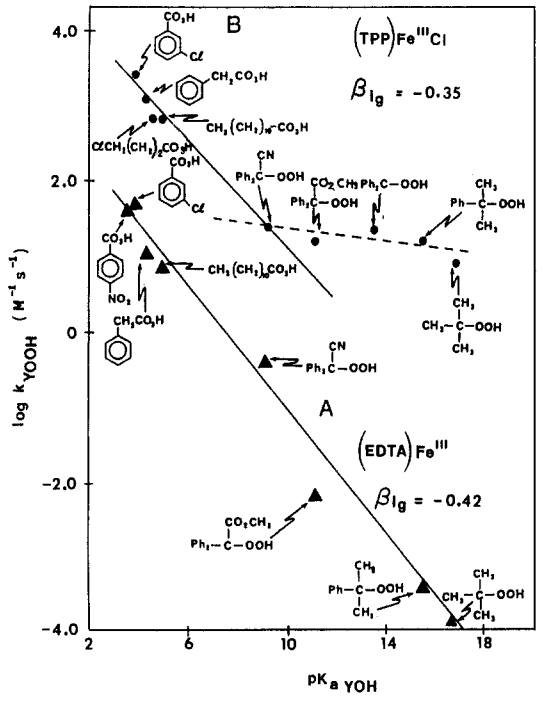


Figure 5. Dependence of the log of rate constants $k = k_{YOOH}$ for reaction 35 and the oxidation of Fe^{III}(EDTA) (methanol, 30 °C) on the pK_a of the carboxylic acid and alcohol leaving groups (from ref 19).

mechanistic aspects have been investigated by Bruice and co-workers.[18,19,272-274] With Fe(TPP)Cl and *N*-oxide **49**, the reaction scheme parallels the two-step sequence 33 for Mn(TPP)L systems. Second-order rate constants

TABLE 9. Kinetics of the Oxidation of Fe(TPP)Cl by Non-Peroxidic Oxo Donors at 30 °C[a]

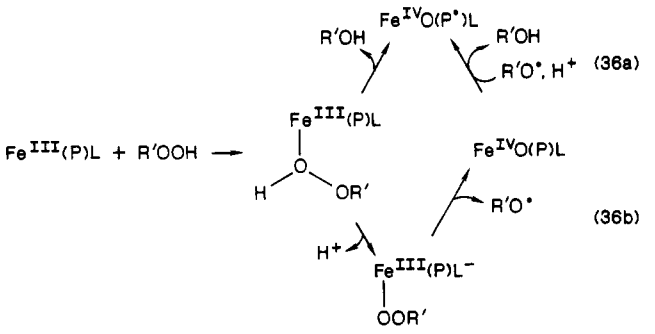
oxidant	k,[b] M^{-1} s^{-1}
$PhI(OAc)_2$	$(3.2 \pm 0.1) \times 10^3$
p-$NCC_6H_4NMe_2O$ (**49**)	72 ± 3
2-(phenylsulfonyl)-3-(*p*-nitrophenyl)oxaziridine (**50**)	$(7.5 \pm 0.1) \times 10^{-2}$

[a] Data from ref 18. [b] Reaction 35.

for reaction 35 with non-peroxidic oxidants are listed in Table 9. Those for percarboxylic acids and alkyl

$$Fe(TPP)Cl + XO \xrightarrow{k} Fe^{IV}O(TPP^{\bullet})Cl + X \quad (35)$$

hydroperoxides are plotted in Figure 5. Reactions were followed by the trapping and radical generation method in reaction 34. Iodosylbenzenediacetate has a rate constant in the range of peracids, **49** reacts with a rate constant comparable to hydroperoxide values, and the oxaziridine **50** is less reactive. The break point in the plot has been interpreted as a change in mechanism.[18,19] The peracid and more acidic hydroperoxide portion has a slope that is the same as that in Figure 3 (solvent difference notwithstanding) and is assigned to heterolytic cleavage, written here as reaction 36a (R′ = R, RCO; L = monoanion). The less acidic hydroperoxide portion conveys a much smaller dependence on leaving group acidity; its approximately linear behavior has not been tested at pK_a < 9. This portion is attributed to the homolytic cleavage reaction 36b, in which proton dissociation apparently precedes O–O bond scission, at least in a polar solvent. In the heterolytic pathway, the proton can be transferred more directly to the oxygen



atom of the leaving group (as in, e.g., **37**). For the homolytic process, achievement of the product oxidation level of heterolysis requires a following reaction such as that with the initial radical product. When R = *t*-Bu, the radical must be captured immediately by the metal center to prevent formation of acetone and methyl radical. The reactions 36 provide a brief description of the likely events under the two mechanisms.

Reaction of Fe^{III}(EDTA) in methanol with *m*-$ClC_6H_4CO_3H$ in the presence of 2,4,6-tri-*tert*-butylphenol proceeds by heterolytic cleavage of the O–O bond generating putative $Fe^{V}O$(EDTA), which has been detected only by its reactivity.[274] Note that there is no break in the plot for Fe^{III}(EDTA) in Figure 5 and that the linear correlation extends over a range of about 10^{12} in leaving group acidity. The oxidation product can be trapped by the phenol and, though unstable, apparently does not decompose, as might be expected, by oxidative decarboxylation of the ligand. These results tend to show that oxidation above Fe(III) by oxo transfer and O–O bond heterolysis of the oxidant are not dependent on a porphyrin ligand.

While the *instantaneous* product of a heterolytic oxo transfer reaction of Fe^{III}(P)L is likely to be $Fe^{V}O$(P)L, spectroscopic properties of the initially detected green species strongly indicate the presence of a porphyrin π-radical monoanion (P•) which is spin-coupled to Fe(IV). This conclusion follows mainly from FeO(TMP)Cl, generated at −80 °C from the reaction of Fe(TMP)Cl and *m*-$ClC_6H_4CO_3H$.[279] The mesityl groups sterically protect the complexes from μ-oxo dimer formation. The Mössbauer spectrum of FeO(TMP)Cl in frozen toluene has been interpreted in terms of an $S = {}^3/_2$ ground state arising from the coupling of ligand ($S = {}^1/_2$) and metal ($S = 1$) spins.[292] This species has a magnetic moment of 4.2 μ_B and is capable of epoxidizing olefins.[279] Further, there can be no question as to the existence of the ferryl (Fe=O) group under conditions more practicable than matrix isolation. Thus, resonance Raman bands at 770–830 cm^{-1} which respond in the expected manner to isotope substitution have been assigned to ν_{FeO} in oxidized synthetic hemes[293] and in ferrylmyoglobin and peroxidases.[294] Bond lengths of 1.60–1.66 Å emerge from the Fe EXAFS of FeO(TMP)(MeOH), FeO(TPP)(*N*-MeIm), and compounds I and II of horseradish peroxidase.[295] These can only be attributed to the Fe=O group. Proton NMR spectral characteristics of oxoiron(IV) porphyrins have been described.[290,296] Schappacher et al.[288] report crystallization of FeO(TpivPP)(THF) contaminated with the structurally similar bromo complex and find that the majority of electron density in the hindered side cavity "could correspond to an oxygen atom with a Fe–O distance of 1.604 (19) Å". The MO treatment of a model of FeO(P)(OH_2) by Tatsumi and Hoffmann[297] leads to the ferryl group electron configuration $\sigma^2\pi^4\pi^{*2}$ ($\pi^* = d_{xz}, d_{yz}$), corresponding to the double-bond description Fe=O.

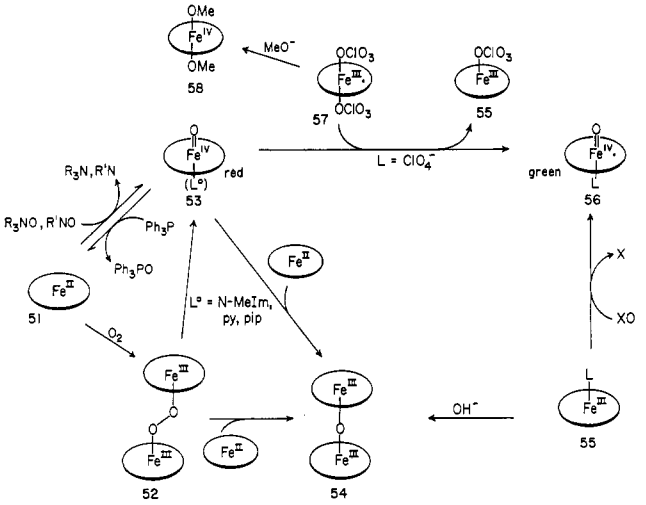


Figure 6. Reaction scheme of iron porphyrins, illustrating oxygen atom transfer and associated reactions. For specification of amine oxides R_3NO and R'NO and the stronger oxidants XO, cf. Table 8.

Oxo transfer and related reactions of iron porphyrins are illustrated in Figure 6. The scheme is readily entered at the Fe(II) or Fe(III) stage. All reactions are performed below ca. −50 °C unless stated otherwise. In notable experiments, Balch and co-workers[290,298] demonstrated that reaction of unligated Fe(P) (**51**) with dioxygen in toluene yields the peroxo dimer **52**, which is cleaved with electron rearrangement by nitrogenous ligands to the Fe(IV) complex FeO(P)L (**53**). Dimer **52** is also cleaved by **51** in reaction 37 to give the μ-oxo dimer **54**. The latter can additionally be obtained by

$$[Fe(P)]_2O_2 + 2Fe(P) \rightarrow 2[Fe(P)]_2O \quad (37)$$

$$2[Fe(P)]_2O_2 \rightarrow 2[Fe(P)]_2O + O_2 \quad (38)$$

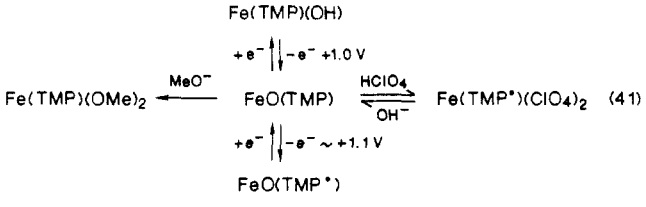
$$FeO(P)L + Fe(P) \rightarrow [Fe(P)]_2O + L \quad (39)$$

$$FeO(P)L + Ph_3P \rightarrow Fe(P) + Ph_3PO + L \quad (40)$$

warming a solution of **52**, which induces the decomposition reaction 38.[298] The simplest route to **53** is by oxo transfer from tertiary or heterocyclic amine oxides to **51**.[277,278] Analogous to the behavior of chromium porphyrins, **53** and **51** spontaneously form **54** in redox reaction 39.[298] At the Fe(III) level, Fe(P)L (**55**) can be converted to the most oxidized member of the set, FeO(P•)L (**56**), by reaction 36. The one-electron link between red **53** and green **56** was proven by oxidation with Fe(P•)(ClO_4)$_2$ as shown, or with chlorine or bromine.[284] The two-electron relationship between **51** and **53** is established by oxo transfer reaction 40. The peroxo dimer is unreactive toward Ph_3P at low temperatures. Not all transformations are possible with different porphyrins. While the hindered TMP ligand permits formation of peroxo dimer **52**, on warming it decomposes to FeO(TMP) and then to Fe(TMP)(OH),[290] which is sterically blocked from forming [Fe(TMP)]$_2$O. Likewise, steric protection of the ferryl group prevents formation of the μ-oxo dimer from FeO(TMP) and Fe(TMP) but does not preclude reaction 40. Treatment of TMP dimer **52** with *N*-MeIm causes rupture of an Fe–O rather than an O–O bond,

giving Fe(TMP)(*N*-MeIm)O_2 and Fe(TMP)(*N*-MeIm)$_2$.[290] The oxidations of two Fe(III) complexes with peroxycarbonate (Table 8) and carbon dioxide[288] are probably successful because of steric shielding of the $Fe^{IV}O$ group by the picket fence porphyrin.

An early indication of the existence of Fe(IV) is found in the oxidations of $[Fe(H_2O)_6]^{2+}$ with hypochlorous acid and ozone in perchloric acid solutions studied by Sutin and co-workers in 1965.[275] From a kinetics analysis it was concluded that the final products, mononuclear and binuclear μ-oxo aquo Fe(III) species, arose by the reaction of an Fe(IV) intermediate with $[Fe(H_2O)_6]^{2+}$. The proposed scheme is similar to that for the oxidation of aqueous Cr(II) (Table 5) except that the binuclear Fe(III) complex more rapidly dissociates. In comparison, chlorine as the oxidant gave >70% $[Fe(H_2O)_5Cl]^{2+}$, a species formed in very minor amount or not at all in the other systems. The intermediate, which must now be considered to contain an Fe^{IV}=O group, has not been directly detected in or isolated from an aqueous system. As is already evident, this group is substantially more accessible in the form of porphyrin complexes in nonaqueous media. Shown in Figure 6 are several ways of producing this group. Iron(IV) can also be reached by two other methods, which rely on different oxidation modes as dependent on the axial ligand in Fe(P)L. When L is a poor π-donor such as Cl^- or ClO_4^-, the first one-electron oxidation is ligand-centered,[299] affording as one example Fe(TMP$^\bullet$)$(ClO_4)_2$ (**57**). Replacement of perchlorate with methoxide causes an internal redox reaction that yields the Fe(IV) complex Fe(TMP)$(OMe)_2$[300] (**58**). With the better π-donor L = OH^-, the reactions 41 occur;[280,301] potentials



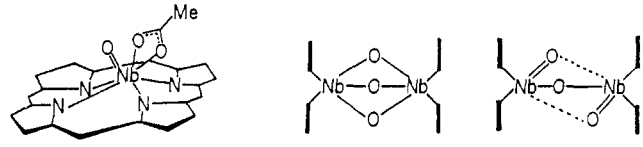
are vs SCE in wet dichloromethane solutions. The first oxidation is metal-based, giving **53**, and the second is ligand-based, producing **56**. Complexes **53** and **57** are interconvertible by acid–base treatment. Despite the instability of oxoiron compounds (only **54** has been isolated in a pure state), impressive progress has been made in identifying and executing oxo transfer and associated reactions. Among the latter are ligand-based oxidations leading to the formation of porphyrin *N*-oxides containing an Fe(III)–O bond.[281] The most immediate benefit of this work is an increased appreciation of accessible active-site oxidation states, and more specific descriptions of them, in heme enzymes such as the peroxidases and, particularly, the cytochrome P-450's.[302]

In consideration of periodic groups beyond iron, Co(IV) and Ni(IV) oxides have been reported.[303] These tend to be nondescript solids of unknown structure. A material formulated as $NiO(OH)_2 \cdot 3H_2O$ has been found to oxidize Me_2SO to Me_2SO_2.[304] Discrete groups M=O are not expected to be stable under ordinary conditions for $d^{5,6}$ metals, inasmuch as the corresponding electron configurations $\sigma^2\pi^4\pi^{*3,4}$ would substantially weaken bonds and reduce bond orders to near 1. In the reaction of Co(TPP)Cl with percarboxylic acids and alkyl hydroperoxides, detectable products do not contain an oxocobalt group.[305] Instead, the reaction proceeds through a doubly oxidized porphyrin and the final product contains Co(III). This illustrates what is likely to be general behavior: ligand-based rather than metal-based oxidation in reactions of oxo donors with $d^{>5}$ complexes. This Co^V=O group may be capable of transitory existence when supported by anionic, oxidatively resistant ligands. It has been noted as a possible intermediate in the oxidation of styrene in the presence of PhIO and Co(III) complexes of tetraanionic chelating ligands.[306] On the other hand, the Ni^{IV}=O intermediate postulated in olefin epoxidation systems mediated by Ni(II) macrocycles appears unlikely.[307] With certain of the tetraaza macrocycles, the intervention of a Ni(II) ligand *N*-oxide similar to a fully characterized Ni(II) porphyrin *N*-oxide complex[308] must be considered.

Turning next to the second and third transition series, no M=O or other of the groups in Figure 1 is known for zirconium or hafnium. Oxo transfer chemistry is fairly extensive with most elements of groups 6–8, and that of molybdenum is the most highly developed of any element.

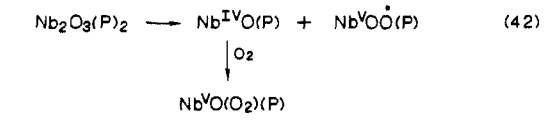
F. Niobium and Tantalum

The Nb^V=O group is a thoroughly established structural element in a variety of compounds, including $[NbOCl_4]^-$ (**8**) and NbO(TPP)(OAc) (**51**), which has the 4:3 coordination pattern with the niobium atom 1 Å above the N_4 plane. NbO(OEP)F has a related cis 4:2



51 52 53

structure with δNb = 0.91 Å.[309] The most pertinent oxo chemistry has been carried out with porphyrin complexes. The preceding two compounds are obtained by acid cleavage of $Nb_2O_3(P)_2$,[48,309] which exhibits shared 4:3 coordination and a bridge structure isomeric with **14**. Depending on the crystalline solvate, the bridge structure of $Nb_2O_3(TPP)_2$ takes the roughly symmetric form **52** with a mean Nb–O bond length of 1.87 (5) Å[48] or the decidedly asymmetric arrangement **53**.[154] In the latter, Nb–O distances range from 1.76 Å, indicative of a slightly perturbed Nb=O group (Table 2), to 2.44 Å, signifying a weak O···Nb interaction. Structure **53** in particular raises the possibility of cleavage reaction 42, a unique type of oxo transfer. Anaerobic photolysis



of $Nb_2O_3(TTP)_2$ in a benzene/alcohol solvent yields NbO(TTP), identified by its EPR spectrum,[310] which is the same as that of the chemical and electrochemical reduction product of **51**.[311] Aerobic photolysis in benzene generates the radical complex $NbO(\dot{O}_2)$(TTP), so designated because its ^{93}Nb hyperfine splitting is only ~3% that of the d^1 complex NbO(TTP). This species is believed to be the active catalyst in the aerobic ep-

oxidation of olefins under visible irradiation. The ligand radical complex NbO_2(TTP) is apparently also produced in photolysis but was not directly detected. Possible oxo transfer reactions not yet explored include formation of NbO_2(P) (or $Nb_2O_3(P)_2$) from NbO(P) and atom donors and the preparation of NbO(P) directly from $Nb_2O_3(P)_2$ by atom abstraction. Other than reaction 42, no metal-based oxo transfer reactions of niobium compounds have been reported.

Oxotantalum groups of any kind are virtually uncharacterized. The Ta^V=O group is most frequently encountered in $[TaOL_5]^{2-}$ (L = halide) but structurally defined only in $K_4Na_2H_2Ta_6O_{19}\cdot 2H_2O$, where terminal and bridging Ta–O bond lengths are 1.786–1.817 and 1.976–2.012 Å,[312] respectively. In general, Ta–O interactions are dominated by an extensive set of peroxide–halide complexes in which peroxide as η^2-O_2^{2-} is isoelectronic with an oxo ligand. Most recently, the Ta=O group has been stabilized in the sterically bulky monomers $TaO(OSi(t\text{-}Bu)_3)_3$, $Cp^*_2TaO(Me)$, and $Cp^*_2TaO(H)$.[313,314] No oxo transfer reactions of tantalum compounds have been described.

G. Molybdenum

This element lies at the epicenter of oxo transfer chemistry. More oxo compounds have been prepared and characterized, more oxo transfer reactions are known, and more catalytic systems based on these reactions have been devised than for any other element. Further, molybdenum forms an extensive set of isopoly- and heteropolyanions,[196] oxomolybdenum(VI) anions are responsible for the aqueous solubility of the element,[315] which in sea water is the highest among the transition elements, and one of the two groups of enzymes implicated in oxo transfer catalysis contains molybdenum. Reference to Figure 1 reveals that molybdenum forms nearly all functional group types; it enters into all bridging interactions in Table 3 except **17** and **19**. The extensive set of oxo transfer reactions is compiled in Table 10. Because of their large number, reactions are considered in several subsets.

1. *Mo(II) → Mo(VI) and Mo(III) → Mo(V)*

There is one example each of these transformations. Shown in Figure 7 are three methods for the preparation of the Mo(VI) phenylhydroxaminato(2–) complex **59** in the bis(*N*,*N*-diethyldithiocarbamate) series.[316,352-354] The reactions of $MoO(S_2CNEt_2)_2$ (**60**) with nitrosobenzene and $MoO_2(S_2CNEt_2)_2$ (**61**) with phenylhydroxylamine are oxidative addition and elimination–substitution processes, respectively. However, the formation of **59** from the Mo(II) dicarbonyl **62** and nitrobenzene in 1,2-dichloroethane must involve atom transfer to the metal center, doubtless in concert with the four-electron reduction and N–O bond cleavage of the ligand. Note that nitrosobenzene affords the Mo(IV) complex **63** whose two-electron relation to **59** is shown by its formation in the reaction of the latter with Ph_3P. Further, **63** is a valence isomer of the Mo(VI) oxo areneimido complex **64**, obtainable from **60** by reaction with arene azides;[353,354] the two have not yet been interconverted.[316] Complexes **59**, **63**, and **64** are among a large number of examples that demonstrate the effective isoelectronic behavior of RNO^{2-} and RN^{2-} with a terminal oxo ligand.

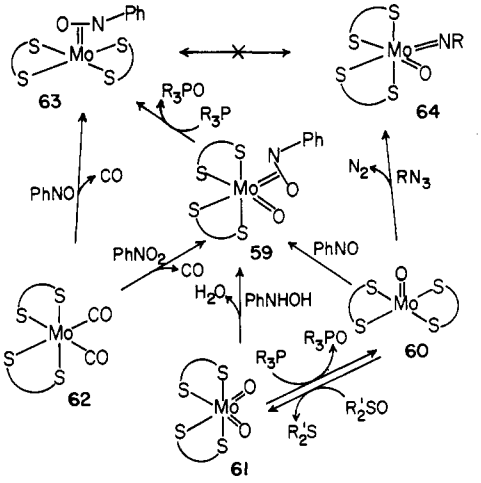
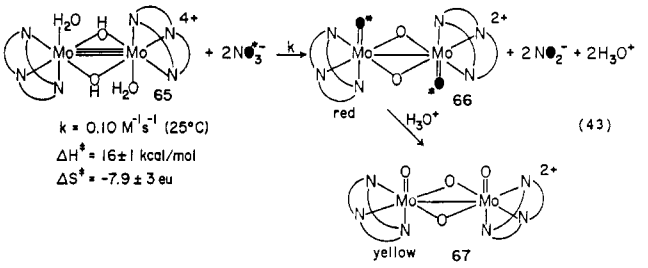


Figure 7. Reaction scheme illustrating three routes to the Mo(VI) complex **59** and the syntheses of valence isomers **63** and **64**. Oxo transfer reactions are **62** → **59**, **59** → **63**, and **60** ⇌ **61**. S⁀S = *N*,*N*-diethyldithiocarbamate(1–).

