Reactivity of Metal Dioxo Complexes

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PERSPECTIVE

Reactivity of Metal Dioxo Complexes

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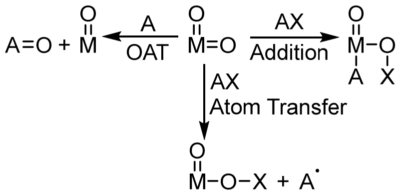
Metal dioxo chemistry and its diverse reactivity are presented with an emphasis on the mechanisms of reactivity. Work from approximately the last decade is surveyed and organized by metal. In particular, the chemistry of cis-dioxo metal complexes is discussed at length. Reactions are grouped by generic types, including addition across a metal oxo bond, oxygen atom transfer, and radical atom transfer reactions. Attention is given to advances in deoxygenation chemistry, oxidation chemistry, and reductive transformations.

Introduction

Interest in metal dioxos can be traced to the seminal work of early bioinorganic chemists and their attempts to mimic the vast reactivity spanned by enzymatic systems. A central theme of this early work is the oxygen atom transfer properties of molybdenum- and tungsten-containing active sites in enzymes.[1,2] Deeper understanding of reactivity in these enzymes led to the inception of molecular metal dioxos and a rich field of reactivity. While oxygen atom transfer remains critical to the reactivity of metal dioxos, other modes of reactivity have emerged and continue to be explored. Among these, addition across a metal oxo bond and radical atom transfer to or from a metal oxo have developed alongside the continuing progress in oxygen atom transfer reactivity.

Themes in Reactivity

Current metal dioxo chemistry can be broken down into three reaction types: oxygen atom transfer (OAT) facilitated by atom abstraction, atom transfer featuring bond homolysis, and heterolytic addition of bonds across a metal oxo functionality (Scheme 1).



Scheme 1: Three primary modes of reactivity in metal dioxos.

Among the most prominent reactivity in metal dioxos is the addition of a polarized σ bond across one of the metal oxo multiple bonds. The vast majority of metal dioxo complexes feature a high oxidation state metal center that can still function as redox active catalysts. In this way, the metal oxo bond functions analogously to a low valent transition metal atom during oxidative additions; the electrons from the metal oxo π bond are distributed among new bonds between M-A and M-O-X (Scheme 1). Following addition, several reactivities are observed: insertion into the M-A bond, homolysis of the O-X bond, or further reactivity such as deprotonation.

High oxidation state metal dioxos are also shown to stabilize radical character at the oxygen atom leading to both radical atom transfer to and from the metal oxo bond. Notably, metal dioxos serve as competent hydrogen atom acceptors to drive C-H activation by forming new MO-H bonds. Radical generation from metal oxo MO-C bonds has also been utilized to form organic radical fragments that couple following homolytic cleavage of the MO-C bond.

Despite their electron deficiency, metal dioxos commonly catalyze reduction reactions. Reactivity of this type may be driven by oxygen atom transfer. Phosphines are common OAT agents and reduce metal centers by accepting one or more oxygen atoms. The reduced metal center afforded by OAT to phosphine may then participate in redox catalysis, often deoxygenating and thereby reducing substrates. These mechanisms are common in dehydration and deoxydehydration reactions where metal dioxos transfer oxygen atoms from substrates to terminal reductants like phosphines.

Consistent interest in metal oxos has yielded numerous reviews of both broad and narrow scope, emphasizing the importance of metal dioxo reactivities. The focus of this perspective will be reports of *cis* metal dioxo complexes published since 2010. Below, we survey the recent literature organized by the identity of the metal. Additionally, reactivity in metal dioxos is sorted by the following generic reaction types:

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bond making, bond breaking, oxygen atom transfer, and deoxygenation of substrates. All reactivity described here features at least one of the mechanisms described in Scheme 1.

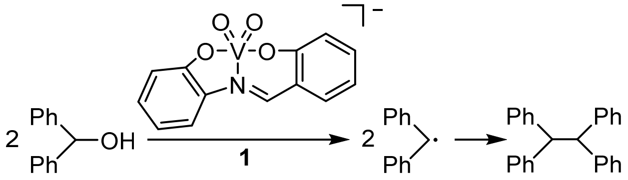
Discussion

Generally, for the cases discussed here, bond making reactions involve C-C, C-P, and C-N bond formation. Bond breaking reactions are largely C-H activation. And finally, deoxygenation reactions include dehydration, deoxydehydration, and direction reduction of carbonyl moieties.

Vanadium

Historically, the vanadyl ion (VO_2^-) has been used for a variety of chemistries, most notably in redox flow batteries[3] Here we discuss reactivity in molecular *cis*-dioxo V(V) complexes reported in recent literature.

Bond Making. Complex 1 catalyzes the reductive coupling of alcohols using the substrate as reductant and coupling partner (Scheme 2). [4]



Scheme 2.