The Mo(III) → Mo(V) conversion by oxo transfer has been proven in reaction 43, which contains several significant features. Reactant $[Mo_2(OH)_2(tacn)_2(OH_2)_2]^{4+}$ (**65**), which likely has the *trans*-diaquo structure analogous to that of $[Mo_2(OH)_2(tacn)_2Cl_2]^{2+}$[355] to which it is directly related by chloride substitution,[356] reacts cleanly with nitrate at pH ~1 to yield $[Mo_2O_4(tacn)_2]^{2+}$ (**66**) and nitrite. To prevent secondary reactions, nitrite was rapidly scavenged by sulfamic acid in the process $NO_2^- + H_2NSO_3H \rightarrow HSO_4^- + N_2 + H_2O$ and detected as dinitrogen. The reaction follows the rate law $-d[\mathbf{65}]/dt = k[\mathbf{65}][NO_3^-]$ with the indicated parameters. An associative mechanism in which nitrate displaces an aquo ligand in the rate-determining step is likely. The use of 90% ^{18}O-enriched nitrate and examination of the ν_{MoO} stretching frequencies have shown that the reaction occurs by atom transfer to, dominantly, the terminal oxo positions. Further, the red product **66** has the syn configuration, by comparison with the dioxygen or perchlorate oxidation product of **65** whose structure has been determined. Thus the reactant and product stereochemistries appear to correspond. Under acid catalysis **66** converts irreversibly to the yellow syn isomer **67**[356] whose structure has been determined by X-ray analysis. The same isomers have been prepared with the larger macrocycle tacd and are distinguishable by absorption and ^{95}Mo NMR spectra.[357] A binuclear reactant is not a requirement for nitrate reduction inasmuch as reaction 44 in acid solu-



$$2[Mo(OH_2)_6]^{3+} + 2NO_3^- \rightarrow [Mo_2O_4(OH_2)_6]^{2+} + 2NO_2^- + 4H_3O^+ \quad (44)$$

tion had been reported some years earlier,[358] but without the ^{18}O labeling experiment necessary to detect atom transfer. The extent to which these reactions are

TABLE 10. Oxo Transfer Reactions of Molybdenum Compounds

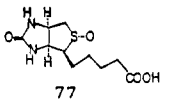
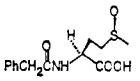
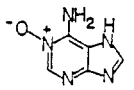
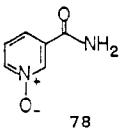
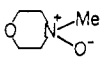
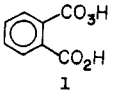
species	reactant	product	ref
		Mo(II) → Mo(VI)	
$Mo(CO)_2(S_2CNEt_2)_2$ (**62**)	$PhNO_2$	$MoO(PhNO)(S_2CNEt_2)_2$ (**59**)	316
		Mo(III) → Mo(V)	
$[Mo_2(OH)_2(tacn)(OH_2)_2]^{4+}$ (**65**)	NO_3^-	$[Mo_2O_4(tacn)_2]^{2+}$ (**66**)	317
		Mo(IV) → Mo(VI)	
$MoO(S_2CNEt_2)_2$ (**60**)	Me_2SO	$MoO_2(S_2CNEt_2)_2$ (**61**)	26, 27, 318–320
$Mo(N\text{-}p\text{-}tol)(S_2CNEt_2)_2$	Me_2SO	$MoO(N\text{-}p\text{-}tol)(S_2CNEt_2)_2$ (**64**)	321, 337
$[MoOCl(dttd)]^-$	Me_2SO	$MoO_2(dttd) + Cl^-$	100
$MoO(L\text{-}NS_2)(DMF)$ (**69**)	Me_2SO	$MoO_2(L\text{-}NS_2)$ (**68**)	322
$MoO(L\text{-}NS_2)(DMF)$	Ph_2SO	$MoO_2(L\text{-}NS_2)$	322
$MoO(L\text{-}NS_2)(DMF)$	$(p\text{-}FC_6H_4)_2SO$	$MoO_2(L\text{-}NS_2)$	323–325
$MoO(L\text{-}NS_2)(DMF)$	 77	$MoO_2(L\text{-}NS_2)$	322
$MoO(L\text{-}NS_2)(DMF)$		$MoO_2(L\text{-}NS_2)$	322
$MoO(S_2CNEt_2)_2$	pyO	$MoO_2(S_2CNEt_2)_2$	27, 320
$Mo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$	pyO	$MoO(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$	326
$MoO(L\text{-}NS_2)(DMF)$	pyO	$MoO_2(L\text{-}NS_2)$	324
$MoO(L\text{-}NS_2)(DMF)$	3-FpyO	$MoO_2(L\text{-}NS_2)$	325
$MoO(L\text{-}NS_2)(DMF)$	 108	$MoO_2(L\text{-}NS_2)$	324
$MoO(L\text{-}NS_2)(DMF)$	 78	$MoO_2(L\text{-}NS_2)$	324
$MoO(S_2CNEt_2)_2$		$MoO_2(S_2CNEt_2)_2$	26
$MoO(L\text{-}NS_2)(DMF)$	$(PhCH_2)_3NO$	$MoO_2(L\text{-}NS_2)$	324
$MoO(S_2CNEt_2)_2$	Ph_3AsO	$MoO_2(S_2CNEt_2)_2$	27
$MoO(L\text{-}NS_2)(DMF)$	Ph_3AsO	$MoO_2(L\text{-}NS_2)$	324
$MoO(S_2CNEt_2)_2$	Ph_3SbO	$MoO_2(S_2CNEt_2)_2$	27
$MoO(S_2CNEt_2)_2$	$t\text{-}BuONO_2$	$MoO_2(S_2CNEt_2)_2$	320
$MoO(S_2CNEt_2)_2$	PhN(O)=NPh	$MoO_2(S_2CNEt_2)_2$	320
$MoO(S_2CNEt_2)_2$	 1	$MoO_2(S_2CNEt_2)_2$	32
$MoO(S_2CNR_2)_2$	Co(saloph)(NO_2)(py) (**79**)	$Mo_2O_3(S_2CNR_2)_4$ (**76**) + Co(saloph)(NO)(py) (**80**)	204
$MoO(L\text{-}NS_2)(DMF)$	NO_3^-	$MoO_2(L\text{-}NS_2)$	327
$MoO(S_2CNEt_2)_2$	NO_3^-	$MoO_2(S_2CNEt_2)_2 + N_2O_2^{2-}$	349
$[MoO(5\text{-}SO_3ssp)(DMF)]^-$	NO_3^-	$[MoO_2(5\text{-}SO_3ssp)(DMF)]^-$	327
		Mo(V) → Mo(VI)	
$[MoOCl_5]^{2-}/[MoOCl_4(DMF)]^-$	NO_3^-	$MoO_2Cl_2(DMF)_2$[a]	328, 329
$MoOCl_3(OPPh_3)_2$	NO_3^-	$MoO_2Cl_2(OPPh_3)_2$[a]	330, 331, 350
$MoOCl_3L$	NO_3^-	MoO_2Cl_2L[a,b]	332, 333
$MoOCl_3(hmpa)_2$	NO_3^-	$MoO_2Cl_2(hmpa)_2$[a]	330
$MoOCl(ox)_2$	NO_3^-	$MoO_2(ox)_2$[a]	333
$MoOCl(tox)_2$	NO_3^-	$MoO_2(tox)_2$[a]	333
MoOCl(sap)(MeOH)	NO_3^- (DMF)	MoO_2(sap)(DMF) + MeOH[a]	333
$MoOCl_3(OPPh_3)_2$	N_2O_4	$MoO_2Cl_2(OPPh_3)_2 + NOCl$	330
		Mo(VI) → Mo(IV/V)	
$MoO_2(S_2CNR_2)_2$	Ph_3P	$MoO(S_2CNR_2)_2 + Mo_2O_3(S_2CNR_2)_4$	26–29, 32, 319, 330, 334–336, 351
$MoO_2(L\text{-}NS_2)$	Ph_3P (DMF)	$MoO(L\text{-}NS_2)(DMF)$	322
$MoO(N\text{-}p\text{-}tol)(S_2CNEt_2)_2$	Ph_3P	$Mo_2O(N\text{-}p\text{-}tol)_2(S_2CNEt_2)_2$	337
$MoO(N\text{-}p\text{-}tol)(S_2CNEt_2)_2$	Ph_3P (excess)	$Mo(N\text{-}p\text{-}tol)(S_2CNEt_2)_2$	321, 337
$MoO(PhNO)(S_2CNEt_2)_2$ (**59**)	Ph_3P	$Mo(PhNO)(S_2CNEt_2)_2$ (**63**)	316
$MoO_2(dttd)$	Ph_3P	$Mo_2O_3(dttd)_2$	100
$MoO_2(dttd)$	Ph_3P (excess)	MoO(dttd)	338
$MoO_2(L\text{-}Cys\text{-}OEt)_2$	Ph_3P	$Mo_2O_3(L\text{-}Cys\text{-}OEt)_4$	339
$MoO_2(S_2CS\text{-}i\text{-}Pr)_2$	Ph_3P (excess)	$MoO(S_2CS\text{-}i\text{-}Pr)_2(PPh_3)$	340
$MoO_2(dme)$	Ph_3P	$Mo_2O_3(dme)_2$	341
$MoO_2(TTP)$ (**12**)	Ph_3P	MoO(TTP)	342, 343
$MoO_2Cl_2(py)_2$	Ph_3P	$Mo_2O_3Cl_4(py)_4$	167

TABLE 10 (Continued)

species	reactant	product	ref
$MoO_2(L\text{-}NS_2)$	$(p\text{-}FC_6H_4)_3P$ (DMF)	$MoO(L\text{-}NS_2)(DMF)$	325
$MoO_2(S_2CNR_2)_2$	Ph_2EtP	$Mo_2O_3(S_2CNR_2)_4$	29
$MoO_2(S_2CNR_2)_2$	Ph_2EtP (excess)	$MoO(S_2CNR_2)_2$	26, 29, 326
$MoO_2(S_2PPh_2)_2$	Ph_2EtP	$Mo_2O_3(S_2PPh_2)_4$	29
$MoO_2(S_2PPh_2)_2$	Ph_2EtP (excess)	$MoO(S_2PPh_2)_2$	29
$MoO_2(S_2P(i\text{-}Pr)_2)_2$	Ph_2EtP (excess)	$MoO(S_2P(i\text{-}Pr)_2)_2$	29
$MoO_2(Cys\text{-}OMe)_2$	Ph_2EtP	$Mo_2O_3(Cys\text{-}OMe)_4$	29
$MoO_2(ox)_2$	Ph_2EtP	$Mo_2O_3(ox)_4$	29
$MoO_2(acac)_2$	Ph_2EtP	$Mo_2O_3(acac)_4$	29
$MoO_2(sap)(DMF)$ (**74**)	Ph_2EtP	$MoO(sap)(DMF)$ (**75**)	344
$MoO_2(sap)(DMF)$	Ph_2EtP, phen	$MoO(sap)(phen)$	344
$MoO_2(ssp)(DMF)$ (**70**)	Ph_2EtP	$MoO(ssp)(DMF)$ (**71**)	344–346
$MoO_2(ssp)(DMF)$	Ph_2EtP, L[b]	MoO(ssp)L	344
$MoO_2(5\text{-}R\text{-}ssp)(DMF)$[c]	Ph_2EtP	$MoO(5\text{-}R\text{-}ssp)(DMF)$	346
$MoO_2(5\text{-}R\text{-}sse)(DMF)$[d] (**72**)	Ph_2EtP	$MoO(5\text{-}R\text{-}sse)(DMF)$ (**73**)	347
$MoO(N\text{-}p\text{-}tol)(S_2CNEt_2)_2$	Ph_2EtP	$Mo_2O(N\text{-}p\text{-}tol)_2(S_2CNEt_2)_4$	337
$MoO(N\text{-}p\text{-}tol)(S_2CNEt_2)_2$	Ph_2EtP, dmac	$Mo(N\text{-}p\text{-}tol)(dmac)(S_2CNEt_2)_2$	337
$MoO_2(dttd)$	Ph_2EtP	$Mo(dttd)(PEtPh_2)$	100
$MoO_2(mpe)$	Ph_2EtP	MoO(mpe)	344
$MoOL_2(S_2CNEt_2)_2$[e]	Ph_2EtP	$MoL_2(PPh_2Et)(S_2CNEt_2)_2$	348
$MoO_2(S_2CNEt_2)_2$	$PhEt_2P$	$MoO(S_2CNEt_2)_2$	26
$MoO_2(dme)$	$PhMe_2P$	$MoO(OPMe_2Ph)(dme)$	341
$MoO_2(dmp)$	$PhMe_2P$	$Mo_2O_3(dmp)_2$	341
$MoO_2(S_2CNEt_2)_2$	Et_3P	$MoO(S_2CNEt_2)_2$	26
$[MoO(S_2CNEt_2)_3]^+$	Ph_3P	$[Mo_2O(S_2CNEt_2)_6]^+$	134
$MoO_2(TTP)$	$(C_6H_{11})_3P$	MoO(TTP)	343
$MoO_2(TTP)$	$(PhO)_3P$	MoO(TTP)	343

[a] Other products $Cl^- + NO_2$. [b] L = bpy, phen. [c] R = Cl, Br, OMe. [d] R = H, Cl, Br, OMe. [e] L = Cl^-, Br^-.

TABLE 11. Enthalpies of Oxo Transfer Reactions of Mo(IV,VI) Dithiocarbamate Complexes (L = $Et_2NCS_2^-$) in 1,2-Dichloroethane[a]

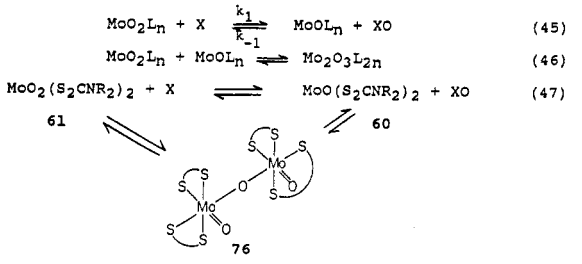
reaction[b]	no.	ΔH, kcal/mol
$Mo_2O_3L_4 = 2MoOL_2 + O(g)$	52	101.0
$MoO_2L_2 = MoOL_2 + O(g)$	53	96.0
$MoO_2L_2 + MoOL_2 = Mo_2O_3L_4$	46	−6.6 (0.5)[c,d]
$MoO_2L_2 + SO_3^{2-} = MoOL_2 + SO_4^{2-}$	54	−28.5 (5.5)
$MoO_2L_2 + Ph_3P = MoOL_2 + Ph_3PO$	55	−29.0 (2.5)[d]
$MoO_2L_2 + MeCHO = MoOL_2 + MeCO_2H$	56	−32.0 (4.0)
$MoOL_2 + H_2O(l) = MoO_2L_2 + H_2$	57	30.1 (4.2)
$MoOL_2 + NO_3^- = MoO_2L_2 + NO_2^-$	58	−4.4 (4.2)
$MoOL_2 + {}^1/_2O_2(g) = MoO_2L_2$	59	−35.0 (3.2)[d]
$MoOL_2 + R'CO_3H = MoO_2L_2 + R'CO_2H$	60	−66.4 (1.2)[d]

[a] All data from ref 32. [b] $R'CO_3H$ = 1. [c] Estimated uncertainty in last digits in parentheses. [d] Direct calorimetric measurement.

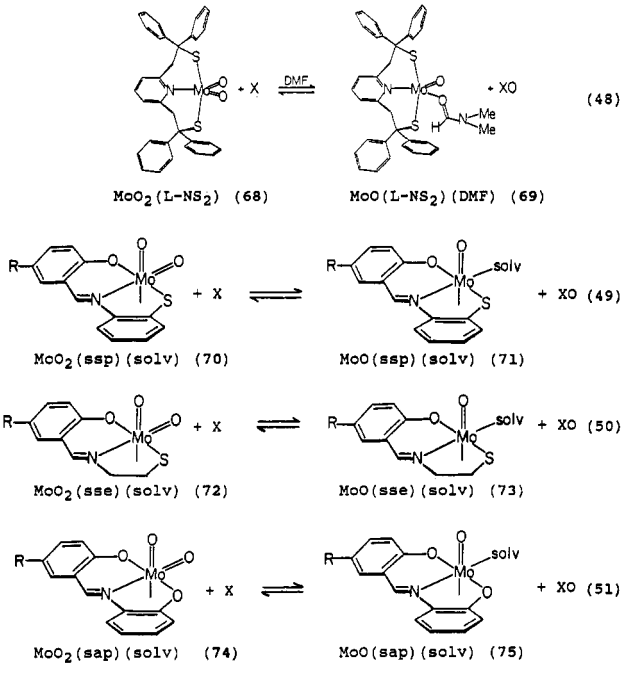
pertinent to the mechanism of action of nitrate reductase[359] is currently uncertain and will depend on the existence of a binuclear active site and the involvement (if any) of Mo(III) in the catalytic cycle.

2. *Mo(VI) → Mo(IV)*

This transformation and its reverse are represented generally by reaction 45. A frequent complication is



the μ-oxo Mo(V) dimer formation reaction 46. Five complexes that figure prominently in oxo transfer are depicted in reactions 47–51. The structures of distorted octahedral **61**, **74** (R = *t*-Bu), and **70** (R = SO_3^-),[327] distorted trigonal-bipyramidal **68**, square-pyramidal **60**, and μ-oxo dimer **76** with a cisoid configuration of bridge **15** have been crystallographically established. The latter configuration is usual in Mo_2O_3 complexes. Complexes **71**, **73**, and **75** are shown as mononuclear but



could be binuclear with phenolate or thiolate bridging atoms. Forward reaction 47 with X = Ph_3P, carried out by Barral et al.[28] in 1972, was the first recognized oxo transfer reaction of a molybdenum compound. When coupled to the aerial oxidation of **60** to **61**, a catalytic cycle for the oxidation of Ph_3P to Ph_3PO was achieved. As shown in section V, this is but one of a number of catalytic cycles based on Mo-mediated oxo transfer reactions.

TABLE 12. Kinetics Data for Oxo Transfer Reactions of Mo(IV,VI) Complexes

complex	X, XO	solvent	t, °C	$(k_1, k_{-1}) \times 10^2$ [a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	ref
$MoO_2(S_2CNEt_2)_2$ (61)	Ph_3P	$1,2\text{-}C_2H_4Cl_2$	25	7.1 (3)[b]			26
	Ph_2EtP	$1,2\text{-}C_2H_4Cl_2$	25	23 (2)			26
	$PhEt_2P$	$1,2\text{-}C_2H_4Cl_2$	25	43 (2)			26
	Et_3P	$1,2\text{-}C_2H_4Cl_2$	25	53 (1)			26
$MoO_2(L\text{-}NS_2)$ (68)	Ph_3P	DMF	23	0.7 (1)			322
	$(p\text{-}FC_6H_4)_3P$	DMF	25	0.97 (4)	11.7	−28.4	325
MoO_2(5-Br-ssp) (70)	Ph_2EtP	DMF	30	0.196 (6)			346
MoO_2(5-Cl-ssp) (70)	Ph_2EtP	DMF	30	0.187 (2)			346
MoO_2(ssp) (70)	Ph_2EtP	DMF	30	0.102 (9)	15.6	−20.7	346, 347
MoO_2(5-MeO-ssp) (70)	Ph_2EtP	DMF	30	0.084 (4)			346
MoO_2(5-Br-sse) (72)	Ph_2EtP	DMF	60	0.35 (3)			345, 347
MoO_2(5-Cl-sse) (72)	Ph_2EtP	DMF	60	0.35 (3)			345, 347
MoO_2(sse) (72)	Ph_2EtP	DMF	30	0.021 (2)	16.8	−19.7	347
			60	0.28 (2)			345, 347
MoO_2(5-MeO-sse) (72)	Ph_2EtP	DMF	60	0.214 (6)			345, 347
$MoO_2(L\text{-Cys-OEt})_2$	Ph_3P	C_6H_6	35	0.029	11	−37	339
$MoO(S_2CNEt_2)_2$ (60)	Me_2SO	$1,2\text{-}C_2H_4Cl_2$	25	0.016 (1)			26
$MoO(L\text{-}NS_2)$(DMF) (69)	Me_2SO	DMF	23	0.150 (3)			322
	Ph_2SO	DMF	23	0.143 (3)			322
	$(p\text{-}FC_6H_4)_2SO$	DMF	25	0.140 (7)	22.1	2.6	325
	d-biotin *S*-oxide (77)	DMF	23	0.136 (3)			322
	Cbz-(*S*)-Met *l*-(S–O)	DMF	23	0.163 (3)			322
	Cbz-(*S*)-Met *d*-(S–O)	DMF	23	0.170 (3)			322
	$3\text{-}FC_5H_4NO$	DMF	25	0.160 (8)	23.4	7.2	325

[a] Reaction 45: k_1 (M^{-1} s^{-1}), k_{-1} (s^{-1}). [b] Estimated uncertainty in the last digit in parentheses.

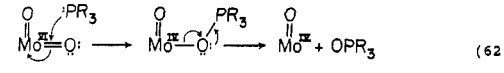
Thermodynamic and kinetics data for the reactions 45 are collected in Tables 11 and 12, respectively. Several points emerge immediately from the enthalpy data for reactions 46 and 52–60, obtained by a combination of direct measurements with auxiliary information and due entirely to Watt et al.[32] First, the impossibility of forming Mo(IV) by unassisted oxygen atom loss is quantitated by the huge positive enthalpies of reactions 52 and 53. Obviously, the oxygen atom removed must be stabilized, as in, e.g., Ph_3PO. For the reaction $Ph_3P + O(g) = Ph_3PO$, $\Delta H = -127$ kcal/mol in 1,2-dichloroethane[32] and -133 ± 6 kcal/mol in the gas phase,[30] accounting for the spontaneity of reaction 55, for which $\Delta H = -29$ kcal/mol by direct measurement. Second, spontaneous oxidation of molybdoenzyme substrates sulfite and acetaldehyde (reactions 54 and 56) is predicted, a matter explored in section V. Third, because of the relatively small, negative ΔH of reaction 46, the occurrence on thermodynamic grounds of the oxo transfer reactions listed does not depend on whether the final molybdenum product is dimer **76**, or **60** or **61** as appropriate. Other thermodynamic data for reactions 46 with related ligands[360-362] (cf. section IV) support a similar conclusion.

The μ-oxo dimer formation reaction 46 is a pervasive event under oxo transfer conditions. When fast and irreversible, a frequent circumstance, it precludes catalysis of substrate oxidation or reduction. When it is reversible and equilibrates rapidly, high stoichiometric yields may be achieved and catalysis is possible. This is the case with the reactions 47. Analysis of the kinetics of oxo transfer is somewhat involved, although a formal solution to this problem has been obtained.[26] In the absence of Mo(V) dimer formation, as for reactions 48–51, oxo transfer kinetics are fairly simple. Complexes **68** and **69**, containing bulky *gem*-diphenyl groups, were designed to prevent bridge formation by steric encumbrance. Other hindered ligands have been synthesized for the same purpose.[363] For reasons presently unclear, μ-oxo species do not appear to be generated in detectable amounts (or at all) in the reactions 49–51 of Schiff base complexes, although there is no evident steric barrier to their formation.

Independent variation of nucleophile and ligand structure have large effects on oxo transfer rates. Tertiary phosphines and phosphites are the general reagents of choice for the Mo(VI) → Mo(IV) conversion. Binuclear final products formed with these reagents (Table 10) are the consequence of dimerization reaction 46 following reaction 45. The only systematic study of nucleophile effects on reaction rates employed the four phosphines in Table 12 with $MoO_2(S_2CNEt_2)_2$. The most basic phosphine (Et_3P) reacts with a rate constant ca. 8 times greater than that of the least basic phosphine (Ph_3P). These and all other phosphine reactions follow rate law 61. The method of analysis of reaction 47 has

$$-d[Mo^{VI}]/dt = k_1[Mo^{VI}][R_3P] \qquad (61)$$

as its only assumption that the system is at equilibrium with respect to the dimerization reaction. As explained elsewhere,[26] prior rate constants for reaction 47 with X = Ph_3P are incorrect. Negative activation entropies indicate an associative process, which is initiated by nucleophilic attack of a Mo^{VI}=O unit, possibly by interaction with the vacant π^*-orbital. Scheme 62 provides a simple description.



(62)

Another manifestation of phosphine reactivity differences is the reduction of **74** to the $Mo^{IV}O$ state in refluxing MeCN/DMF by Ph_2EtP[344] but not Ph_3P. A key observation is that reaction 48 with X = Ph_3P and reactions 49 and 50 with X = Ph_2EtP proceed smoothly at 30–60 °C. In contrast, under the same conditions the dialkoxide analogue of **68** ($MoO_2(L\text{-}NO_2)$(solv)[99]) and **74** do not react with Ph_3P or Ph_2EtP, respectively, at any appreciable rate. This illustrates the general behavior that S-ligated complexes are more readily reduced than their O-ligated counterparts, the indicated donor atoms being anionic. Particularly resistant com-

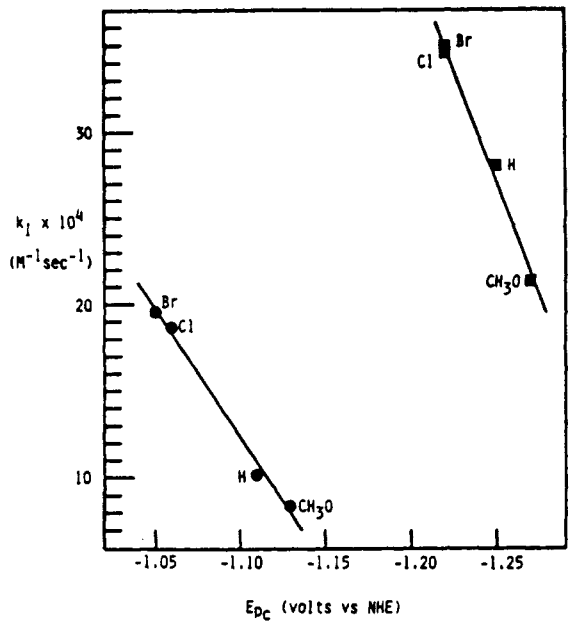


Figure 8. Correlation of rate constants for forward reactions 49 (●; at 30 °C) and 50 (■; at 60 °C) with X = Ph_2EtP in DMF with the peak potential for the Mo(VI) → Mo(V) reduction (R = Br, Cl, H, OMe) (from ref 347).

plexes may yield to the exceptionally basic phosphine $[2,4,6\text{-}(MeO)_3C_6H_2]_3P$.[364] Shown in Figure 8 is a linear correlation of second-order rate constants and reduction potentials for sets of complexes **70** and **72** with different R substituents. The potential of the irreversible Mo(VI/V) reduction is taken as an index of relative reducibility, a not unreasonable assumption for complexes of such similar structures. Although the spreads in data are small, the correlation appears to be real. Topich and Lyon[347] first formulated a donor atom reactivity series for the reduction of $Mo^{VI}O_2$ complexes by phosphines. Qualitative reactivity observations and the data of Table 12 lead to the kinetics series 63. It is intended

$$S_4\ (61) > NS_2\ (68) > ONS\ (70, 72) \gg NO_2\ (74) \quad (63)$$

only as a rough guide in predicting or regulating reactivity. Of all $Mo^{VI}O_2$ species examined, $MoO_2(S_2CNEt_2)_2$ is the most kinetically facile oxygen atom donor. For example, with Ph_2EtP it reacts over 200 and 1000 times faster than **70** and **72**, respectively.

3. *Mo(IV) → Mo(VI)*

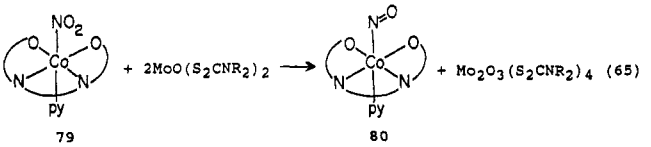
Reaction enthalpies of $MoO(S_2CNEt_2)_2$ in Table 11 indicate ready oxidation by dioxygen and the inability of water to act as an oxo donor, properties which extend to the Mo(IV) complexes in reactions 48–51. The first examples of oxo transfer from substrate (other than dioxygen) to molybdenum were provided by Mitchell and Scarle[320] in 1975, who qualitatively showed oxidation of **60** in reaction 45 with XO = Me_2SO, pyO, and several other donors. However, the reactions claimed for Ph_3PO, N_2O, and nitrate are incorrect.[29,330] Subsequently, a variety of substrates have been reduced, principally heterocyclic, imino, and tertiary amine *N*-oxides and sulfoxides (Table 10). Among these are certain molybdoenzyme substrates, including Ph_2SO, *d*-biotin *S*-oxide (**77**), and nicotinamide *N*-oxide (**78**).

The kinetics of substrate reduction in reaction 48 follow scheme 64, where XO = *S*-oxide and *N*-oxide.[322,325] The rate of substrate reduction is first

$$\begin{array}{ccc} MoO(L\text{-}NS_2)(DMF) + XO & \rightleftharpoons & MoO(L\text{-}NS_2)(XO) + DMF \\ & & \downarrow k_{-1} \\ & & MoO_2(L\text{-}NS_2) + X \end{array} \quad (64)$$

order in complex **69** and XO, and at sufficiently high [XO] is independent of substrate concentration. Under these conditions, the ligand binding equilibrium is shifted essentially completely toward the adduct, from which product is formed in a first-order reaction. Complex **69** is well configured to bind substrate by solvent displacement; ligand constraints[99] render a six-coordinate solution structure unlikely. Given the substantial differences in local structure around the sulfur atoms and the small range of binding constants,[322] it is highly probable that *S*-oxide substrates bind through their oxygen atoms. Scheme 64 is likely of general applicability. Complexes **71**, **73**, and **75** offer one or two binding sites to potential substrates; their structures are unknown in detail. The concentration variations required to detect the ligand binding step in the reaction of **60** with Me_2SO were not carried out, but this complex has been shown to bind weakly other neutral ligands.[365] Rate constants for reactions of dithiocarbamate and L-NS_2 complexes with common substrates show the reciprocal behavior expected if intrinsic reducibility/oxidizability contributes significantly to activation energies. Thus, for reduction by Ph_3P k_1(**61**):k_1(**68**) = 10:1 and for oxidation by Me_2SO k_{-1}(**69**):k_{-1}(**60**) = 9.4:1. The nearly constant factor of 10 is accidental.

Other reactions in this category include the oxidation of **60** by Ph_3AsO, Ph_3SbO, *t*-$BuONO_2$, and percarboxylic acid **1**. The R = SO_3^- derivative of **71** and complex **69** are cleanly oxidized by nitrate in DMF solution to **70** and **68**, respectively, with formation of nitrite, which was scavenged by sulfamic acid. Lastly, reaction 65 is an example of an infrequently encoun-



79 80

tered process which is simultaneously a ligand-based reduction and a metal-centered oxidation. No measurable reaction occurs between Co(saloph)(NO)(py) (**80**) and $MoO_2(S_2CNR_2)_2$, showing that nitrito complex **79** is a stronger oxidant than the latter. Because **79** is reduced by Ph_3P and **80** is oxidized by dioxygen, **79** is a catalyst for the aerial oxidation of the phosphine.[204]

4. *Thermodynamic Aspects of the Mo(VI) ⇌ Mo(IV) Conversions*

A sufficient number of substrates have been tested in reaction 45 to facilitate an inquiry into the range of molybdenum-mediated oxo transfer reactions and the factors that render molybdenum complexes competent in this respect. Our initial approach to this problem has been described.[324] Substrate reactions are reduced to a common thermodynamic basis by use of available data for reaction 66. Reaction enthalpies are calculated

$$X + {}^1/_2O_2(g) \rightarrow XO \quad (66)$$

from bond dissociation energies or related information[30,32,366–369] and ΔH = 59.55 (2) kcal/mol for ${}^1/_2O_2(g)$

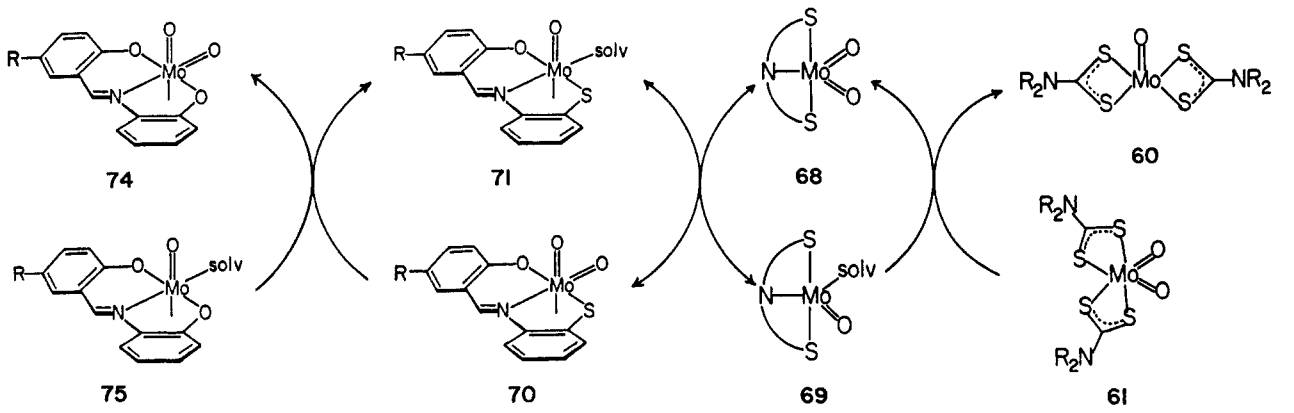


Figure 9. Schematic depiction of intermetal oxo transfer reactions of Mo(IV,VI) complexes. Spontaneous reactions occur from left to right; the middle reaction is an equilibrium that favors **69** and **70** (from ref 324).

→ O(g) and are collected in Table 13. Included as "calibration" points for the observer are values for the oxidation of methane and dihydrogen. The ΔH value for reaction 59 (Table 11) allows complexes **60** and **61** to be accurately placed in the table. The reaction enthalpies do not constitute a precisely comparable set owing to differences in physical state and solvent and in uncertainties in auxiliary data used to calculate the ΔH values. With these points noted, Table 13 provides a thermodynamic series with a utility analogous to that of a series of half-reactions and their standard potentials. Combinations of the reactions 66 and 59 lead to the net reaction 45 and an estimate of its ΔH value. Such a reaction is spontaneous by the criterion of a negative ΔH. Free energy data would be preferable; however, the limited results available[324] (not given) lead to the same conclusions. Thus, a Mo(IV) complex can reduce to X any substrate XO which occurs in a reaction with a more positive ΔH, and a Mo(VI) complex can oxidize to XO any substrate X which occurs in a reaction with a less positive ΔH. Where kinetics permit and competing reactions are unimportant, these predictions are upheld by the reactions of the pair **60/61**. It is assumed that the ΔH values for the formation of azoxybenzene and (phenylmethylene)benzenamine *N*-oxide are reasonable estimates for heterocyclic *N*-oxides, for which data are unavailable. The only possibly contrary result is based on the indirectly evaluated $\Delta H = -44$ kcal/mol for Ph_3AsO. As already noted, this compound *oxidizes* **60**, and **69** as well. We conclude that the correct value for the oxidation is >−35 kcal/mol.

In the absence of necessary thermodynamic data, other complexes can be roughly interleaved in the series of Table 13 by qualitative observations of reactivity. To do so, we anticipate the occurrence of *intermetal* oxo transfer described in section IV and refer to Figure 9. This depicts the spontaneous reaction of $Mo^{VI}O_2$ and $Mo^{IV}O$ complexes with different ligands. The oxo *donor* order is **61** > **68** > **70** > **74** and the oxo *acceptor* order is **75** > **71** > **69** > **60**. Correlations with kinetics results are apparent. Thus the couples **69/68** > **71/70** > **75/74**, arranged in the order of increasing ΔH of oxidation, all lie *below* **60/61**. Because reaction 67 is spontaneous,[324]

$$MoO_2(L\text{-}NS_2) + 2PhSH \xrightarrow{DMF} MoO(L\text{-}NS_2)(DMF) + PhSSPh + H_2O \quad (67)$$

ΔH for the oxidation of **69** falls within the approximate

TABLE 13. Thermodynamic Data for the Reaction X + $^1/_2O_2$ = XO

X[a]	XO[a]	ΔH,[b] kcal/mol
o-$C_6H_4(CO_2H)_2$	*o*-$C_6H_4(CO_2H)(CO_3H)$	+28
N_2(g)	N_2O(g)	+20
t-BuOH	*t*-BuOOH	+15[d,f]
$S_2O_3^{2-}$(aq)	**$S_2O_4^{2-}$(aq)**	+12
PhCH=NPh(g)	PhCH=N(O)Ph(g)	−4[e]
ClO_2^-(aq)	**ClO_3^-(aq)**	−8
MeONO(g)	$MeONO_2$(g)	−13
PhN=NPh(g)	PhN=N(O)Ph(g)	−17[e]
NO_2^-(aq)	**NO_3^-(aq)**	−25 (−32[c,g])
C_2H_4(g)	C_2H_4O(g)	−25
Me_2S(g)	**Me_2SO(g)**	−27
CH_4(g)	CH_3OH(g)	−30
Ph_3As	Ph_3AsO	>−35 (−44[d,f,h])
$MoO(S_2CNEt_2)_2$ (**60**)	$MoO_2(S_2CNEt_2)_2$ (**61**)	−35[c,g]
$(MeO)_2SO$(g)	$(MeO)_2SO_2$(g)	−49
MeNC(g)	MeNCO(g)	−50
Me_2SO(g)	Me_2SO_2(g)	−52
2PhSH	PhSSPh + H_2O	−54[i]
H_2(g)	H_2O(g)	−58
MeCHO(g)	$MeCO_2H$(g)	−64
HCO_2^-(aq)	HCO_3^-(aq)	−64
SO_3^{2-}(aq)	SO_4^{2-}	−65 (−64[c,g])
Ph_3P(g)	Ph_3PO(g)	−67 (−67[c,g])
CO(g)	CO_2(g)	−68
n-Bu_3P(g)	*n*-Bu_3PO(g)	−80[i]
Si_2Me_6(g)	Si_2OMe_6(g)	−99[i]

[a] Enzyme substrates in boldface. [b] Calculated from $\Delta H°_f$ data in ref 367 and 369 unless otherwise noted. [c] Reference 32. [d] Reference 30. [e] Reference 368. [f] Benzene solution. [g] 1,2-Dichloroethane solution. [h] See text. [i] Reference 366.

limits of −35 to −54 kcal/mol. Numerous predictions are offered by the thermodynamic reaction series, among them the reduction of isocyanates, sulfones, and water by highly oxidizable Mo(IV) complexes with $\Delta H \lesssim -60$ kcal/mol and the oxidation of sulfides by oxometal complexes with $\Delta H \gtrsim -27$ kcal/mol. As will be developed in section V, complexes **60/61** and **68/69** are thermodynamically competent to oxidize or reduce the substrates of many molybdoenzymes.

5. *Mo(V) → Mo(VI)*

This transformation has usually been effected by the minimal reaction 68 in dry DMF or dichloromethane with complicated kinetics. Nitrogen dioxide can be

$$[Mo^VO]^{3+} + NO_3^- \rightarrow [Mo^{VI}O_2]^{2+} + NO_2 \quad (68)$$

quantitated as nitrite following the hydrolysis reaction $2NO_2 + H_2O \rightarrow HNO_2 + H^+ + NO_3^-$. The complexes listed as products in Table 10 are not necessarily final

TABLE 14. Oxo Transfer Reactions of Tungsten Compounds

species	reactant	product	ref
		W(II) → W(IV)	
$CpW(CO)_2(MeC(O)C_2H_2)$ (81)	NO	$CpW(O)Me(C_2H_2)$ (**82a**) + $CpW(O)(COMe)(C_2H_2)$ (**82b**)	374
$WCl_2(PMePh_2)_4$	CO_2	$WOCl_2(CO)(PMePh_2)_2$	377
$WCl_2(PMePh_2)_4$	C_2H_4O	$WOCl_2(PMePh_2)_2(C_2H_4)$	377
		W(III) → W(VI)	
$W_2(O\text{-}t\text{-}Bu)_6$ (83)	PhNO	$W_2O(NPh)_2(O\text{-}t\text{-}Bu)_6$ (84)	375
		W(VI) → W(IV)	
$WOCl_4$	Ph_3P	$WCl_4(PPh_3)_2 + WOCl_4(OPPh_3)\cdot PPh_3$	376

products inasmuch as substitution of neutral ligands by excess chloride or nitrate after oxidation has been reported in several cases. Kinetics analyses of reaction 68[328-333] lead to the sequence 69–71, in which neutral

$$MoOCl_3L_2 \rightleftharpoons MoOCl_3L + L \quad (69)$$

$$MoOCl_3L + NO_3^- \rightleftharpoons [MoOCl_3L(ONO_2)]^- \quad (70)$$

$$[MoOCl_3L(ONO_2)]^- \rightarrow [MoO_2Cl_3L]^- + NO_2 \quad (71)$$

ligand dissociation and substrate binding are followed by atom and electron transfer in the slow step. If the z axis is along the Mo=O bond, the ground-state configuration of Mo(V) is $4d_{xy}^1$. As proposed by Garner et al.,[350] efficient electron transfer requires overlap of $4d_{xy}$ and the nitrate π^*-orbital, which is only possible when nitrate is monodentate and cis to the oxo ligand. Consequently, in some cases after nitrate binding and before electron transfer, isomerization to the cis configuration may be required. With complexes containing a bidentate ligand such as $MoOCl_3(bpy)$, dissociation reaction 72, occurring prior to nitrate binding and

$$MoOCl_3(L\text{-}L) \rightarrow [MoOCl_2(L\text{-}L)]^+ + Cl^- \quad (72)$$

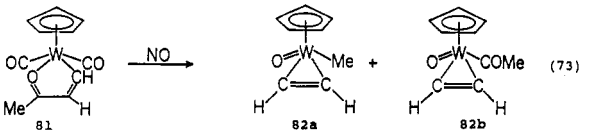
producing charge separation, appears to be the rate-determining step in DMF.[332,333] Oxygen-18 experiments to confirm that the source of the added atom in the Mo(VI) product is nitrate (possibly superfluous in the nonaqueous conditions employed) have not been reported for these reactions. Any close relevance of these reactions to those of nitrate reductases requires that the latter bind substrate in the Mo(V) state and generate product by the disproportionation of NO_2. There is no unambiguous evidence that either of these conditions is met.

Oxidation of Mo(V) as $MoOCl_3(OPPh_3)_2$ in a reaction of essential stoichiometry $Mo^VO + NO_2^- \rightarrow Mo^{VI} + NO$ has been observed in a complicated system in dichloromethane solution.[370] The Mo(VI) products in dilute solution are unidentified. In concentrated solutions with a high initial $[NO_2^-]$:[Mo] ratio, a salt of $[Mo_8O_{26}]^{4-}$ was isolated.

H. Tungsten

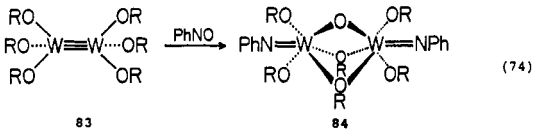
Few if any parallels in the oxo transfer chemistry of molybdenum and tungsten have been discovered or developed. This situation is due in part to lack of a commensurate research effort in tungsten chemistry. Nonetheless, with the possible exception of linear $W^{IV}O_2$, the corresponding oxotungsten functional groups are known[371-373] (Figure 1); of these, $W^{VI}O_3$ has not been structurally defined. Similarly, bridge groups **13–16** have been recognized (Table 2), but a detailed structure of **16** is lacking.

The few types of oxo transfer reactions reported thus far are listed in Table 14. Reaction 73 is described as



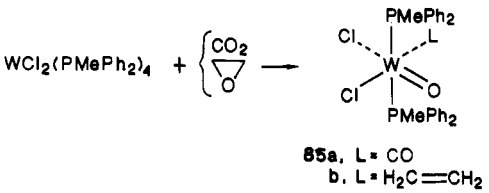
(73)

instantaneous in toluene at −78 °C and is one of very few oxo transfer systems initially containing nitrogen monoxide. However, it is not known whether NO or a reduction product such as N_2O arising from its reaction with **81** is the actual atom donor. Oxotungsten cyclopentadienyl complexes are available by other routes,[104] as are oxotungsten(IV) olefin complexes.[64] Products **82a** and **82b** are the only examples of Cp–oxo–olefin complexes of tungsten. Reaction 74 (R = t-Bu) is complex, involving the destruction of the W≡W bond of **83** with formation of W=N bonds and retention of binuclearity in product **84**, which consists of two faced-shared octahedra. The reaction does have an oxo



(74)

transfer component inasmuch as ligands $2PhN^{2-} + O^{2-}$ can be considered to arise from the six-electron metal oxidation induced by the 2 equiv of nitrosobenzene used in synthesis. The exact stoichiometry of the reaction is unknown; the source of the bridging oxo ligand is likely nitrosobenzene, but this has not been established. The C–O bond cleavage of carbon dioxide to an oxo–carbonyl complex in reaction 75 is unprecedented. The



(75)

reaction occurs in benzene solution at ambient temperature and 1 atm of CO_2. Product **85a** contains a W^{IV}=O group with a bond distance of 1.689 (6) Å as part of a distorted octahedral structure.[377] The W(II) precursor also reacts with ethylene oxide to yield the oxo–olefin product **85b**. Earlier, $WOCl_2(PMePh_2)_2L$ (L = CO, CH_2=CHR) had been prepared and found to be resistant to rearrangement reactions affording CO_2 or epoxides,[64] a result now understandable in terms of the occurrence of the reverse reactions 75. It and related reactions[377] are doubtless driven in part by the stability of the oxotungsten(IV) unit.

TABLE 15. Oxo Transfer Reactions of Technetium and Rhenium Compounds

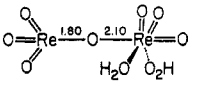
species	reactant	product	ref
	Tc(V) → Tc(III)		
$TcOCl_2(HBpz_3)$	Ph_3P (PhMe, Δ)	$TcCl_2(HBpz_3)(PPh_3)$	398
$TcOCl_2(HBpz_3)$	Ph_3P (CH_2Cl_2)	$TcCl_2(HBpz_3)(OPPh_3)$	398
	Tc(V) → Tc(IV)		
$[TcO(MoS_4)_2]^-$	Ph_3P	$Tc(PPh_3)_2(MoS_4)_2(OH_2)$	387
	Re(V) → Re(VII)		
$ReCl_5$	Cl_2O	$ReO_3Cl + Cl_2$	388
	Re(VII) → Re(V)		
$[ReO_4]^-$	Ph_3P, HL[a]	$ReOL_3(PPh_3)_2$	389
$[ReO_4]^-$	Ph_3P, HL,[a] EtOH	$ReOL_2(OEt)(PPh_3)_2$	389
$[ReO_4]^-$	dppe, H^+	$[ReO_2(dppe)]^+$	399
Re_2O_7	Et_3P, L[b]	$[ReO_2L_4][ReO_4]$	392
Cp^*ReO_3 (88)	Ph_3P	$Cp^*_2Re_2O_4$ (91)	390, 397
Cp^*ReO_3	Ph_3P, O_2	$Cp^*_2Re_2O_3(ReO_4)_2$ (89)	391
Cp^*ReO_3	Ph_3P, O_2	$[Cp^*_3Re_3O_6]^{2+}$ (90)	396
	Re(VII) → Re(III)		
$[ReO_4]^-$	$PhMe_2P$, HL[a]	$ReL_3(PMe_2Ph)_3$	403
$[ReO_4]^-$	Ph_2MeP, HCl	$ReCl_3(PMePh_2)_3$	403
	Re(V) → Re(III)		
$ReOL_3(PPh_3)_2$[c] (trans)	Ph_3P, RCN[d]	$ReL_3(RCN)(PPh_3)_2$	400
$ReOCl_3(PPh_3)_2$ (trans)	Ph_2PH	$ReCl_2(PPh_2)(PHPh_2)_3$	401
$ReOCl_3(dppe)$	$PhEt_2P$	$ReCl_3(dppe)(PEt_2Ph)$	402
$ReOCl_3(PPh_3)_2$	Ph_3P, TlS_2CNEt_2	$ReCl_2(S_2CNEt_2)(PPh_3)_2$	404
$ReOCl_2(S_2CNEt_2)(PPh_3)$	Ph_3P	$ReCl_2(S_2CNEt_2)(PPh_3)_2$	404
$ReOCl_3(PPh_3)_2$	R_3P[e]	$ReCl_3(PR_3)_3$	393
$ReOCl_2(HBpz_3)$	Ph_3P	$ReCl_2(HBpz_3)(PPh_3)$	386
$ReO_2I(PPh_3)_2$	MeCCMe	$Re(O)I(MeCCMe)_2$ (96) + Ph_3PO + Ph_3P	394
$Cp^*ReO(O_2CCPh_2)$ (93)	CO	$Cp^*Re(CO)_2(OC(O)CPh_2)$ (95)	395
$Cp^*ReO(OC(O)NPh)$ (92)	CO	$Cp^*Re(CO)_2(OC(O)NPh)$ (94)	395
Cp^*ReOCl_2	CO	$Cp^*Re(CO)_2Cl_2$	395

[a] HL = HCl, HBr. [b] L = py, 4-Mepy. [c] L = Cl^-, Br^-. [d] R = Me, *n*-Pr. [e] R_3 = *n*-Pr_3, *n*-Bu_3, Me_2Ph, Et_2Ph, *n*-Pr_2Ph, *n*-Bu_2Ph, $EtPh_2$.

The $W^{VI}O_2 \rightarrow W^{IV}O$ reduction, analogous to a frequent and usually facile process in molybdenum chemistry, has not been reported. In this laboratory, the complexes MO_2(5-*t*-Busap)(MeOH) (M = Mo, W) have been prepared and shown to have a distorted octahedral structure with methanol trans to one of mutually cis oxo ligands.[327] As yet, no means of reductive oxo transfer of the tungsten complex has been found. In contrast to the clean reduction of $MoO_2(S_2CNR_2)_2$ to $MoO(S_2CNR_2)_2$ by tertiary phosphines, $WO_2(S_2CNMe_2)_2$ is claimed to yield uncharacterized products.[378] The only apparent W(VI) reduction by oxo transfer is that in the system $WOCl_4/Ph_3P$, where about half of the reactant is converted to the W(IV) product $WCl_4(PPh_3)_2$. Given the generally lesser stability of W(IV), it is probable that reactions of $W^{VI}O_2$ complexes will be slower, or not proceed at all, vs those of $Mo^{VI}O_2$ analogues; i.e., in the thermodynamic series of Table 13 the $W^{IV}O/W^{VI}O_2$ reaction will have a substantially more negative ΔH. Particularly intriguing is the possibility that W(IV) may be an exceptionally potent reductant by oxo transfer. Investigation of this and other aspects of tungsten oxo transfer chemistry requires prior development of routes to soluble mononuclear $W^{IV}O$ complexes. Very few such (nonorganometallic) complexes are known. The best characterized, including $[WO(OH)(CN)_4]^{3-}$[379] and $WOCl_2(PR_3)_3$,[380] contain π-acid ligands; their susceptibility to oxidation by atom transfer has not been examined.

I. Technetium and Rhenium

The groups M^VO, linear M^VO_2, and $M^{VII}O_3$ of these elements have been well characterized in stable compounds. Bent ReO_2 is known only in the pseudotetrahedral Re(VI) complex $ReO_2(mes)_2$. The trioxo group has been found in only a few compounds, among these Tc_2O_7, Cp^*ReO_3, and $Re_2O_7(H_2O)_2$. The latter, historically referred to as "perrhenic acid", consists of the discrete molecules **86** with tetrahedral and distorted



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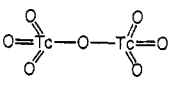

87

octahedral coordination. Unlike its technetium analogue **87**, crystalline Re_2O_7 is not molecular, consisting instead of tetrahedral ReO_4 and distorted octahedral ReO_6 units linked by oxo bridging to build polymeric double layers.[381] Existence of the $Re^{VII}O_4$ group, in a compound formulated as $Ba_3[ReO_4(OH)_2]_2$, is based on infrared spectral evidence only.[382] Tabulations of oxotechnetium compounds are available elsewhere.[383-385] Rouschias' summary of rhenium chemistry in 1974[386] remains a useful source of oxorhenium compounds and their syntheses and reactions. Oxo transfer reactions are collected in Table 15. All are reductive transformations except for the preparation of ReO_3Cl from $ReCl_5$ and chlorine dioxide.

The Tc(V) → Tc(III) reductive oxo transfer is well established with $TcOCl_2(HBpz_3)$. It and its Re(V) analogue react with excess Ph_3P in refluxing toluene to afford phosphine adducts in good yield. In dichloromethane at room temperature, the Tc(V) complex is reduced to the Ph_3PO adduct but the Re(V) complex does not react. This is in keeping with the Mo/W comparison above, i.e., another manifestation of the greater difficulty in reducing a third-row vs a second-

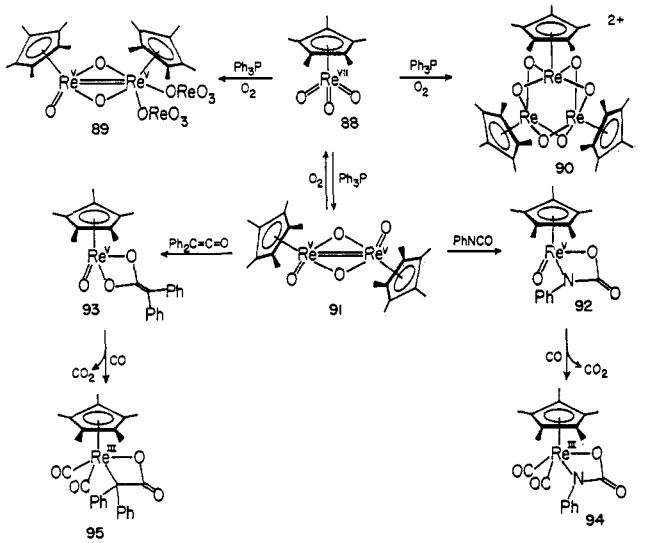


Figure 10. Functionalization and oxo transfer reactions of Cp^*ReO_3.

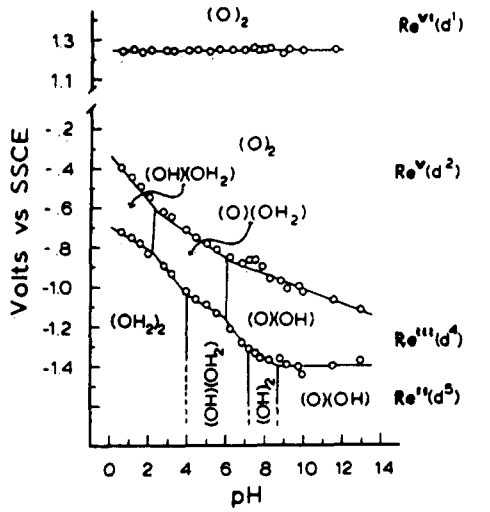


Figure 11. Half-wave potential vs pH diagram for an aqueous system based on $[ReO_2(py)_4]^+$ showing species distribution over the pH range 0.5–13. Potentials are referenced to SCE; vertical lines denote pK_a values (from ref 409).

row transition element in the same oxidation state and coordination environment. The complex $[TcO(edt)_2]^{1-}$ is reported not to react with Ph_3P in refluxing acetonitrile,[405] an inertness that is probably due to the instability of Tc(III) in the electron-rich environment of the dithiolate ligands. In the only other oxo transfer reaction of a Tc(V) complex, $[TcO(MoS_4)_2]^-$ was converted to an apparent Tc(IV) product. Neither this material nor the course of the reaction has been characterized in detail.

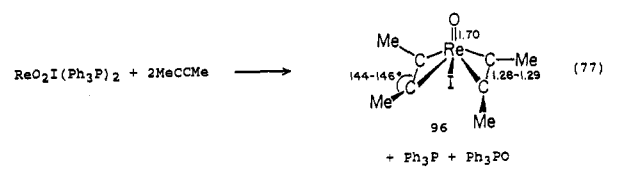
Reduction of perrhenate yields Re(V) or Re(III) products depending on the phosphine and reaction conditions. One of the Re(V) products, *trans*-$ReOCl_3(PPh_3)_2$, is perhaps the most versatile precursor compound in Re(V) chemistry. It is subject to reduction with phosphines, providing an entry to Re(III) compounds. Reaction 76 is nearly quantitative in re-

$$\textit{trans}\text{-}ReOCl_3(PPh_3)_2 + Ph_3P + MeCN \rightarrow ReCl_3(MeCN)(PPh_3)_2 + Ph_3PO \quad (76)$$

fluxing acetonitrile, and Ph_3PO is formed in an amount corresponding to this stoichiometry.[400] Inasmuch as Ph_3P does not appear to reduce $ReOCl_3(PPh_3)_2$ directly, apparently for steric reasons, it is probable that the first step in the reaction is reversible substitution of one phosphine by solvent. Phosphine then attacks the solvate complex $ReOCl_3(MeCN)(PPh_3)$ to give product. The low-yield reduction of $ReOCl_3(PPh_3)_2$ in a refluxing nitrile solvent without added phosphine proceeds by this path. The more basic dialkylphenylphosphines and alkyldiphenylphosphines displace Ph_3P from $ReOCl_3(PPh_3)_2$ and reduce Re(V) to Re(III), affording *mer*-$ReCl_3(PR_3)_3$. Reduction of Re_2O_7 with Et_3P affords a route to complexes with the linear Re^VO_2 group.

Of particular interest among Re(VII) → Re(V) → Re(III) transformations are those commencing with Cp^*ReO_3 (**88**) and carried out by Herrmann and coworkers.[390,391,395-397] These are summarized in Figure 10 and together with several other reactions[396] constitute the most thorough reactivity study of any trioxometal group. In the presence of trace or large amounts of dioxygen, **88** is converted to **89** or mixed-valence **90**, respectively. The latter is the first example of the $Re_3(\mu\text{-}O)_6$ core unit. In the absence of dioxygen, **88** is reduced to the diamagnetic dimer **91**, the only rhenium compound known with bridge **18**. This compound is cleaved with phenyl isocyanate to **92** and with diphenylketene to **93**. Both of these are reduced with carbon monoxide at 50 atm, to the Re(III) dicarbonyls **94** and **95** (with linkage isomerization), respectively. Stabilization of this relatively reducing oxidation state of rhenium by carbon monoxide must be a substantial driving force for presumed oxo transfer to form carbon dioxide. Isotope labeling to check this step has not been reported.

Although its stoichiometry involves two rather than one added ligand(s), reaction 77 is an instance of generalized reaction 10 whereby binding of an exogenous ligand induces oxo transfer. This reaction has been



(77)

classified under Re(V) → Re(III). However, the product, Re(O)I(MeCCMe)$_2$ (**96**), is electronically ambiguous in that the C–C bond distances and C–C–C bond angles are suggestive of an extent of reduction of the acetylenes and therewith an effectively higher metal oxidation state. This is one of the very few cases in which the generalization of stabilization of a M=O group by a metal oxidation state of ≥4+ is not clearly upheld.

Unlike the $Mo^{VI}O_2$ group, no oxo transfer reactions have been described for the Re^VO_2 group. However, this group has certain reactivity features that are instructive for oxometal groups generally. Taking $[ReO_2(en)_2]^+$ as an example, the complex undergoes the successive protonation reactions 78[406-408] with the indicated pK_a values.[406] Upon reduction below Re(V), the complexes

$$\underset{\text{yellow}}{[ReO_2(en)_2]^+} \overset{H^+}{\underset{3.26}{\rightleftharpoons}} \underset{\text{pink}}{[ReO(OH)(en)_2]^{2+}} \overset{H^+}{\underset{-0.9}{\rightleftharpoons}} \underset{\text{blue}}{[Re(OH)_2(en)_2]^{3+}} \quad (78)$$

become much more basic. The system based on $[ReO_2(py)_4]^+$ has been the most thoroughly examined.[409]

Species distribution as a function of pH and potential is shown in Figure 11. The Re(VI) complex $[ReO_2(py)_4]^{2+}$ is not protonated over the entire pH range. $[ReO_2(py)_4]^+$ behaves as in the above series but with pK_a values larger by about 3 units. The most intriguing result is the existence of oxo complexes $[Re^{III}O(OH)(py)_4]$ and $[Re^{II}O(OH)(py)_4]^-$ above pH = pK_a = 6.0 and 8.7, respectively. These two complexes, whose formulations have not been confirmed by isolation, are apparent exceptions to the M=O group stability generalization. Both are capable to some extent of stabilizing π-bonding interactions, with maximum bond orders of 1.5 (Re(II), d^5) and 2 (Re(III), d^4). Despite the relatively weak Re–O bonds, it is unlikely that these complexes would be reducible by oxo transfer to Re(0,I) without stabilizing these oxidation states with π-acceptors.

Oxidation of the Re^VO_2 group in $[ReO_2(en)_2]^+$ has been investigated in aqueous solution with several reagents capable of oxo transfer.[410] Using the ^{18}O-enriched complex, reaction with permanganate, hypochlorite, and ozone resulted in the inclusion of 1.71, 1.91, and 1.95 atoms of oxygen in the product, $[ReO_4]^-$. In systems containing unenriched complex and oxidant and enriched water, 2.16 (ClO^-) and 1.62 (O_3) atoms of oxygen from solvent were incorporated in the product. Hence, direct oxo transfer, which could at most involve one atom of oxygen to generate Re(VII), is a minor or negligible pathway in these oxidations.

J. Ruthenium and Osmium

Owing to the accessibility of oxidation states IV–VIII, the oxo chemistry of these elements is extensive. The tetraoxides are the best known compounds; RuO_4 is less stable and a generally stronger oxidant than OsO_4. Their use as oxidants in organic chemistry has been reviewed,[33-35] and a descriptive account of the chemistry of the higher oxidation states is available.[411] The monograph by Seddon and Seddon[412] provides exhaustive coverage of oxoruthenium compounds. Well-characterized complexes with terminal oxo ligands are most frequently encountered with, but are not restricted to, the IV, VI, and VIII states.

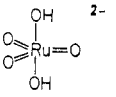
Diamagnetic molecules containing the linear $Ru^{VI}O_2$ and $Os^{VI}O_2$ groups are numerous. Recent work[413,414] has provided crystallographic verification of the linearity of $Ru^{VI}O_2$; that property of the $Os^{VI}O_2$ group had been similarly established much earlier (Table 2). Distorted tetrahedral $OsO_2(mes)_2$ provides the only instance of a bent configuration of the latter group. Monooxo species are less common. As shown by reactions 79 and 80, the reduction $Ru^{VI}O_2 \rightarrow Ru^{IV}O$ has been effected

$$[RuO_2(tmc)]^{2+} + Ph_3P \rightarrow [RuO(tmc)Cl]^+ + Ph_3PO \quad (79)$$

$$RuO_2(py)_2(OAc)_2 + Ph_3P \rightarrow \text{“}RuO(py)_2(OAc)_2\text{”} + Ph_3PO \quad (80)$$

in two instances with Ph_3P. Reaction 79 was carried out in an acetone suspension of the complex with excess phosphine.[415] The product complex has trans stereochemistry and a triplet ground state; the chloride ligand must derive from perchlorate but it is not known how this ion was reduced. In reaction 80, Ph_3P is rapidly and quantitatively converted to the oxide.[414] The nature of the Ru(IV) product has not been fully established. Among monooxo complexes, detailed structures are available only for $[RuO(tmc)Cl]^+$ and $OsO(O_2C_2H_4)_2$ (9).

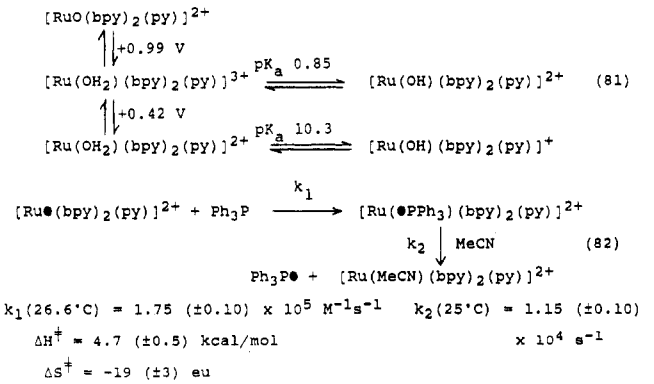
Several $Os^{VIII}O_3$ complexes have been reported; of these, OsO_3F_2 and $[OsO_3F_3]^-$ are the most securely identified but no X-ray structural determinations have been performed (excluding the tetrahedral derivatives $OsO_3(NR)$ and $[OsO_3N]^-$ of OsO_4[118,119,411]). The only example of a RuO_3 group has been found in the compound originally formulated as $BaRuO_4 \cdot H_2O$. This is actually $Ba[RuO_3(OH)_2]$ whose anion **97** is trigonal



97

bipyramidal with the $Ru^{VI}O_3$ group in the equatorial plane.[110] This arrangement permits extensive Ru–O π-bonding. The mean Ru–O bond length of 1.754 (5) Å is comparable to those in RuO_4 (1.705 Å[416]) and $KRuO_4$ (1.79 Å[417]). No other planar MO_3 groups have been recognized. Structure 7 of the $Os^{VIII}O_4$ group in complexes such as $[OsO_4(OH)_2]^{2-}$ and $[OsO_4F_2]^{2-}$[8,411] has been inferred from spectroscopic data.[382] There is no clear evidence for the existence of the RuO_4 *group*. The oxo transfer reactions in Table 16 are both oxidative and reductive in nature. Of the oxo metal groups in Figure 1, $Ru^{IV}O$, $Ru^{VI}O_2$, $Os^{VI}O_2$, and $Os^{VIII}O_4$ are implicated in these reactions.

As developed by Meyer and co-workers, the oxo transfer chemistry of ruthenium derives from several key complexes containing pyridine or polypyridyl ligands. The first of these, $[Ru(bpy)_2(py)(OH_2)]^{2+}$, is the starting material for the preparation of $[RuO(bpy)_2(py)]^{2+}$, by far the most thoroughly studied of the very few *mono*oxoruthenium complexes reported. This complex was originally obtained from the aquo complex by oxidation with Ce(IV) in acid solution[425] and subsequently by oxo transfer from hypochlorite. It is the terminal oxidized member of the reversible redox/acid–base series 81 and, as with several other series



members, has been isolated as a stable salt.[425,435] Note the factor of about 10 in pK_a values between the Ru(II) and Ru(III) complexes, a behavior due largely to the stabilization of hydroxide by back-bonding to Ru(III). The complex $[RuO(bpy)_2(PEt_3)]^{2+}$ is prepared in a similar manner and generates an analogous series.[428] $[RuO(bpy)_2(py)]^{2+}$ is cleanly reduced to the Ru(II) state by Ph_3P in reaction sequence 82.[424] The transfer of the ^{18}O label from complex to substrate is complete. The first step is the fastest reductive oxo transfer step yet

TABLE 16. Oxo Transfer Reactions of Ruthenium and Osmium Compounds.

species	reactant	product	ref
		Ru(II) → Ru(III)	
$[Ru(OH_2)_6]^{2+}$	ClO_4^-	$[Ru(OH_2)_6]^{3+}$	418
$[Ru(bpy)_2(py)(OH_2)]^{2+}$	NO_3^-	$[Ru(bpy)_2(py)(OH_2)]^{3+}$	419
		Ru(II) → Ru(IV)	
Ru(TTP)(CO)	m-$ClC_6H_4CO_3H$	$[Ru(TTP)(m\text{-}ClC_6H_4CO_2)]_2O$ + $[Ru(TTP)(OH)]_2O$ (99)	420
Ru(TPP)(CO)(MeOH)	t-BuOOH	$[Ru(TPP)(OMe)]_2O$	150
Ru(OEP)(CO)(MeOH)	t-BuOOH	$[Ru(OEP)(OMe)]_2O$	150
Ru(OEP)(CO)(solv)	t-BuOOH	$[Ru(OEP)(OH)]_2O$	421
$[Ru(bpy)_2(py)(OH_2)]^{2+}$	NaOCl	$[RuO(bpy)_2(py)]^{2+}$	422
$[Ru(trpy)(bpy)(OH_2)]^{2+}$	NaOCl	$[RuO(trpy)(bpy)]^{2+}$	422
		Ru(II) → Ru(VI)	
Ru(TMP)(CO)(solv) (98)	PhIO	RuO_2(TMP) (100)	420
Ru(TMP)(CO)(solv)	m-$ClC_6H_4CO_3H$	RuO_2(TMP)	420
		Ru(III) → Ru(IV)	
Ru(OEP)(PPh_3)Br	PhIO	RuO(OEP)Br	423
		Ru(IV) → Ru(II)	
$[RuO(bpy)_2(py)]^{2+}$	Ph_3P (MeCN)	$[Ru(bpy)_2(py)(MeCN)]^{2+}$	424–426
$[RuO(bpy)_2(py)]^{2+}$	Me_2S (MeCN)	$[Ru(bpy)_2(py)(MeCN)]^{2+}$	427
$[RuO(bpy)_2(py)]^{2+}$	Me_2SO (MeCN)	$[Ru(bpy)_2(py)(MeCN)]^{2+}$ + Me_2SO_2	427
$[RuO(bpy)_2(PEt_3)]^{2+}$	Ph_3P	$[Ru(bpy)_2(PEt_3)(solv)]^{2+}$	428
		Ru(VI) → Ru(IV)	
$[RuO_2(tmc)]^{2+}$	Ph_3P	$[RuO(tmc)Cl]^+$	415
$RuO_2(py)_2(OAc)_2$	Ph_3P	$RuO(py)_2(OAc)_2$	414
		Ru(VI) → Ru(II)	
RuO_2(TMP) (100)	$(MeO)_3P$	Ru(TMP)$(P(OMe)_3)_2$ (101)	420
		Ru(VIII) → Ru(IV)	
RuO_4	Ph_2S	RuO_2 + Ph_2SO + Ph_2SO_2	429
RuO_4	MeS(p-tol)	RuO_2 + $MeSO_2$(p-tol)	429
RuO_4	$MeSCH_2Ph$	RuO_2 + $MeSO_2CH_2Ph$	429
		Os(II) → Os(VI)	
Os(OEP)(CO)(MeOH)	t-BuOOH	OsO_2(OEP)	421
		Os(VI) → Os(III)	
"OsO(PPh_3)$_2Br_3$"[e]	R_2PhP[a]	$Os(PPhR_2)_3Br_3$	393
$[OsO_2(bpbH_2)]^{2+}$	Ph_3P, Cl^-	Os(bpb)(PPh_3)Cl	432
		Os(VI) → Os(IV)	
OsO_2(salen)	Ph_3P (ROH[d])	Os(salen)$(OR)_2$	434
$[OsO_2(hba\text{-}b)]^{2-}$	Ph_3P	$Os(PPh_3)_2$(hba-b)	430
$[OsO_2(chba\text{-}dcb)]^{2-}$	Ph_3P	$Os(PPh_3)_2$(chba-dcb)	431
$[OsO_2(chba\text{-}dcb)]^{2-}$	Ph_3P, 4-Rpy[c]	$Os(4\text{-}Rpy)_2$(chba-dcb)	430
$[OsO_2(chba\text{-}dcb)]^{2-}$	Ph_3P, t-BuNC	$Os(t\text{-}BuNC)_2$(chba-dcb)	431
$[OsO_2(chba\text{-}Et)]^{2-}$ (102)	Ph_3P, 4-Rpy[b]	$Os(4\text{-}Rpy)_2$(chba-Et) (103)	431
$[OsO_2(chba\text{-}Et)]^{2-}$	Ph_3P, O_2	$[Os_2O(OPPh_3)_2(chba\text{-}Et)_2]^{2-}$	153
$OsO_2Cl_2(PPh_3)_2$	Ph_3P, HCl	$Os(PPh_3)_2Cl_4$	445
$OsO_2Br_2(PPh_3)_2$	Ph_3P, HBr	$Os(PPh_3)_2Br_4$	446
		Os(VIII) → Os(VI)	
OsO_4	Ph_3P, HCl	$OsO_2Cl_2(PPh_3)_2$	445
OsO_4	Ph_2RP[d]	$OsO_2Cl_2(PRPh_2)_2$	446
OsO_4	$PhEt_2P$	$OsO_2Cl_2(PEt_2Ph)_2$	446
OsO_4	Ph_3P, HBr	$OsO_2Br_2(PPh_3)_2$	446
$[OsO_4(OH)_2]^{2-}$	Me_2SO	$[OsO_2(OH)_4]^{2-}$ + Me_2SO_2	433

[a] R = alkyl. [b] R = py, 4-t-Bupy. [c] R = MeO, Et, Me, Cl, Br, MeCO. [d] R = Me, Et. [e] A mixture of $OsO_2Br_2(PPh_3)_2$ and $OsBr_4(PPh_3)_2$.[446]

measured. The rapidity of this reaction must be largely due to the high electron affinity of Ru(IV), a property reflected by the potentials of series 81. The second step is a solvolysis of the Ru(II) product liberating oxidized substrate. Inasmuch as the oxoruthenium(IV) complex has a triplet ground state and the initial Ru(II) product doubtless is diamagnetic, the reaction is, to a first approximation, spin-forbidden. How this forbiddance is lifted and to what extent a spin change is manifested in the activation parameters are unclear.

Two apparent one-electron oxidations of Ru(II) may occur by oxo transfer, although this has not been definitely established in either case. Reduction of nitrate by Ru(II) has been demonstrated in the form of reaction 83,[419] where sulfamate has been used to scavenge the nitrous acid product. The proposed sequence 84 for an

$$2[Ru(bpy)_2(py)(OH_2)]^{2+} + NO_3^- + 3H^+ + NH_2SO_3^- \rightarrow 2[Ru(bpy)_2(py)(OH_2)]^{3+} + N_2 + HSO_4^- + 2H_2O \quad (83)$$

$$[Ru^{II}(ONO_2)] \xrightarrow[H^+ \; HNO_2]{} [Ru^{IV}{=}O] \xrightarrow[2H^+]{[Ru(OH_2)]} 2[Ru^{III}(OH_2)] \quad (84)$$

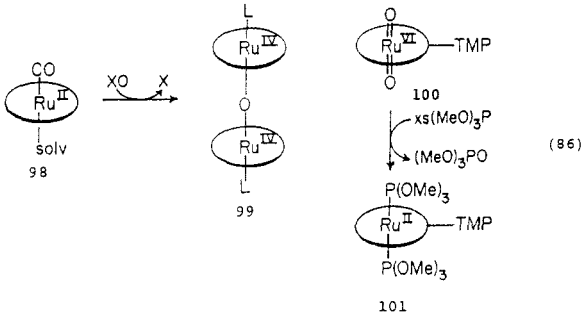
oxo transfer pathway is plausible. The step following substrate binding is proton-induced intramolecular oxo transfer; protonation of a terminal oxygen atom of nitrate enhances electron deficiency at the nitrogen atom,

leading to rupture of the RuO–N bond in concert with the formation of the Ru^{IV}=O group. The final step is an example of reaction 8 followed by protolytic cleavage of the oxo bridge. In acid solution $[Ru(OH_2)_6]^{2+}$ is oxidized to $[Ru(OH_2)_6]^{3+}$ by perchlorate, which is reduced to chlorate. From comparative kinetics, the rate of reduction of perchlorate is limited by the rate of substitution by this ion at Ru(II).[418] The proposed mechanism of this reaction is consistent with oxo transfer and, although less explicit than pathway 84, is analogous to it. Both these reactions are included in Table 16 as likely oxo transfer processes. Lastly, note is taken of reaction 85, which has been incorporated in

$$[Ru(bpy)_2(py)(NO_2)]^{2+} + Ph_3P \rightarrow [Ru(bpy)_2(py)(NO)]^{2+} + Ph_3PO \quad (85)$$

an electrocatalytic cycle for the oxidation of Ph_3P.[436] This is an oxo transfer reaction which is both ligand-based and metal-mediated in that both ligand and metal are reduced. However, as with reaction 20 there is no involvement of an oxometal group. These reactions are representative of a larger set and are recognized as cases of secondary reaction 11.

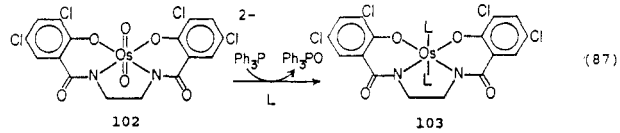
Reaction of solvated Ru(P)(CO) (**98**) containing an unhindered porphyrin with several different oxo donors affords the μ-oxo Ru(IV) dimer $[Ru(P)L]_2O$ (**99**) with a linear bridge. These and other oxo transfers are summarized by the reactions 86. Use of the hindered



(86)

ligand TMP, however, leads to diamagnetic RuO_2(TMP) (**100**) whose $Ru^{VI}O_2$ group is expected to have the trans arrangement found in nearly all $Os^{VI}O_2$ complexes. No intermediates were detected spectrophotometrically, suggesting a faster reaction of initially formed RuO(TMP) than of Ru(TMP)(CO) with the oxidant or, possibly, rapid disproportionation of the former to reactant and RuO_2(TMP). This complex is reduced to the Ru(II) level (**101**) by trimethyl phosphite and executes olefin epoxidation.[437] Ru(TMP), devoid of axial ligands and therefore exceptionally reactive, has recently been isolated.[438] This complex and RuO(TMP) are transient intermediates in the proposed mechanism of olefin epoxidation catalyzed by RuO_2(TMP).[437] The monooxoruthenium(IV) complex might be accessible by stoichiometric reaction of Ru(TMP) with a suitable donor; with dioxygen RuO_2(TMP) is formed,[438] consistent with the catalytic scheme. The only monooxoruthenium porphyrin species claimed to have been detected is RuO(OEP)Br, from the oxidation of Ru(OEP)(PPh_3)Br with PhIO.[423] The complex is formulated to contain Ru(IV) and a porphyrin radical and is thus isoelectronic with active oxygenation catalysts in iron porphyrin systems. The *trans*-$Ru^{VI}O_2$ group is accessible by other means,[413,414,439-442] including the Ce(IV) (but not *t*-BuOOH) oxidation of $[Ru(bpy)_2(OH)(OH_2)]^{2+}$ to $[RuO_2(bpy)_2]$.[439] *cis*-$[RuO_2(bpy)_2]^{2+}$ has been identified spectroscopically.[443] The two isomers exhibit distinct, proton-linked redox series; no oxo transfer reactions have been reported.

Even oxidation states in the Os(II)–Os(VIII) set are represented in oxo transfer chemistry. Parallels with ruthenium are few, but probably could be developed. No Os(II) → Os(IV) transformations are known, but OsO_2(OEP) is obtainable by the oxidation of Os(OEP)(CO)L with *t*-BuOOH (L = MeOH) or hydrogen peroxide (L = py).[444] The Os(IV) analogues of **99** have been obtained by aerial oxidation of Os(OEP)(CO)(MeOH).[421] Reactions of the *trans*-$Os^{VI}O_2$ group have been most extensively examined in complexes such as $[OsO_2(chba\text{-}Et)]^{2-}$ (**102**). The tetranegative ligand can



(87)

accommodate oxidation states in the II–VI range and, owing to its electron-rich nature, is effective in stabilizing Os(VI). These complexes are reducible to the Os(IV) species **103** by Ph_3P in the presence of neutral ligand L in reaction 87. The trans configuration of the L = py product has been established crystallographically.[431] Reaction 88 is listed in Table 16 as the only Os(VIII) → Os(VI) transformation that is a likely oxo transfer process; however, proof of actual atom transfer is lacking.

$$[OsO_4(OH)_2]^{2-} + Me_2SO + H_2O \rightarrow [OsO_2(OH)_4]^{2-} + Me_2SO_2 \quad (88)$$

The oxo transfer reaction of the species "OsO(PPh_3)$_2$Br$_3$" must involve instead $OsO_2Br_2(PPh_3)_2$ inasmuch as the former has been shown to be a mixture of the latter and *trans*-Os(PPh_3)$_2$Br$_4$.[445,446] Several different types of complexes are accessible from the reduction of OsO_4 with tertiary phosphines. It appears that the probable sequence of events is OsO_4 → $OsO_2L_2(PR_3)_2$ → *trans*-Os$(PR_3)_2L_4$ → *mer*-Os$(PR_3)_3L_3$ (L = Cl^-, Br^-).[446] Examples of the first two steps are found in Table 16. Depending on reaction conditions, a given system may proceed to different extents, including reaching the Os(III) state. The latter was the case in certain early work on OsO_4/PR_3/HCl or HBr systems[393] and tended to obscure the probable oxo transfer steps. Recent reactions of tertiary phosphines and arsines with OsO_4 at low temperatures afford $Os^{VI}O_2$ complexes rather than further reduction products,[447] consistent with the preceding scheme.

IV. Intermetal Oxo Transfer Reactions

In these reactions, oxometal groups are the atom donors and metal centers with or without oxo ligands are the acceptors. Two types of reactions are recognized, resulting in complete oxo transfer to the acceptor or incomplete transfer affording a detectable oxo-bridged species which may or may not be the final product under the reaction conditions employed. The term "complete" refers to the absence of bridged complexes among the products, not to the extent of the overall reaction. Both types of reactions lead to metal-centered oxidation and reduction of reactants, a de-

TABLE 17. Complete Intermetal Oxo Transfer Reactions

reactants	products	ref
$M^{IV}O + M^{VI}O_2 \rightleftharpoons M^{VI}O_2 + M^{IV}O$ (89)		
MoO(L-NS_2)(DMF) (**69**) + $MoO_2(S_2CNEt_2)_2$ (**61**)	MoO_2(L-NS_2) (**68**) + $MoO(S_2CNEt_2)_2$ (**60**)	324
MoO(ssp)(DMF) (**71**) + MoO_2(L-NS_2)	MoO_2(ssp)(DMF) (**70**) + MoO(L-NS_2)(DMF)	324
MoO(sap)(DMF) (**75**) + MoO_2(ssp)(DMF) (**72**)	MoO_2(sap)(DMF) (**74**) + MoO(ssp)(DMF)	324
$M^{VI}O_2 + M^{II} \rightarrow 2M^{IV}O$ (90)		
$MoO_2(S_2CNR_2)_2$ + $Mo(CO)_2(S_2CNR_2)_2$	$MoO(S_2CNR_2)_2$ + 2CO	378
$W(CO)(R_1CCR_2)(S_2CNR_2)_2$ + $Mo_2O_3(S_2P(OEt)_2)_4$	$WO(R_1CCR_2)(S_2CNR_2)_2$[a] + $2MoO(S_2P(OEt)_2)_2$ + CO	448
$Mo(CO)(R_1CCR_2)(S_2CNEt_2)_2$ + $Mo_2O_3(S_2P(OEt)_2)_4$	$MoO(R_1CCR_2)(S_2CNEt_2)_2$[b]	448
$W(CO)_2(PPh_3)(S_2CNR_2)_2$ + $2Mo_2O_3(S_2P(OEt)_2)_4$	$WO_2(S_2CNR_2)_2$ + $4MoO(S_2P(OEt)_2)_2$ + 2CO + Ph_3P	378
$M^{VI}O_2 + M^{IV} \rightarrow 2M^{V}O$ (91)		
$MoO_2(acac)_2$ + $MoCl_2(acac)_2$	$MoOCl(acac)_2$	449

[a] $R_1 = R_2 = H$; $R_1 = H$, $R_2 = Ph$. [b] $R_1 = R_2 = p$-MeC_6H_4CO; other products not specified.

fining requirement of intermetal oxo transfer. Reactions with incomplete transfer result in the formation of bridge **13** in scheme 13. In these cases, the bridged complexes are relatively stable intermediates in inner-sphere electron transfer.

A. Complete Oxo Transfer

Reactions of this type, which are not numerous, are classified according to oxidation state changes in reactions 89–91 in Table 17. Reactions 89 are not degenerate owing to the presence of different ligands. They are displayed in Figure 9, whose scheme was devised to establish directly relative oxo transfer propensities of Mo(IV,VI) complexes. In this set, $MoO_2(S_2CNEt_2)_2$ is the strongest donor and MoO(sap)(DMF) is the strongest acceptor. Reaction rates permitting, this scheme is capable of expansion to other complexes of the same and different metals. Reactions 90 are irreversible owing to the loss of carbon monoxide. They are classified as shown because of the probability that in three of the systems the common reactant is $MoO_2(S_2P(OEt)_2)_2$, which exists in equilibrium with the μ-oxo Mo(V) and $Mo^{IV}O$ complexes.[450] This complex has never been isolated. The last of these reactions probably proceeds through a $W^{IV}O$ intermediate. This is the only known route to $WO_2(S_2CNR_2)_2$ complexes. Methods which readily afford the Mo(VI) dithiocarbamates fail with tungsten, for reasons unknown. The single example of reaction 91 involves both oxo and chloro ligand exchange. The probable course of reaction is, first, oxo transfer to yield $MoO(acac)_2$ and $MoOCl_2(acac)_2$, followed by chlorine atom transfer. A similar reaction between $MoO(S_2CNEt_2)_2$ and $MoOCl_2(S_2CNEt_2)_2$, to give $MoOCl(S_2CNEt_2)_2$, is claimed but not described.[449] If the foregoing interpretations are correct, complete intermetal oxo transfers are analogous to the simplest oxo transfer, reaction 7, each event being an atom transfer with a two-electron change.

B. Formation of Inner-Sphere Binuclear Complexes

Reactions which proceed with "incomplete" oxo transfer are considerably more common than the complete type. They are readily organized in terms of redox changes into reactions 92–96, which are compiled in Table 18. To emphasize the defining features of this reaction type, it may be helpful to observe that the

TABLE 18. Formation of Binuclear μ-Oxo Complexes by Intermetal Oxo Transfer

reactants	product	ref
$M^{IV}O + M^{I} \rightarrow M^{III}$–O–$M^{II}$ (92)		
FeO(TPP)(py) + $[Cu(pyazIm)]^+$	$[(TPP)FeOCu(pyazIm)]^+$	454
$M^{IV}O + M^{II} \rightarrow M^{III}$–O–$M^{III}$ (93)		
$[VO(OH_2)_5]^{2+}$ + $[V(OH_2)_6]^{2+}$	$[(H_2O)_5V$–O–$V(OH_2)_5]^{4+}$	222
CrO(P) + Cr(P)	(P)CrOCr(P)[a]	9, 50, 239
CrO(TPP) + MnL	(TPP)CrOMnL·H_2O[e]	451
CrO(TPP) + FeL	(TPP)CrOFeL·H_2O[e,f]	451
CrO(TPP) + $Fe(S_2CNEt_2)_2$	(TPP)CrOFe$(S_2CNEt_2)_2$	451
CrO(P) + $Fe(TPP)(pip)_2$	(P)CrOFe(TPP)[b]	132, 452
CrO(TPP) + $Fe(TMeP)(pip)_2$	(TPP)CrOFe(TMeP)	132
CrO(TPP) + Fe(Pc)	(TPP)CrOFe(Pc)	132
FeO(P)L[a] + Fe(P)	(P)FeOFe(P)	290, 298
$M^{IV}O + M'^{IV}O \rightarrow M^{III}$–O–$M'^{V}$(=O) (94)		
CrO(TPP) + $MoO(S_2CNEt_2)_2$	(TPP)CrOMoO$(S_2CNEt_2)_2$·H_2O	451
$M^{VI}O_2 + M^{II} \rightarrow M^{V}$(=O)–O–$M^{III}$ (95)		
$MoO_2(S_2CNEt_2)_2$ + FeL	$(Et_2NCS_2)_2$Mo(O)OFeL[g]	451
$M^{VI}O_2 + M^{IV}O \rightleftharpoons M^{V}$(=O)–O–$M^{V}$(=O) (96)		
$MoO_2(S_2CNR_2)_2$ + $MoO(S_2CNR_2)_2$	$Mo_2O_3(S_2CNR_2)_4$	26, 28, 29, 32, 326, 340, 360, 362, 453
$MoO_2(SSeCNEt_2)_2$ + $MoO(SSeCNEt_2)_2$	$Mo_2O_3(SSeCNEt_2)_4$	362
$MoO_2(Se_2CNEt_2)_2$ + $MoO(Se_2CNEt_2)_2$	$Mo_2O_3(Se_2CNEt_2)_4$	362
$MoO_2(S_2CS$-*i*-$Pr)_2$ + $MoO(S_2CS$-*i*-$Pr)_2$	$Mo_2O_3(S_2CS$-*i*-$Pr)_4$	361
MoO(N-*p*-tol)$(S_2CNEt_2)_2$ + Mo(N-*p*-tol)$(S_2CNEt_2)_2$	Mo_2O(N-*p*-tol)$_2(S_2CNEt_2)_4$	321, 337
$MoO_2(S_2PPh_2)_2$ + $MoO(S_2PPh_2)_2$	$Mo_2O_3(S_2PPh_2)_4$	29, 361
$MoO_2(S_2CNR_2)_2$ + $MoO(S_2P(OEt)_2)_2$	$Mo_2O_3(S_2CNR_2)_2(S_2P(OEt)_2)_2$	450
$MoO_2(S_2PPh_2)_2$ + $MoO(S_2P(OEt)_2)_2$	$Mo_2O_3(S_2PPh_2)_2(S_2P(OEt)_2)_2$	450
$MoO_2(S_2P(OEt)_2)_2$ + $MoO(S_2P(OEt)_2)_2$	$Mo_2O_3(S_2P(OEt)_2)_4$	450

[a] P = TPP, TMeP, TCP, TXP, TTP, TFP, TPFP, OEP. [b] P = TPP, TTP, TFP, TMP, TXP. [c] L = py, pip, *N*-MeIm. [d] P = TPP, TmTP, TMeP, OEP. [e] L = salah, salmah. [f] L = salen, saloph. [g] L = salen, salmah.

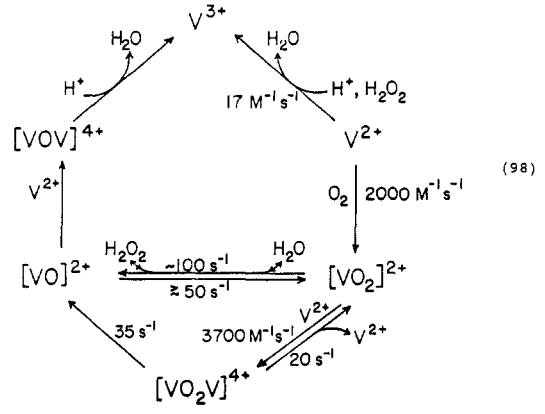
reaction 97[455] and related processes[162,456] are *not* of this

$$[VO(OH_2)_5]^{2+} + [VO_2(OH_2)_4]^{+} \rightarrow [(H_2O)_5V(=O)-O-V(=O)(OH_2)_5]^{3+} \quad (97)$$

type. The product contains bridge unit **15**, which, although electronically delocalized in most cases, is an adduct of the two reactants with no net redox change. This reaction is one of many in which a metal ion interacts with the oxo ligand of an oxometal complex without electron transfer. Among other examples are the reactions of the macrocyclic complex TiO(L-N_4) with a number of M(II,III) complexes.[457] Bridged complexes are formed and no electron transfer is expected with the M(III) reactants. In the reaction product of Fe(salen), the Ti–O bond distance (1.701 (6) Å) is ~0.1 Å longer than usual Ti=O distances (Table 1) and 0.14 Å shorter than the most pertinent Ti^{IV}–O–Ti^{IV} distance.[458] Also, the bridge Fe–O bond (1.935 (6) Å) is ~0.1 Å longer than those in $[Fe(salen)]_2O$ (Table 2). Structural evidence, which is all that is available, does not favor electron transfer. This compound and that formed from Mn(salen) are not included in Table 18.

Two probable examples of reaction 93, the oxidations of $[Cr(OH_2)_2]^{2+}$ (Table 5) and $[Fe(OH_2)_2]^{2+}$ (Table 8) to the corresponding $[M(OH_2)_6]^{3+}$ ions with oxo transfer reagents, have already been cited. In neither case was the putative oxometal(IV) intermediate detected. Of all metal ions in aqueous solution, the oxo reaction chemistry of vanadium is the best defined and justifies a closer look.

Leading aspects of the reactions of $[V(OH_2)_6]^{2+}$ under oxidizing conditions are summarized in scheme 98 (aquo ligands omitted); all reactions were carried out in acid solutions. Both hydrogen peroxide and dioxygen ox-



idize V^{2+} to V^{3+}.[459,460] However, the major reaction pathways differ. The most recent study of the V^{2+}/H_2O_2 system did not detect $[VO]^{2+}$ as a reaction intermediate.[459] With dioxygen, V^{2+} is first oxidized to the transient V(IV) peroxo species $[VO_2]^{2+}$ in a reaction much faster than expected if aquo ligand substitution is rate-limiting. Rapid reaction with excess V^{2+} yields the presumed V(III) peroxo dimer $[VO_2V]^{4+}$, which forms 2 equiv of $[VO]^{2+}$ by an internal redox process similar to the conversion **52** → **53** in heme chemistry (Figure 6). In the presence of excess V^{2+}, intermetal oxo transfer reaction 99 forms the μ-oxo V(III) dimer

$$V^{2+} + VO^{2+} \xrightarrow{k_1} [VOV]^{4+} \xrightarrow[2H^+]{k_2} 2V^{3+} + H_2O \quad (99)$$

$[VOV]^{4+}$. This reaction is sufficiently fast that the

$$d[VOV^{4+}]/dt = k_1[V^{2+}][VO^{2+}] - k_2[VOV^{4+}][H^+] \quad (100)$$

intense brown color of the dimer (λ_{max} 425 nm) develops more rapidly than the overall reaction leading to V^{3+}. The V(III) formulation is confirmed by appearance of the same chromophore in partially hydrolyzed solutions of V(III).[222] Rate law 100 from the work of Newton and Baker[222] describes the net rate of formation of the intermediate, which is decomposed to V^{3+} by protonation. The full kinetics analysis indicates that about 65% of the overall reaction proceeds by an inner-sphere mechanism via the persistent intermediate $[VOV]^{4+}$. The remainder of the reaction follows an outer-sphere pathway in which vanadyl is reduced to V^{3+} with concomitant protonation and elimination of the oxo ligand as water. Scheme 98 may be of some generality for the oxidation of aquo metal ions with $d^{\leq 6}$ configurations. Rush and Bielski[459] have pointed out that the scheme and results for other metal ions are consistent with the autoxidation mechanism of Ochiai,[461] who recognized oxygen–metal species whose formation has since been detected. The vanadyl ion has also been shown to react with $[Ru(NH_3)_5(OH_2)]^{2+}$, giving the stable binuclear complex $[(H_3N)_5RuOV(OH_2)_n]^{4+}$.[462] The same product is obtained from $[Ru(NH_3)_5Cl]^{2+}$ and V^{3+}. Its electronic structure is not known in any detail, and while potentially ambiguous, the existence of a perturbed ν_{VO} stretch at 975 cm^{-1} favors the Ru(II)/V(IV) description. In this event, the second method of preparation involves an electron transfer step prior to product formation, and both methods are metal-binding reactions at the oxo ligand rather than intermetal oxo transfer.

Reaction 93 has been used effectively as a means of synthesis of oxo-bridged homo- and heteronuclear complexes, primarily by the reaction of CrO(P) with strongly reducing Cr(II), Mn(II), and Fe(II) complexes. The products are antiferromagnetic. A linear Cr–O–Fe bridge has been established in crystalline (TPP)(py)-CrOFe(TMeP); pyridine is coordinated to Cr(III). Dimensional data have not been reported. Single examples are known for reactions 94 and 95. Product structures have not been determined.

Reaction 96 is a particular case of reaction 8 (a = 1) and affords complexes such as **76** with bridge **15**. It has been established only in molybdenum systems thus far, but the isolation of $W_2O_3(S_2CNR_2)_4$ compounds[463] suggests that it may extend to tungsten as well. A number of Re_2O_3 complexes are known[386,404,464,465] containing the linear Re(V) bridge **14**, which should assemble from appropriate $Re^{V}O_2$ and $Re^{V}O$ species. One realized route appears to be by condensation of two $Re^{V}O(OH)$ complexes. There is no evidence that this bridge is formed by intermetal oxo transfer. Reactions of molybdenum complexes may be reversible or irreversible, those of the latter type being common and often leading to relatively insoluble Mo_2O_3 complexes which have not been studied further. The tabulated examples are restricted to reversible reactions.

In an important contribution, the Osaka group has determined the kinetics and equilibrium thermodynamics of a number of these reactions. The results are summarized in Table 19. Rate constants k_1 and k_{-1} were determined by the concentration jump method and equilibrium constants were calculated from them. Other equilibrium data were obtained from temperature

TABLE 19. Kinetics and Thermodynamic Data for the Dissociation Reaction

$$Mo_2O_3L_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MoO_2L_2 + MoOL_2 \text{ (in 1,2-}Cl_2C_2H_4\text{, 25 °C)}$$

L	k_1, s^{-1}	$10^{-2}k_{-1}$, M^{-1} s^{-1}	10^3K_{eq}, M	ΔH^*, kcal/mol	ΔS^*, eu	ΔH, kcal/mol	ΔS, eu	ref
$Et_2NCS_2^-$	2.93 (29)	14.7 (2.20)	2.0 (2)	17.0 (4)[a]	0.1 (9)	12.1 (6)	28 (3)	360
				[5.1 (2)][b]	[-27.0 (5)]			
						6.0 (6)		32
Et_2NCSSe^-	3.78 (11)	9 (1)	4.2 (5)	18.8 (4)	7.3 (2)	15 (1)	40 (7)	360
				[3.8 (1.1)]	[-32 (8)]			
$Et_2NCSe_2^-$	10.8 (1)	8.3 (1.0)	13.0 (2)	12.8 (1.1)	-10.9 (8)	5.9 (6)	11 (4)	360
				[6.8 (1.6)]	[-22 (6)]			
i-$PrSCS_2^-$	12.2 (8.6)	320 (22)	0.38 (27)	18.9 (7)	9.7 (4.9)	13 (1)	32 (7)[c]	361
				[6.1 (6)]	[-19 (4)]			
$(EtO)_2PS_2^-$	1.74 (6)	4.5	3.9 (2)	17.4	2 (6)	13.5 (8)	35 (7)	362
				[3.9]	[-33 (2)]			
$Ph_2PS_2^-$	0.50 (2)	8.7 (8)	0.58 (6)	17.0	-2.7 (1.6)	6.5 (1)	7.4 (4.5)	362
				[10.5]	[-10.0 (8)]			

[a] Estimated uncertainty in last digit(s) in parentheses. [b] Bracketed values refer to the *reverse* of the title reaction. [c] Reported incorrectly as a negative value.

dependencies of equilibrium constants determined spectrophotometrically. The presence of three oxo species in solutions prepared from isolated oxo dimer complexes was established from electronic and IR spectra. Note that the majority of the data refer to the reverse of reaction 46 (n = 2), dimer dissociation. While uncertainties in some of the data are appreciable, the following major aspects of these reactions emerge: (i) in the millimolar concentration range the equilibria favor the mononuclear complexes; (ii) the introduction of selenium in the ligands destabilizes the dimer complexes; (iii) activation entropies for dissociation are small positive or negative quantities while those for the reverse process are larger negative values; (iv) equilibrium entropy changes accompanying dissociation are variable but positive. Concerning iii, a reasonable conclusion from the small activation entropies is that in the transition state the Mo–O–Mo bridge bond is weakened but the binuclear structure remains intact. Because the bridging and terminal oxo ligands in the dimer and in the $Mo^{VI}O_2$ product are always cis, subsequent bond cleavage and product formation require rather minor rearrangement of only the chelate ligands. Lastly, the dissociation of $Mo_2O_3(S_2CS\text{-}i\text{-}Pr)_4$ is accompanied by a slower decomposition of $MoO_2(S_2CS\text{-}i\text{-}Pr)_2$ to (i-PrSC(S)S)$_2$ and $Mo_2O_4(S_2CS\text{-}i\text{-}Pr)_2$. This is one example of the formation of bridge unit **18** (scheme 13) by autoreduction of a $Mo^{VI}O_2$ complex containing sufficiently reducing ligands.

V. Catalytic Oxo Transfer

To the extent that they are understood, all systems that execute catalysis by metal-centered oxo transfer include as one step the forward or reverse reaction 7. This is coupled to an oxidation or a reduction step that may, or may not, be an oxo transfer reaction. Described next are synthetic systems followed by an examination of atom transfer as a possible reaction pathway for the molybdenum hydroxylases. Excluded from consideration are ligand-based oxo transfer systems and catalytic oxygenations of purely organic substrates.

A. Synthetic Systems

Specific reactions 101–104 have been catalyzed in the cycles of the same number in Figure 12. The observations of Barral et al.[28] led to the first example of catalysis containing a step clearly recognized as oxo transfer. Cycle 102a was initiated in chlorobenzene

$$Ph_3P + {}^1/_2O_2 \rightarrow Ph_3PO \quad (101a)^{289}$$

$$Ph_3P + R_3NO \rightarrow Ph_3PO + R_3N \quad (101b)^{277,278}$$

$$Ph_3P + {}^1/_2O_2 \rightarrow Ph_3PO \quad (102a)^{28,466,467}$$

$$Ph_3P + Ph_3AsO \rightarrow Ph_3PO + Ph_3As \quad (102b)^{27}$$

$$PhCH(OH)COPh + {}^1/_2O_2 \rightarrow PhCOCOPh + H_2O \quad (102c)^{468}$$

$$Ph_3P + Me_2SO \rightarrow Ph_3PO + Me_2S \quad (103a)^{322,469}$$

$$(R_F)_3P + (R_F)_2SO \rightarrow (R_F)_3PO + (R_F)_2S \quad (103b)^{325}$$

$$2R_FSH + (R_F)_2SO \rightarrow R_FSSR_F + (R_F)_2S + H_2O \quad (103c)^{324}$$

$$(R_F)_3P + 3\text{-FpyO} \rightarrow (R_F)_3PO + 3\text{-Fpy} \quad (103d)^{325}$$

$$2HCO_2H + 2NO_2^- + 2H^+ \rightarrow 2CO_2 + 3N_2O + H_2O \quad (104)^{349}$$

solution in the presence of air and with a large Ph_3P:$MoO_2(S_2CNR_2)_2$ mol ratio. Oxygen atom abstraction by the phosphine gave **60** and the phosphine oxide, which presumably exist as a weak complex (as shown) before largely dissociating. The highly air-sensitive Mo(IV) complex is then reoxidized to the Mo(VI) state **61**. All other catalytic systems in Figure 12 function in an analogous fashion. Intermediates such as that in scheme 62 have been proposed in some cases but never detected; these are omitted from the cycles. A feature of cycle 102 is the possible existence of Mo(V) oxo dimer **76** in equilibrium with the oxomolybdenum(IV,VI) complexes. This does not preclude catalysis since the equilibrium is labile and thus presents to the substrate a finite concentration of the monomeric catalyst **61**. This equilibrium can be repressed if in, e.g., substrate oxidation the concentration of Mo(IV) under turnover conditions is maintained at a very low level by rapid reoxidation to the Mo(VI) catalyst. With dithiocarbamate complexes, formation of **76** is readily observed by the appearance of a purple color. The complexes $MoO_2(Cys\text{·}OR)_2$ (R = Me, Et, i-Pr, CH_2Ph) also catalyze reaction 102a.[466,467] Efficiency is improved when a small amount of water is added to the DMF solvent; turnover numbers are low (0.003–0.02 min^{-1}).[467] A Mo(V) complex, proposed to be $MoO(OH)(Cys\text{·}OR)_2$,

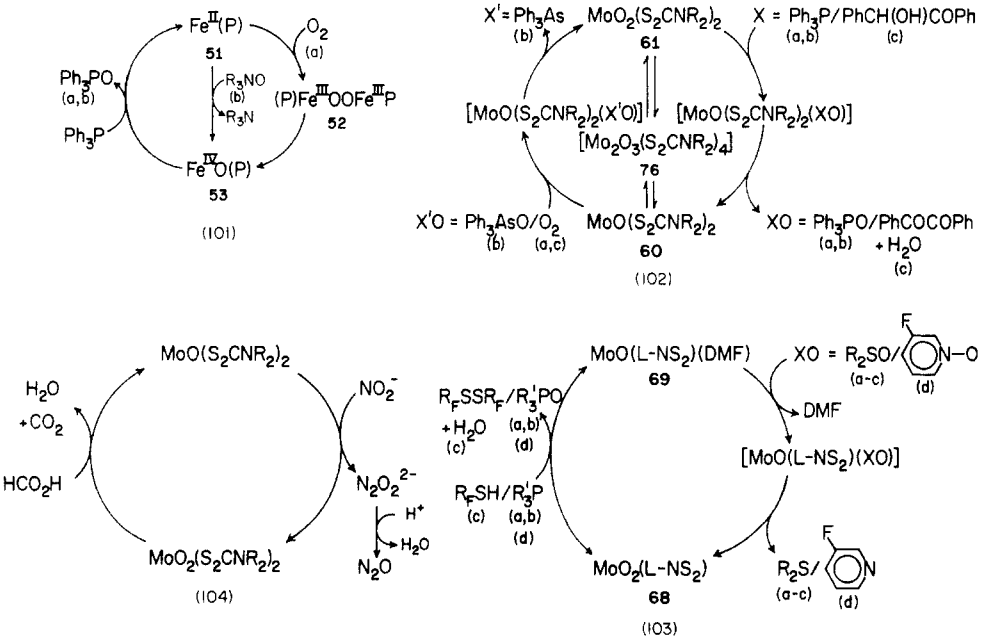


Figure 12. Catalytic cycles for reactions 101–104; cycles are designated according to reaction number, and letters in parentheses refer to reactions in a given cycle. In cycle 103 R = Me, R_F and R′ = Ph, R_F.

has been detected as a reaction product with Ph_3P in the presence of water. Its small concentration suggests that it is not on the major reaction pathway, which is likely to be oxo transfer from Mo(VI) to substrate. The catalytic cycle is broken by the formation of μ-oxo dimers, which in the case of $Mo_2O_3(Cys{\cdot}OR)_4$ is not known to be reversible. Cycle 101 is an alternative catalytic oxidation system for Ph_3P. Addition of excess phosphine to **51** in toluene solution at −80 °C gives Fe(P)$(PPh_3)_2$, which with dioxygen forms the peroxo dimer **52**. This complex and the phosphine do not react at −80 °C for several days. When the system is warmed, **52** generates oxo complex **53**, which reacts with substrate to complete one turnover. Alternatively, **53** may be generated in one step by reaction of **51** with a tertiary amine oxide. Catalytic activity is terminated by formation of (P)FeOFe(P) (**54**) from **51** and **53**.

As already observed, reaction 102b proceeds because the P–O bond energy exceeds the As–O bond energy by ca. 27 kcal/mol. Uncatalyzed, essentially quantitative oxo transfer is observed after 4.5 h at 110 °C; however, there is no reaction at 40 °C after 20 h or at room temperature after 21 days.[470] The reaction is catalyzed by the Mo(VI,IV) dithiocarbamates, some 40 turnovers occurring over 20 h at 40 °C. Pyridine *N*-oxide, azoxybenzene, Me_2SO, and Ph_3SbO were also catalytically reduced in the presence of Ph_3P.[27]

The aerial oxidation of benzoin to benzil (reaction 102c) has been effected in DMF solutions with $MoO_2(S_2CNR_2)_2$, $MoO_2(Cys{\cdot}OR)_2$, and $MoO_2(Cys{\cdot}NHR)_2$ as catalysts. Reactions are not rapid, the initial first-order rate constants being 0.012–0.048 s^{-1} at 30 °C. The first step is thought to be protonation of an oxo ligand, followed by coordination of the benzoin anion and a second proton transfer to form water and generate benzil. Catalysis runs down because of formation of μ-oxo Mo(V) dimers and catalyst deactivation by water produced in substrate oxidation.

Catalyst systems based on complexes **68**/**69** have been developed in the form of the cycles 103 in DMF solutions. The substrates of interest are several sulfoxides and 3-fluoropyridine *N*-oxide, which are catalytically reduced in the presence of Ph_3P or $(R_F)_3P$. Several of these systems have been followed through at least 500 turnovers at ambient temperature with little catalyst decomposition. Because of ligand design, μ-oxo dimer formation does not intervene. Use of the R_F = *p*-C_6H_4F group allows ^{19}F monitoring of the relative concentrations of the various components, whose signals are fully resolved, in reactions 103b–d. Reaction 103a is typical of catalyzed systems of this sort containing tertiary phosphines as reductants. No reaction occurs between Me_2SO and Ph_3P for at least 1 h at 189 °C.[471] However, in the presence of catalytic amounts of **68** at ambient temperature, ^{31}P NMR spectra showed progressive oxidation of Ph_3P to Ph_3PO, and Me_2S was formed in practically quantitative yield at the completion of the reaction. The first step in the reaction was found to be essentially first order in **68** with an initial second-order rate constant of 0.006 M^{-1} s^{-1}. This is in good agreement with the value in the absence of Me_2SO (Table 12), showing that the first step is the reduction of **68** by Ph_3P. The catalytic rate is limited by the rate of oxo removal from **68** by the phosphine, as seen from the ratio of the second-order rate constants for sulfoxide reduction and phosphine oxidation, 0.5:0.007 = 70:1. Cycles 102 and 103 should be expandable to a wider variety of substrates and oxidants or reductants. Reaction 103c is only very slowly catalyzed by **69** but it does show that an electron donor, in addition to an oxygen atom acceptor, can function as a reductant in oxo transfer catalysis.

Reaction 104 is catalyzed in DMF solution at ambient temperature by Mo(IV) or Mo(VI) dithiocarbamates. Demonstration of individual reactions 105 and 106 has been claimed.[349] In the first of these, hyponitrite ap-

$$MoO(S_2CNEt_2)_2 + NO_2^- \rightarrow MoO_2(S_2CNEt_2)_2 + {}^1/_2N_2O_2^{2-} \quad (105)$$

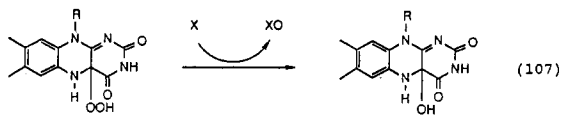
$$MoO_2(S_2CNEt_2)_2 + HCO_2H \rightarrow MoO(S_2CNEt_2)_2 + CO_2 + H_2O \quad (106)$$

pears to arise from the dimerization of the initial product NO^-. $MoO_2(S_2CNEt_2)_2$ and $MoO(S_2CNEt_2)_2$ were reported not to react with nitrite and nitrate, respectively, in DMF. Reaction 106 is slower but proceeds quantitatively at 40 °C. The stoichiometric quantity of carbon dioxide was evolved and the isolated solid contained mainly the Mo(IV) complex. No reaction occurs between formic acid and nitrite in DMF. In the complete system, initial rates of formation of N_2O and CO_2 conformed to the reaction stoichiometry. These observations tend to support the catalysis of reaction 104 by the indicated reaction cycle.

B. Enzymes and Analogue Reaction Systems

1. Enzymes

Biological oxygenation reactions are mediated by both metal and non-metal prosthetic groups. With respect to the substrates considered here, flavomonooxygenases account for the great majority of oxidation reactions at nitrogen and sulfur atoms when metals are not directly involved in catalysis. Such reactions result in the physiological processing of xenobiotics.[472] While not of immediate concern here, it is noted that these reactions can be minimally represented by the scheme 107

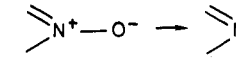


104 105 (107)

wherein the 4a-hydroperoxyflavin **104** (generated from NADPH-reduced flavin and dioxygen) is the atom transfer agent, delivering an oxygen atom derived from dioxygen to substrate X and being reduced to the hydroxyflavin **105**. Examples include the oxidations of sulfides, selenides, triethyl phosphite, and iodide to the corresponding oxides by bacterial cyclohexanone monooxygenase.[473]

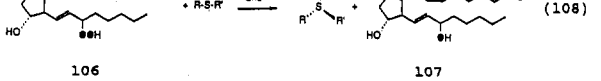
Listed in Table 20 are substrates and enzymes which, together with suitable electron carriers, comprise systems that possibly or definitely operate by means of catalytic primary oxo transfer. All enzymes are known or believed to be molybdoenzymes except for cytochrome P-450[302] and the peroxidases,[500] which contain heme, and the dioxygenase, which has non-heme iron. This listing is representative but certainly not exhaustive. Several of these enzymes, particularly xanthine and aldehyde oxidases, are well characterized while others have not been highly purified. In several cases the enzymes have not been isolated but have been shown to have Mo-dependent activity. For example, when *E. coli* was grown anaerobically with glycerol as the carbon and energy source and Me_2SO as the sole electron acceptor, DMSO reductase activity was induced. Growth was inhibited and activity was reduced in the presence of sodium tungstate.[483] In another instance, cell-free extracts of cultures of *P. mirabilis* were found to have much reduced chlorate reductase activity when the organism was grown in the presence of tungstate.[488] Inasmuch as the replacement of molybdenum by tungsten in other cases removes catalytic activity (vide infra), the clear implication of these findings is that the enzymes responsible for the reductase activities are molybdoenzymes.

TABLE 20. Substrates in Enzymatic Reactions Known or Likely To Proceed by Primary Oxo Transfer

reaction/substrate	enzyme	ref
		
nicotinamide *N*-oxide (78)	milk, liver XO	474, 475
	liver AO	476
	TANO reductase[b]	477
nicotinic acid *N*-oxide	TANO reductase[b]	477
α-, γ-picoline *N*-oxide	TANO reductase[b]	477
quinoline *N*-oxide	liver AO	478
adenine 1-oxide	milk XO	479
adenosine *N*-oxide	TANO reductase[b]	477
guanine 3-oxide	milk XO	479
8-hydroxyguanine 3-oxide	milk XO	479
$R_3NO \rightarrow R_3N$		
Me_3NO	TANO reductase[b]	477, 480, 481
cyclobenzaprine *N*-oxide	liver AO	482
imipramine *N*-oxide	liver AO	482
$NO_3^- \rightarrow NO_2^-$	nitrate reductase	359
$RS(O)R' \rightarrow RSR'$		
Me_2SO	DMSO reductase[b]	483
Ph_2SO	liver AO	478, 484, 485
$(PhCH_2)_2SO$	liver AO	478, 484
phenothiazine *S*-oxide	liver AO	478, 484
d-biotin *d*-*S*-oxide	*d*-biotin *d*-*S*-oxide reductase[l]	486
d-biotin methyl ester *d*-*S*-oxide	liver AO	478
sulindac[a]	liver AO	484
$SO_3^{2-} \rightarrow SO_4^{2-}$	liver sulfite oxidase	487
$ClO_3^- \rightarrow ClO_2^-$	chlorate reductase[c]	488, 489
$RSR' \rightarrow RS(O)R'$		
$PhSCH_2R$[g]	liver cytochrome P-450	490
(*p*-tol)SR[h]	liver cytochrome P-450	491, 492
p-RC_6H_4SMe[i]	liver cytochrome P-450	493, 494
	horseradish peroxidase	495
	chloroperoxidase	495
2-alkylthiachromans[j]	liver cytochrome P-450	492
MeSPh	prostaglandin cyclooxygenase–hydroperoxidase[e]	496
p-$HOC_6H_4SCH_2COCO_2^-$	4-hydroxyphenylpyruvate dioxygenase[d]	497
sulindac sulfide[f]	prostaglandin cyclooxygenase–hydroperoxidase[e]	498
$RS(O)R' \rightarrow RS(O)_2R'$		
p-$RC_6H_4S(O)Me$[k]	liver cytochrome P-450	490, 499

[a] *cis*-5-Fluoro-2-methyl-1-[*p*-(methylsulfinyl)benzylidenyl]indene-3-acetic acid. [b] From *E. coli*. TANO = tertiary amine *N*-oxide. [c] From *Proteus mirabilis*. [d] From *Pseudomonas*. [e] From ram seminal vesicles. [f] *cis*-5-Fluoro-2-methyl-1-[*p*-(methylthio)benzylidenyl]indene-3-acetic acid. [g] R = H, Ph, CN, *p*-$C_6H_4NO_2$, COPh. [h] R = Me, Et, *t*-Bu, CH_2Ph. [i] R = H, Me, OMe, O-*i*-Pr, Cl, NO_2. [j] Also acyclic and other cyclic sulfides. [k] R = H, Me, OMe, Cl. [l] From *E. coli*.

In the majority of cases, there is little or no information on reaction pathways. However, in some systems significant experiments involving ^{18}O labeling have been performed. Two of these are summarized in the sulfide oxidation reaction 108 catalyzed by prostaglandin cyclooxygenase–hydroperoxidase. This enzyme effects the oxidation of methyl phenyl sulfide and sulindac sulfide to the corresponding sulfoxides, in which process the 15-hydroperoxyprostaglandin **106** is reduced to the prostaglandin **107**. The oxygen atom acquired by both substrates arises exclusively from **106**, which was prepared enzymatically with dioxygen as the source



106 107 (108)

of ^{18}O.[498] The heme prosthetic group is presumably like that of other peroxidases such as yeast cytochrome *c* peroxidase, which in the Fe(III) state has imidazole and aquo axial ligands.[501] Reaction with the hydroperoxide, as with simpler hydroperoxides, likely affords the Fe^{IV}=O group (there being no precedent for Fe^{V}=O) and a second oxidizing equivalent created as a porphyrin or protein side chain group radical.

Experiments with cytochrome P-450 have involved microsomal and purified preparations from rabbit and rat liver. No important differences were observed between the two types of preparations. Reaction 109

$$RSR' + O_2 + NADPH + H^+ \rightarrow RS(O)R' + NADP^+ + H_2O \quad (109)$$

describes the overall oxidation of sulfides catalyzed by P-450's. When a microsomal oxidation of PhSMe was conducted in ^{18}O-labeled phosphate buffer, only about 1% of oxygen in the product arose from solvent.[490,493] Further, the oxidation products of thioanisoles incubated with horseradish peroxidase or chloroperoxidase and labeled hydrogen peroxide contained mainly ^{18}O atoms.[495] In the resting state of *Pseudomonas putida* cytochrome P-450 the axial Fe(III) ligands are cysteinyl sulfur and water.[502] When the substrate, camphor, is bound, the aquo ligand is displaced and Fe(III) becomes five-coordinate.[503] A similar situation can be expected with mammalian enzymes. Thus, in the peroxidase above and in the P-450 enzymes the heme groups are well set up to develop ferryl units, such as that directly detected in horseradish peroxidase by EXAFS spectroscopy,[295] upon reaction with a suitable oxo donor. Such reactions place the catalytic site in an oxidation state two electrons more oxidized than the resting state, which contains Fe(III) bound to a porphyrin dianion, and raises the question of the mechanism of atom transfer to sulfides. Two limiting pathways are shown in scheme 110: direct atom transfer and electron

$$[Fe^{IV}O(P\cdot)L]^+ + RSR' \rightarrow \begin{cases} [Fe^{III}(P)L]^+ + RS(O)R' \\ Fe^{IV}O(P)L + RSR' \end{cases} \quad (110)$$

transfer to produce a sulfenium cation and half-reduced catalyst followed by atom (formally O^-) transfer. For the sake of definiteness, 1 oxidizing equiv is stored in the porphyrin and is quenched in the first electron transfer. The near-linear correlation between log V_{max} for the oxidation of NADPH in reaction 109 and peak potentials for the irreversible oxidation of para-substituted thioanisoles has been interpreted to favor a path in which electron transfer precedes atom transfer.[493,494] The correlation is such that an increase in the electron-donating ability of the sulfide substituent increases the rate of oxidation of NADPH. The two pathways will be difficult to distinguish experimentally. Cytochrome P-450 will oxidize sulfoxides to sulfones in a process analogous to reaction 109 but more sluggish in rate. The sulfide:sulfoxide ratio of V_{max} values is 5.6:1 for *p*-methoxyphenyl methyl sulfide and sulfoxide, the most reactive substrates tested. The same reactivity correlation was observed,[499] suggesting the possible intermediacy of $RS^+(O)R'$. Model systems capable of sulfide and sulfoxide oxidation with oxoheme catalysts should be accessible. Stoichiometric reactions should be useful in attempts to detect electron-transfer intermediates in scheme 110. It has not been established whether the Fe^{IV}=O group alone, in a complex such as **53** (as opposed to **56**), is capable of oxidizing sulfides and sulfoxides.

4-Hydroxyphenylpyruvate dioxygenase catalyzes the sulfoxidation of 4-hydroxyphenylthiopyruvate, with dioxygen being the source of oxygen atoms. The possibility of an Fe^{IV}=O oxidant at the non-heme catalytic site has been recognized;[497] isotope labeling experiments have not been performed.

The remaining enzymes in Table 20 are molybdoenzymes and are usually referred to as the molybdenum hydroxylases. Detailed accounts of their properties are available.[6,7,504-506] Noting that reactions catalyzed by a number of these enzymes conform to generalized reaction 1 in which an oxygen atom is added to or subtracted from substrate, we have introduced the nomenclature "oxotransferases".[99,507] Following the recent considerations by Friedman et al.,[508] it may be preferable to restrict the latter term to enzymes which catalyze oxo transfer without intervention by any other reactant than substrate and to employ "hydroxylase" for those enzymes which require water to hydrolyze oxidized substrate from the active site in the catalytic reaction. At present, the latter enzymes appear to be xanthine oxidase (XnO), aldehyde oxidase (AO), and perhaps formate dehydrogenase, all of which effect the transformation

$$\gtrless C-H \rightarrow \gtrless C-OH.$$

Formate dehydrogenase actually produces CO_2; this may arise from the dehydration of bicarbonate, although other pathways are possible. In the usual enzyme systems, the oxygen atoms transferred derive from water, and dioxygen is the terminal electron acceptor. For XnO the overall reaction is xanthine + H_2O + O_2 → uric acid + H_2O_2. In their native, fully oxidized forms XnO and AO contain $Mo^{VI}OS$ units. When inactive, both enzymes have an oxo in place of a sulfido ligand. In the following discussion, attention is confined to enzymes which appear to include primary oxo transfer in their reaction cycles. Williams[509] and Stiefel,[510] both in 1973, recognized the possibility of oxo transfer and concomitant two-electron reduction of molybdenum in the action of nitrate reductase, which reduces substrate to nitrite. Shortly thereafter, Garner et al.[350] postulated atom transfer in the reduction of nitrate by Mo(V) (reaction 71), and Wentworth[511] explicitly proposed the atom transfer conversion $Mo^{IV}O$ → $Mo^{VI}O_2$, a primary oxo transfer reaction, in the enzymatic reduction of nitrate. This reaction has now been achieved in system 48 with XO = NO_3^- and sulfamate as a scavenger of nitrite.[327]

Sulfite oxidase is a mammalian enzyme located principally in the liver. Purified enzymes have molecular weights of 55 000–60 000 and are composed of two subunits, one containing molybdenum and the other a *b*-type cytochrome which acts as an internal electron-transfer center.[487,506,512] Sulfite is the only known substrate; the overall process is reaction 111. A proposed

$$SO_3^{2-} + 2Fe^{III}\text{-cyt-}c + H_2O \rightarrow SO_4^{2-} + 2Fe^{II}\text{-cyt-}c + 2H^+ \quad (111)$$

catalytic cycle[506] is shown as scheme 112 in Figure 13.

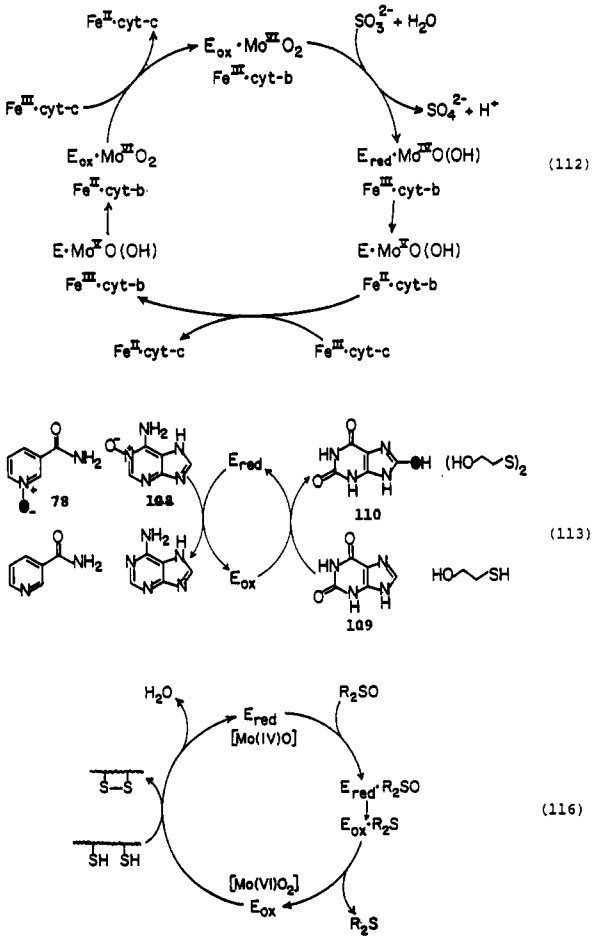


Figure 13. Upper: Catalytic cycle 112 for sulfite oxidase (E = enzyme, cyt = cytochrome; adapted from ref 506). Middle: catalytic cycle 113 for the reduction of nicotinamide *N*-oxide (**78**) and adenine 1-oxide (**107**) by xanthine oxidase with xanthine (**108**) or mercaptoethanol as electron donor. Lower: proposed catalytic cycle 116 for the enzymatic reduction of sulfoxides.[322]

Starting with the oxidized state, the first reaction is oxo transfer to substrate affording product sulfate and $Mo^{IV}O$. A reasonable possibility is that the vacated oxo coordination site is filled by hydroxide derived from water. A sequence of internal and external single electron transfers, the latter with cytochrome *c* as the carrier, recovers the oxidized form of the enzyme. In this scheme the EPR-active Mo(V) species appear in that part of the sequence connecting fully oxidized and reduced enzyme, and not in the substrate oxidation step. Isotope labeling experiments have not been reported. Tungsten-containing sulfite oxidase is completely inactive in sulfite oxidation and is apparently not reducible below the W(V) state,[513] thereby preventing a primary oxo transfer step.

In contrast to sulfite oxidase, AO and XnO are promiscuous enzymes that accept a wide variety of alternative substrates. Indeed, because of its broad substrate specificity and lack of knowledge of true physiological function, Rajagopalan[514] considers AO to have been misnamed. Xanthine oxidase will not only oxidize a variety of purines, pyrimidines, pyridines, and aldehydes,[514] it will also tolerate oxidants other than dioxygen. This is illustrated in scheme 113 of Figure 13, which provides a simplified interpretation of the interesting experiments of Murray et al.[474] in 1966 and of subsequent observations by Stöhrer and Brown[479] in 1969. Nicotinamide *N*-oxide (**78**) or adenine 1-oxide (**108**) acts as an oxo donor to the reduced form of the enzyme, returning it to its oxidized state, which then reacts with its "natural" substrate xanthine (**109**) to afford uric acid (**110**). Further, **109** can be replaced with another electron donor such as mercaptoethanol. These results show that XnO is also an *N*-oxide reductase. Of substantial importance is the finding that when **78** was labeled with ^{18}O, 54% and 67% of the label appeared in the product with the milk and liver enzymes, respectively. There was no incorporation of ^{18}O in **110** when $^{18}O_2$ was the oxidant; consequently, water provides the oxygen atom introduced into xanthine, a matter further confirmed by the use of $H_2{}^{18}O$.[475] Transfer of the isotope supports the direct oxo transfer pathway as depicted in scheme 113. (While there is no evidence that the flavin is a site of catalysis, demonstration of isotope transfer with deflavo XnO would be desirable.) The lack of complete transfer indicates exchange of enzyme oxo ligands with bulk solvent and/or another reaction pathway. The information in Table 20 indicates that AO is also an *N*-oxide and *S*-oxide reductase. Further, most molybdoenzymes (not listed) accept nitrate as an alternative substrate.

The proof of one enzymatic catalysis involving a primary oxo transfer step implies that there could be others. The most probable cases at present, in addition to sulfite oxidase, are nitrate, *S*-oxide, *N*-oxide, and chlorate reductases. However, no isotope labeling experiments intended to trace ^{18}O atoms introduced in substrate have been performed. A particularly interesting possibility would be the capture of these atoms by a tertiary phosphine in an enzymatic reduction of the preceding substrates by phosphine. Proof of such a cycle would provide powerful evidence of the ability of biological molybdenum sites to execute primary oxo transfer. However, the well-established ability of $Mo^{IV}O$ complexes to reduce most enzyme substrate types and several actual substrates (Table 10) leaves no doubt as to the intrinsic competence of the $Mo^{IV}{=}O$ group as reductant by atom transfer.

Lastly, note is made of the observation of catalysis of the reversible intermolecular oxo transfer reaction 114 by the nitrite dehydrogenase of *Nitrobacter agilis*.[508] This reaction is one of several overall ^{18}O atom

$$NO_2{}^{18}O^- + {}^{15}NO_2^- \rightleftharpoons NO_2^- + {}^{15}NO_2{}^{18}O^- \quad (114)$$

transfers between different isotopic species that result in the formation of double-labeled nitrate and nitrite at similar rates. When exchange with solvent water is taken into account, the key point is the generation of the double-labeled ions. These cannot arise in the observed amounts without atom transfer to the catalyst followed by oxo transfer to reduced substrate. Double-labeling experiments should have other applications in this respect. Unfortunately, it is not known if the catalyst in this case is a molybdoenzyme.[508]

2. Analogues

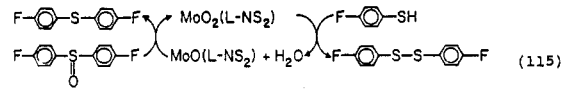
Analogue reaction systems of heme oxygenases, with particular reference to mechanism of action of cytochrome P-450,[302] have been extensively pursued using metalloporphyrins as catalysts in oxygenations of organic substrates.[34,37] Work with other substrates has been directed toward the development of functional

models of the catalytic sites of the molybdenum oxotransferases. Much of the research has been conducted in this laboratory. Because the approach and many of the results have been recently summarized,[507,515] only a resume of the leading aspects is provided here.

Several requirements must be met for a molybdenum complex to qualify as an active-site analogue. (i) It must approach or achieve the composition of the coordination unit, as deduced from a combination of EXAFS and EPR results for the enzymes.[516-519] (ii) It must not be subject to intermetal oxo transfer reaction 46, leading to μ-oxo Mo(V) dimers of the sorts listed in Tables 3 and 18. (iii) The oxidized (Mo(VI)) and reduced (Mo(V,IV)) complexes should be interconvertible in both directions by atom and/or electron transfer in order that catalysis be achieved. Concerning i, EXAFS and EPR results have been used to deduce probable *minimal* coordination units for several enzymes. No protein crystal structures are available. For example, these results indicate the units $Mo^{VI}OS(SR)_2$ and $Mo^{IV}O(SH)(SR)_2$ for the oxidized and reduced forms, respectively, of xanthine dehydrogenase. There is little doubt that these units are also found in XnO and AO. The units $Mo^{VI}O_2(SR)_{2,3}$ and $Mo^{IV}O(OH)(SR)_{2,3}$ are considered to apply to sulfite oxidase (scheme 112), to nitrate reductase from *Chlorella*, and to the cyanolyzed (inactive) forms of xanthine dehydrogenase and XnO. Nitrogen and oxygen atoms may also be present in the coordination spheres. Molybdenum–oxo bond lengths are in good agreement with those in Table 2 and Mo–S bond lengths, which are in the 2.36–2.54-Å range, correspond to thiolate (not thioether) binding. Active sites are mononuclear. $Mo^{V}_2O_3$ bridges **15** are presumably prevented from forming during oxo transfer because of protein structural constraints and thus are biologically irrelevant. Complexes containing these bridges are frequently irreversibly formed, in which case they cannot support catalytic or even stoichiometric conversions of substrates.

Reaction system 48 is currently the most highly developed analogue system for molybdenum oxotransferases. As already noted, complexes **68** and **69** are designed so as to prevent μ-oxo dimer formation. The mean Mo–O and Mo–S bond lengths in **68**, 1.705 (3) and 2.416 (5) Å, respectively, fall within the range for corresponding bonds in enzymes; diffraction-quality crystals of **69** have not been obtained. The presence of one N atom donor in these complexes is not inconsistent with the EXAFS results.

As shown in Table 10, reactions with a variety of substrates prove that reaction 48 can occur in the forward and reverse directions. Among the substrates shown to react cleanly in reduction are certain *N*-oxides and *S*-oxides that are enzyme substrates, including *d*-biotin *S*-oxide (**77**), and nitrate. The substrate oxides have also been catalytically reduced in scheme 103, where a tertiary phosphine is a convenient and effective reductant of the oxidized catalyst. Demonstration of *S*-oxide reduction in certain reconstituted enzymatic systems including the cysteinyl-containing redox protein thioredoxin has suggested that thiol may be an electron source for reduction of these substrates. It has not been established that the enzymes in question are Mo dependent. However, this is not the case for *d*-biotin *S*-oxide reductase, which is a molybdoenzyme and appears to utilize a cysteinyl-containing protein different from thioredoxin or glutaredoxin.[486] Following observation of clean reduction of **68** to **69** by arenethiols, cycle 115 was demonstrated by use of ^{19}F NMR spec-



troscopy.[323] This shows that electrons can be transferred from thiol to substrate via a credible model of an oxotransferase active site. Further, $MoO(S_2CNEt_2)_2$ can be obtained in good yield from the reduction of $MoO_2(S_2CNEt_2)_2$ with benzenethiol[520] and is an *S*-oxide reductant (Table 10). These results have been used to devise cycle 116 in Figure 13, proposed for the enzymatic reduction of *S*-oxides to sulfides.[322] Allowance is made for the likely existence of enzyme complexes of oxidized and reduced substrate. It should be kept in mind that the nature of the active site of the *S*-oxide reductase is uninvestigated; in particular, the presence or absence of a terminal sulfido ligand has not been established. Whatever the deficiencies of cycle 116, all steps have the virtue of being based on demonstrated analogue chemistry.

Under the oxo transfer hypothesis, the Mo(V) state is developed in the electron transfer sequence following catalysis; i.e., this state is not directly involved in the bond-breaking/bond-making step. In, e.g., cycle 116 the thiol reduces Mo(VI) in two one-electron steps. Because of the spectroscopic unresponsiveness of diamagnetic Mo(IV,VI), except in the more recently applied X-ray absorption spectroscopy, Mo(V) enzymatic states had for some time been the only ones directly observable. A large body of EPR data exists, especially for XnO. One goal of analogue chemistry is the development of models of the Mo(V) states whose spectroscopic similarities to the enzymes permit deductions of active-site structural features. While a treatment of this matter is beyond the purview of this article, it is noted that electrochemical and EPR evidence have established series 117 (L = dme) whose terminal member exhibits

$$[Mo^{VI}O_2L] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Mo^{V}O_2L]^- \xrightarrow{H^+} [Mo^{V}O(OH)L] \quad (117)$$

^1H and ^{17}O hyperfine splittings similar to those of enzyme states.[521] $MoO_2(dme)$ is unusual among $Mo^{VI}O_2$ comlexes in supporting a reversible one-electron reduction (at −1.28 V vs SCE in THF[341]). In the presence of water, the highly basic $Mo^{V}O_2$ group is protonated, a behavior analogous to that in dioxorhenium(V) systems (reaction 78). With other ligands, generation of $Mo^{V}O(OH)$ and $Mo^{V}O(SH)$ centers has been claimed by coupled reduction and protonation.[522] At the very least, these results increase the viability of a cis-$Mo^{V}O(OH)$ enzyme state such as is represented in scheme 112.

It has already been observed that oxidations of the enzyme substrates sulfite and acetaldehyde in Table 11 by $MoO_2(S_2CNEt_2)_2$ are rather strongly exothermic and that the reduction of nitrate by $MoO(S_2CNEt_2)_2$ is, at the least, approximately thermoneutral. More generally, the placement of these complexes, **60**, and **61** in the thermodynamic series of Table 13 is such that, on thermodynamic grounds, they are competent to oxidize

or reduce all enzymatic substrates for which thermochemical data are available. Clean oxidations of aldehydes, xanthine and related bases, formate, and sulfite by $Mo^{VI}O_2$ species have not been reported or substantiated by subsequent work if reported. Reductions of chlorate and dithionite by Mo^{IV}=O complexes have not been described. Oxidations of aldehydes, in particular, have been attempted in several laboratories without success.[523,524] Photochemical oxidation of benzaldehyde with $MoO_2(S_2CNEt_2)_2$ in dichloromethane or chloroform affording benzoic acid and $MoO(S_2CNEt_2)_2$ has been observed.[525] One Mo(VI) complex MoO_2L (L = N_2S_2 tetradentate) is reduced to Mo(V) in the presence of excess sulfite.[526] The oxidation product of sulfite was not described. Successful transformations of other enzymatic substrates are summarized in Table 10. It is emphasized that no $Mo^{VI}OS$ complexes have yet been prepared that are suitable analogues for the active sites of XnO and AO. Consequently, it is not known if a sulfido ligand is obligatory to the reduction of the substrates of these enzymes in analogue systems.

All Mo^{IV}=O complexes tested, including those in reactions 47–51, reduce Me_2SO, the thermodynamically most resistant of the oxidized enzyme substrates in Table 13. This indicates that the coordination unit does not play a major role in setting reactivity toward this substrate and those with less negative ΔH values. The resistance of complex 74 to reduction by tertiary phosphines underscores the beneficial effects of anionic sulfur ligands in stabilizing Mo^{IV}=O. The stoichiometric reduction of enzymatic substrate XO by a Mo^{IV}=O complex is, therefore, a necessary but not sufficient thermodynamic criterion for a functional oxotransferase active-site analogue. Required for sufficiency in the general case are factors which permit atom transfer to or from substrate and then regeneration of the initial Mo(IV,VI) state by atom or electron transfer. A possible role of sulfur ligands, projected from the behavior of synthetic systems, is modulation of effective (atom transfer) or real (electron transfer) potentials into a physiologically accessible range, thereby permitting catalysis. An "incorrect" ligand set could place the oxidized enzyme at a potential too negative to permit reduction to Mo(IV), either by two one-electron transfers as in the return portion of a cycle 116 or by atom transfer as in the initial event of cycle 112.

At parity of coordination environment, the most significant difference between molybdenum and tungsten complexes is the more negative reduction potentials of the latter. This has been most clearly shown by the important work of Heath et al.[527] on the hexachlorometalates. Values of $E_W - E_{Mo}$ for the reversible couples $[MCl_6]^{z/z-1}$ in dichloromethane are −0.61 (0/1−), −0.65 (1−/2−), and −0.87 V (2−/3−). Potential differences for oxo complexes of the two metals are collected elsewhere.[324] Among the more recent results are those for the three-membered series 118[528] (R = 2,3,5,6-

$$[MO(SR)_4] \underset{}{\overset{-0.25\ V}{\rightleftharpoons}} [MO(SR)_4]^- \overset{-0.24\ V}{\rightleftharpoons} [MO(SR)_4]^{2-} \quad (118)$$

Me_4C_6H) where the redox-active orbital has nonbonding metal d_{xy} character. These further exemplify the negative potential differences, which tend to be attenuated by electron-delocalizing ligands.[324]

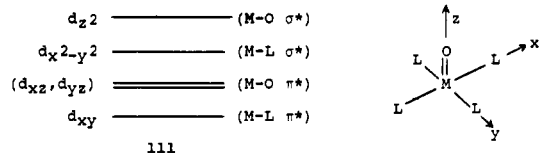
The inactivity of tungsten-containing sulfite oxidase[513] and of bacterial enzymes from organisms grown up in the presence of tungstate instead of molybdate[483] almost certainly derives from the more negative potentials of corresponding tungsten redox couples. This explanation had been offered by several investigators, but until less than 10 years ago there were insufficient experimental data to establish the consistently negative potential differences in comparative pairs of synthetic complexes. These data suggest that W(VI/V/IV) potentials in enzymes would be cathodically shifted compared to those of the native molybdo forms, possibly rendering difficult or impossible the attainment of a catalytic cycle with physiological electron carriers. Another contributing factor could be relative M=O bond energies, which are estimated to favor W=O by about 10–20 kcal/mol in $MOCl_4$ and MO_2Cl_2.[529] In oxo transfer this would make a $W^{VI}O_2$ complex a poorer oxidant and a $W^{IV}O$ complex a better reductant than their molybdenum counterparts. Clearly, much remains to be learned about the comparative atom and electron transfer chemistry of tungsten and molybdenum.

VI. Summary and Conclusions

At this stage of development of oxo transfer chemistry, two considerations are paramount: the types and numbers of oxometal functional groups and the factors effecting their stabilities; a rationalization of known reactivities extendable as a predictive basis for new reactions. These matters are explored and summarized in the following sections.

A. Functional Group Electronic and Geometrical Structures

The generalization concerning stabilization of oxometal groups in terms of an oxidation state not less than 4+ and no more than four d electrons is based in large part on MO calculations. The results of earlier semiempirical treatments[111,530–533] and those of multiple-scattering $X\alpha$[534,535] and ab initio SCF[536] analyses for, mainly, d^1 complexes of the types $[MOL_{4,5}]^{z-}$ (M = V(IV), Cr(V), Mo(V), L = halide) concur in a $^2B_2$ ground state and $M^{\delta+}$=$O^{\delta-}$ polarization of the oxometal group. Calculations of the naked ions $[MO]^{2+,3+}$ yield the same ground state. All but the ab initio calculation (of $[CrOCl_4]^-$) lead to the energy level scheme 111, in which



111

the principal bonding interactions of the d orbitals are indicated. The d_{xy} orbital is nearly nonbonding, its main interactions being in-plane π-bonding. From the scheme, it is evident that any configuration $d^{>4}$ would reduce the π-bond order below 1 and destabilize oxometal bonding. Further, d^4 configurations are not generally accessible in transition elements to the right of group 8 owing to the extremely high oxidation states required. The combinations $M^{\geq 4+}$ ($d^{\leq 4}$) are clearly optimal for development of the M=O group. The metal formal charge can be considered to reduce the

basicity of the oxo ligand such that it is sufficiently nonnucleophilic to survive electrophilic attack under normally accessible experimental conditions. The Re(II,III) complexes in Figure 11 stabilized under basic conditions provide, as already noted, apparent exceptions to the foregoing generalization.

The remaining oxometal groups in Figure 1 are stabilized under the conditions of the M=O group, with recognition that with the exception of $[RuO_3(OH)_2]^{2-}$ (97) tri- and tetraoxo groups require d^0 metal ions. Reduction of oxo ligand basicity by high metal oxidation states is again a pertinent factor here. The great majority of d^2 MO_2 groups are linear, doubtless for the bonding reasons introduced earlier. However, there are several exceptions. Already mentioned are $MO_2(mes)_2$ (M = Re(VI), Os(VI))[105] whose nonlinear, highly distorted tetrahedral configurations may reflect a compromise between linear MO_2 and tetrahedral MO_2L_2. Oxidation of *cis*-$[M(bpy)_2(OH_2)_2]^{2+}$ (M = Ru, Os) by excess Ce(IV) in aqueous solution affords *cis*-$[MO_2(bpy)_2]^{2+}$, isolated as perchlorate salts.[443,537] Stereochemistry was assigned on the basis of two MO_2 stretching frequencies. These may be kinetic products inasmuch as *cis*-$[OsO_2(bpy)_2]^{2+}$ is converted to the trans isomer in refluxing acetonitrile.[537] No oxo transfer chemistry has been reported and no X-ray crystal structures are available for these complexes. The trigonal planar configuration of the RuO_3 group in **97** is unique. Its stability vs other arrangements in five- and six-coordination has not been investigated theoretically or experimentally.

B. Spontaneous Oxo Transfer: Evolution of a Reactivity Scale

A common thermodynamic basis for reactivity in terms of the "half-reactions" 66 has already been introduced in the form of Table 13 and applied successfully to the reactions of Mo(IV,VI) complexes. Here the criterion of spontaneity for primary oxo transfer reaction 7 is a negative ΔH for the combined half-reactions. This method is extended in this section, first to aqueous solution, and then to a larger reaction set making use of reactivity information already compiled.

1. Aqueous Solution

In this medium ample standard potential data are available to permit calculation of free energy changes at 298 K for a large set of known or potential oxo donors and acceptors. Data are assembled in Table 21. The exact values depend on the choice of $E°$ values and, in some cases, of pK_a data. Where comparisons can be made, $\Delta G°$ and ΔH values run parallel and the order in Table 13 is maintained even though the majority of entries there do not refer to aqueous solution at pH 0 or 14. Further, $\Delta G° > \Delta H$, leading to the expected negative ΔS values, which are usually in the −10 to −20 eu range. On this scale, ozone is the strongest oxo donor and cyanide is (marginally) the strongest acceptor. Reactions 2 and 3 are predicted to be spontaneous with large driving forces.

Principal interest attends the position of metal species in the reactivity series. The V^{2+}/VO^{2+} couple can be directly calculated from available potentials. The value for the Ti^{2+}/TiO^{2+} couple was similarly obtained but, given the uncertainty in potentials involving Ti^{2+} in aqueous solution,[538] the value of −62.9 kcal/mol is likely an upper limit. The placement of other couples in the table is conjectural; each is placed in the highest position consistent with the information available. Their real positions may be lower, but not higher. The reaction of Fe^{2+} with ozone affords about 40% of product as a binuclear complex.[275] Clearly this result is not restrictive in the placement of the Fe^{2+}/FeO^{2+} couple. If an Fe(IV) pathway exists in oxidation by HOCl (~15% binuclear product), then $\Delta G° \lesssim +12$ kcal/mol for this couple. Similarly, if the oxidation of Cr^{2+} by chlorate[234] has a primary oxo transfer pathway, $\Delta G° \lesssim -5$ kcal/mol for the Cr^{2+}/CrO^{2+} couple. The order of these two couples cannot be established from the data available. Oxidation of Mn(TCPP) with excess hypochlorite is claimed to give MnO(TCPP),[247] but the reason for the excess oxidant is not clear. The oxidation of $[Ru(bpy)_2(py)(OH_2)]^{2+}$ to $[RuO(bpy)_2(py)]^{2+}$ by hypochlorite at pH 10.5 has been reported.[422] These observations suggest $\Delta G° \lesssim +22$ kcal/mol for the two couples; their order is unestablished.

Numerous predictions follow from the table. Among the more interesting are the reduction of *S*-oxides and sulfones by V^{2+}, and recognition of perbromate and Ti^{2+} as an exceptionally potent oxo donor and acceptor, respectively. Reduction of pyrO (reaction 24) and 2,2′-bipyridine-4,4′-disulfonic acid *N,N′*-dioxide by V^{2+} [221] by atom transfer is consistent with $\Delta G° \approx -22$ kcal/mol for py + $^1/_2O_2$ = pyO estimated from polarographic potentials[539] and pK_a values. Reduction of the protonated *N*-oxide is only slightly less favorable. It is evident that Ti(II,IV) and V(II,IV) oxo transfer chemistry will be dominated by oxidation of the II state

TABLE 21. Thermodynamic Data for the Reaction X + $^1/_2O_2$ → XO in Aqueous Solution

X	XO	$\Delta G°_{298}$,[a] kcal/mol
O_2	O_3	+39.0
BrO_3^-	BrO_4^-	+28.8
$N_2(g)$	$N_2O(g)$	+25.0
H_2O	H_2O_2	+24.6
Cl^-	ClO^-	+22.6
Mn(TCPP)	MnO(TCPP)	
$[Ru(bpy)_2(py)(OH_2)]^{2+}$	$[RuO(bpy)_2(py)]^{2+}$	
Br^-	BrO^-	+16.8
ClO^-	ClO_2^-	+12.9
Cl^-	HOCl	+12.4
Fe^{2+}	FeO^{2+}	
I^-	IO^-	+3.28
ClO_3^-	ClO_4^-	−1.25
ClO_2^-	ClO_3^-	−4.89
Cr^{2+}	CrO^{2+}	
$HSeO_3^-$	$HSeO_4^-$	−9.23
SeO_3^{2-}	SeO_4^{2-}	−15.4
NO_2^-	NO_3^-	−18.1
$Me_2S(g)$	$Me_2SO(g)$	−21.2
$Me_2SO(g)$	$Me_2SO_2(g)$	−45.7
MeSH	$Me_2S_2 + H_2O$	−48.6
V^{2+}	VO^{2+}	−52.9
HSO_3^-	HSO_4^-	−54.4
HCN	HOCN	−55.7
HCO_2^-	HCO_3^-	−56.4
$H_2(g)$	H_2O	−56.7
SO_3^{2-}	SO_4^{2-}	−59.0
CO	CO_2	−61.6
Ti^{2+}	TiO^{2+}	−62.9[b]
CN^-	OCN^-	−63.2

[a] Calculated with data from ref 22. [b] See text. Standard potentials: $O_2 + 2H^+ + 2e^- = H_2O$, 1.229 V; $O_2 + H_2O + 2e^- = 2OH^-$, 0.401 V.

TABLE 22. Rudimentary Scale of Oxo Transfer Reactivity in Nonaqueous Media

X/XO	ΔH, kcal/mol	category	couple
ROH/ROOH PhI/PhIO	≲+15	A	Cr(P)Cl/CrO(P)Cl, Mn(P)Cl/MnO(P)Cl $[Cr(salen)(OH_2)_2]^+/[CrO(salen)]^+$
R_2S/R_2SO	≳−27	B	$Fe(P)Cl/FeO(P^{\bullet})Cl$, $[Ru(bpy)(py)(MeCN)]^{2+}/[RuO(bpy)_2(py)]^{2+}$
	−35	C	$MoO(S_2CNR_2)_2/MoO_2(S_2CNR_2)_2$ >
	≲−35		$MoO(L\text{-}NS_2)(DMF)/MoO_2(L\text{-}NS_2)$ > $MoO(ssp)(DMF)/MoO_2(ssp)(DMF)$
Ph_3P/Ph_3PO	≳−67	D	$Cr(P)/CrO(P)$, $Mn(P)L_2/MnO(P)$, $Fe(P)L_n/FeO(P)L$, $MoO(P)/MoO_2(P)$, $MCl_2(HBpz_3)(PPh_3)/MOCl_2(HBpz_3)$ (M = Tc, Re), $ReL_3(RCN)(PPh_3)_2/ReOL_3(PPh_3)_2$, $[RuO(tmc)Cl]^+/[RuO_2(tmc)]^{2+}$, "$RuO(py)_2(OAc)_2$"/$RuO_2(py)_2(OAc)_2$
R'_3P/R'_3PO[a]	≲−67	E	$MO(sap)(DMF)/MO_2(sap)(DMF)$ (M = Mo, W)

[a] $R_3 = Ph_{3-n}R_n$, n = 1–3, R = alkyl.

owing to highly unfavorable free energies of reduction of TiO^{2+} and VO^{2+}, properties that are likely to carry over to these M^{IV}=O groups in nearly any environment. Owing to oxidation by water, Ti^{2+} is unlikely to have any significant aqueous chemistry, at least near ambient temperature.

However uncertain the placement of couples of unknown potentials, the free energy data in Table 21 offer a start in interpreting aqueous oxo transfer reactions, with the caveat that slow kinetics and competing reactions may negate predictions. In aqueous solution demonstrated metal-centered oxo transfer reactions are few, and it is clear that alternative pathways such as those composed of sequences of inner-sphere one-electron steps may predominate in some cases.[20] Free energy changes for other substrate half-reactions of interest are accessible from standard potentials, but no other thermodynamic data on primary metal-centered oxo transfer in aqueous solution are available.

2. Non-Aqueous Solutions

Collected in Table 22 are couples of thermal primary oxo transfer reactions, arranged so as to convey the upper or lower limit of ΔH for a particular half-reaction as it can be deduced from known reactivity. Except for the molybdenum reaction pairs **69/68** and **71/70**, couples in a given category of the table cannot be internally ordered. Four sets of X/XO substrate couples have been selected as markers because they have been involved in the largest number of reactions; the enthalpy changes of their half-reactions in Table 13 are indicated.

The most reactive set contains RCO_2H/RCO_3H, ROH/ROOH, and PhI/PhIO. Owing to the extensive use of PhIO, it is unfortunate that its ΔH value is unknown; however, it is clear that its reactivity is comparable to that of *t*-BuOOH or a percarboxylic acid. Because all complexes that react with the latter reagent also react with the former, ΔH of the couples whose reduced member is subject to oxidation by these reagents cannot exceed about +15 kcal/mol, the upper limit for category A.

In category B, the lower limit of about −27 kcal/mol is set by reduction of the oxidized member of a couple by Me_2S. Thus $[RuO(bpy)_2(py)]^{2+}$ is reduced in a reaction analogous to scheme 64 with a pseudo-first-order rate constant of 14 s^{-1} and $\Delta S^{\ddagger}$ = −39 (3) eu.[427] Consistent with its position, $[RuO(bpy)_2(py)]^{2+}$ also oxidizes Me_2SO and Ph_3P. The $Fe(P)Cl/FeO(P^{\bullet})Cl$ couple has been placed in this category on the basis of enzymatic reaction 110. Oxidation of an organic sulfide has not been investigated in a synthetic heme system. Also, it has not been established whether $FeO(P)L_n$ (n = 0, 1) can oxidize sulfides; such complexes are assigned to a lower category. If the placement of the foregoing couple is accepted, its ΔH value is bracketed between the approximate limits of +15 and −27 kcal/mol.

Category C contains molybdenum complexes which have an upper limit of −35 kcal/mol based on the measured enthalpy change for reaction 59, and whose relative ΔH order is established by the intermetal oxo transfer series in Figure 9. Because the Mo(VI) species are all reduced by Ph_3P, their ΔH values lie between the approximate limits of −35 and −67 kcal/mol. As already noted, because of the occurrence of reaction 67, the lower limit of ΔH for the $MoO(L\text{-}NS_2)(DMF)/MoO_2(L\text{-}NS_2)$ couple is nearer −54 kcal/mol.

Category D contains couples whose lower limit of about −67 kcal/mol on ΔH is defined by reduction of the oxidized member by Ph_3P. Like category A, this is obviously a quite unrestrictive category, to which numerous other couples (especially from Table 10) could be added. Because of the statement that FeO(TmTP)(*N*-MeIm) with Ph_3As "reacts to form Ph_3AsO",[290] the lower limit of the generalized $Fe(P)L_n/FeO(P)L$ couple might be as high as about −35 kcal/mol. While this result is included in Table 8, it has not been documented; consequently, at least for now, the foregoing couple is placed in category D.

Category E is based on the *negative* evidence that neither $MoO_2(sap)(DMF)$[344] nor its tungsten analogue[327] reacts with Ph_3P even under forcing conditions. The former is cleanly reduced with Ph_2EtP but the latter remains resistant to reduction. It is probable that numerous other couples belong to this category, including some of those reducible by alkylaryl- or trialkylphosphines (Tables 10 and 15). Unfortunately, parallel trials with Ph_3P are not reported, making it uncertain that the more nucleophilic phosphines are *required* for reduction. It is likely that Ti^{IV}=O and V^{IV}=O complexes such as the porphyrinates fall in this category, given the relative instabilities of their M(II) states. Attempts to reduce such species by oxo transfer have not been described.

Not included in Table 22 are reactions that depart from the defining primary reaction 7, such as those involving clusters or more than two-electron changes. The oxidation of, e.g., M(P)(CO)L to $MO_2(P)$ (M = Ru, Os) with category A donors is a four-electron reaction.

The same reaction effected with less reactive oxidants has not been reported. Reaction 87 and related Os(VI) → Os(IV) reductions (Table 16) are overall two-electron reactions conducted with >2 equiv of Ph_3P. In some cases at least, these reactions appear to proceed with formation of intermediates below oxidation state IV, which are then oxidized with air or hydrogen peroxide. In both systems, means of access to and the stability of M^{IV}=O complexes remain undefined.

Table 13 and the reactivity scales of Tables 21 and 22 have the merit of providing some thermodynamic basis of choice of oxo donor or acceptor for a particular reaction in question. Additional half-reaction enthalpies can be calculated from $\Delta H°_f$ data.[367,369] It is improbable that more reactive donors will be required for any purpose. The same cannot be said of acceptors, given the existence of category E. Strongly basic phosphines[364] offer one possibility, as do oxophilic silicon compounds as judged from ΔH = −99 kcal/mol for Si_2Me_6/Si_2OMe_6, marking the disilane as the strongest acceptor on the scale of Table 13. Its Si–Si bond dissociation energy of 80.5 kcal/mol[540] may, however, limit its utility. Reagents which reduce phosphine oxides to phosphines,[541] such as the more electrophilic Si_2Cl_6,[542] and $HSiCl_3$[543,544] and $PhSiH_3$[544,545] have not been explored in metal-centered oxo transfer and hold promise. The critical task of sequencing oxo transfer reactivities of substrates and metal complexes can best be achieved by direct calorimetry, as pioneered by Watt et al.[32] In the absence of such measurements and with reference to metal complexes, considerable refinement of the current rough order should be possible in two ways: by examining reactions with marker X/XO couples of known ΔH, and by investigating intermetal reactions with the intention of defining atom transfer cascades such as that in Figure 9. While the qualitative thermodynamic aspects of reactivity have been emphasized in this section, it is appropriate to underscore again the results in Figures 3–5 and Table 12. These represent the beginnings of a systematic definition of the kinetics and mechanisms of oxygen atom transfer, one generalization from which is that all primary reactions proceed by an inner-sphere pathway.

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Abbreviations

abh	acetylbenzoylhydrazonide(1–)
acac	acetylacetonate(1–)
acen	*N,N'*-ethylenebis(acetylacetone iminate)-(2–)
AO	aldehyde oxidase
$bpbH_2$	1,2-bis(2′-pyridinecarboxamido)benzene
bpy	2,2′-bipyridine
chba-Et	1,2-bis(3,5-dichloro-2-hydroxybenzamido)-ethane(4–)
chba-dcb	1,2-bis(3,5-dichloro-2-hydroxybenzamido)-4,5-dichlorobenzene(4–)
Cl_8TPP	*meso*-tetrakis(2,6-dichlorophenyl)-porphyrinate(2–)
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
cpdc	4-chloropyridine-2,6-dicarboxylate(2–)
cyclam	1,5,8,12-tetraazacyclotetradecane
Cys	cysteinyl
dmac	dimethyl acetylenedicarboxylate
dme	*N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-ethylenediamine(2–)
dmp	*N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-propylenediamine(2–)
DPEP	deoxophylloerythroetioporphyrinate(2–)
dppe	1,2-bis(diphenylphosphino)ethane
dttd	2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane(2–)
edt	ethane-1,2-dithiolate(2–)
EDTA	ethylenediamine-*N,N,N',N'*-tetraacetate-(4–)
en	ethylenediamine
EXAFS	extended X-ray absorption fine structure
FFP	face-to-face porphyrinate(4–)
hba-b	1,2-bis(2-hydroxybenzamido)benzene(4–)
$HBpz_3$	tris(pyrazolyl)hydroborate(1–)
HEDTA	*N*-(hydroxyethyl)ethylenediamine-*N,N',N'*-triacetate(3–)
hmpa	hexamethylphosphoramide
Im	imidazole
imep	2,6-bis[1-((2-(imidazol-4-yl)ethyl)imino)-ethyl]pyridine
L	ligand (generalized)
L-N_4	unsaturated tetraaza macrocycle ($C_{22}H_{22}N_4^{2-}$)
L-NO_2	2,6-bis(2,2-diphenyl-2-oxidoethyl)-pyridinate(2–)
L-NS_2	2,6-bis(2,2-diphenyl-2-sulfidoethyl)-pyridinate(2–)
mes	mesityl
Me_3tacn	*N,N',N''*-trimethyl-1,4,7-triazacyclononane
Me_8TPP	*meso*-tetrakis(2,6-dimethylphenyl)-porphyrinate(2–)
mpe	*N,N'*-bis(2-mercapto-2-methylpropyl)-ethylenediamine(2–)
NTA	nitrilotriacetate(3–)
●	^{18}O
OEP	octaethylporphyrinate(2–)
$OEPMe_2$	α,γ-dimethyl-α,γ-dihydrooctaethyl-porphyrinate(2–)
ox	8-hydroxyquinolinate(1–)
Pc	phthalocyaninate(2–)
peida	((1-(2-pyridyl)ethyl)imino)diacetate(2–)
pen·OMe	penicillamine *O*-methyl ester(1–)
phen	1,10-phenanthroline
pmida	((2-pyridylmethyl)imino)diacetate(2–)
pip	piperidine
P	porphyrinate(2–)
py	pyridine
pyO	pyridine *N*-oxide
pyr	pyrazine
pyrO	pyrazine *N*-oxide

R_F	*p*-fluorophenyl
salah	1,7-bis(salicylideneamino)-4-azaheptane(2–)
salen	1,2-bis(salicylideneamino)ethane(2–)
salmah	1,7-bis(salicyclideneamino)-4-aza-4-methylheptane(2–)
saloph	1,2-bis(salicylideneamino)benzene(2–)
salpn	1,2-bis(salicyclideneamino)propane(2–)
saltmen	2,3-dimethyl-2,3-bis(salicylideneamino)butane(2–)
sae	2-(salicylideneamino)ethanethiolate(2–)
sap	2-(salicyclideneamino)phenolate(2–)
SCE	saturated calomel electrode
solv	solvate
ssp	2-(salicylideneamino)benzenethiolate(2–)
tacd	1,5,9-triazacyclodecane
tacn	1,4,7-triazacyclononane
TCP	*meso*-tetrakis(*p*-chlorophenyl)porphyrinate(2–)
TCPP	*meso*-tetrakis(*p*-carboxyphenyl)porphyrinate(6–), sodium salt
TFP	*meso*-tetrakis(*p*-fluorophenyl)porphyrinate(2–)
tmc	1,5,9,13-tetraaza-1,5,9,13-tetramethylcyclohexadecane
TMP	*meso*-tetramesitylporphyrinate(2–)
TMeP	*meso*-tetrakis(*p*-methoxyphenyl)porphyrinate(2–)
TmTP	*meso*-tetrakis(*m*-tolyl)porphyrinate(2–)
tol	tolyl
tox	8-mercaptoquinolinate(1–)
TPFP	*meso*-tetrakis(*p*-(trifluoromethyl)phenyl)-porphyrinate(2–)
TPFPP	*meso*-tetrakis(pentafluorophenyl)-porphyrinate(2–)
TpivPP	*meso*-tetrakis(*o*-pivamidophenyl)-porphyrinate(2–)
TPP	*meso*-tetraphenylporphyrinate(2–)
TPyEA	tris(2-pyrazol-1-ylethyl)amine
trpy	2,2′,2″-tripyridyl
TTP	*meso*-tetrakis(*p*-tolyl)porphyrinate(2–)
TXP	*meso*-tetrakis(3,5-xylyl)porphyrinate(2–)
X	reduced substrate (generalized)
XnO	xanthine oxidase
XO	oxidized substrate (generalized)

Registry No. O, 17778-80-2.

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