The vanadium dioxo complex catalyzes the deoxygenation of allylic and benzylic alcohols to their corresponding radicals. Radical recombination gives the coupled alkane. Notably, when fluorene is present during the reaction hydrogen atom transfer (net reduction by two protons and two electrons) takes place, preventing radical coupling of substrate. The fluorene radical resulting from hydrogen atom abstraction also serves as a competent radical coupling partner and results in a statistical mixture of alkane products.[5] Density functional theory (DFT) calculations support a mechanism where hydrogen transfer from the substrate reduces 1 to a V(III) oxo-aquo complex. The V(III) oxo-aquo complex generates two equivalents of substrate radical. Catalysis may occur through multiple pathways involving V(III) and V(IV) species and reoxidation of these vanadium intermediates is posited to occur by disproportionation of two V(IV) species or between a V(V) and V(III) species.

Bond Breaking.

Vanadium dioxos and their related vanadium oxo-peroxo complexes are active towards hydrogen atom abstraction (eg. Scheme 1, generic "Atom Transfer" reaction). Mayer and coworkers reported the ability of $[(^tBu_2\text{-bpy})_2VO_2]^+$ to slowly activate weak C-H and O-H bonds. [6] The group independently synthesized the oxo-peroxo complex, $[(^tBu_2\text{-bpy})_2VO(O_2)]^+$, by exposing the known oxo-hydroxo complex, $[(^tBu_2\text{-bpy})_2VOOH]^+$ to air in tetrahydrofuran, which gave nearly quantitative yields over a matter of days. [7] $[(^tBu_2\text{-bpy})_2VO(O_2)]^+$ activates weak O-H bonds in hydroquinone and TEMPOH but is significantly less reactive than the dioxo complex $[(^tBu_2\text{-bpy})_2VO_2]^+$.

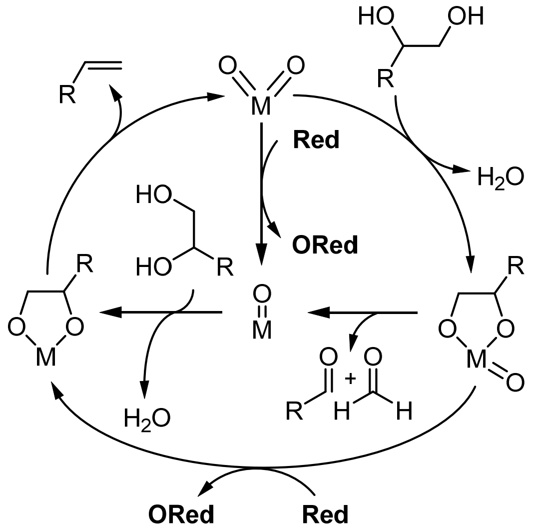
Warren and coworkers investigated the enhancement of this reported C-H activation in the dioxo and oxo-peroxo vanadium complexes under broadband UV-visible irradiation. [8] A ligand-to-metal charge transfer (LMCT) generates a charge-separated radical with an estimated 2 V reduction potential for the dioxo vanadium complex $[^tBu_2\text{-bpy})_2VO_2]^+$, initiating C-H activation and generation of organic radicals. Activation of weak C-H bonds is observed for both $[(^tBu_2\text{-bpy})_2VO_2]^+$ and $[(^tBu_2\text{-bpy})_2VO(O_2)]^+$ in aerobic conditions suggesting a common catalytic intermediate between the dioxo and oxo-peroxo complexes.

Other examples of vanadium dioxo C-H activation are reported in a series of complexes bearing scorpionate ligands.[9] Carboxylation of the gaseous alkanes methane and ethane was achieved using peroxydisulfates whereas hydroxylation of the liquid alkanes cyclohexane and cyclopentane employed hydrogen peroxide as the terminal oxidant.

While not explicitly a monometallic dioxo complex, another notable example of C-H activation by V-O bonds has been reported by Liu and coworkers.[10–12] In these reports, the vanadium oxo source is a precatalyst. The active form of the catalyst is believed to be a vanadium oxo bridged dimer bearing terminal sulfate groups. The coordination of the sulfates to the vanadium center stabilizes radical character at the sulfur oxygen bond upon electrochemical oxidation. DFT calculations suggest rapid hydrogen atom abstraction from methane following electrochemical oxidation. While the vanadium oxo bond is not directly involved in substrate oxidation, these results present a unique reactivity undoubtedly enabled by radical stabilization by the vanadium oxo moiety. Later reports by Liu and coworkers suggest titanium and chromium oxos may afford similar reactivity, stabilizing electrochemically generated sulfur oxo radicals and enabling the oxidation of methane.

Deoxygenation. Deoxydehydration (DODH) is the reduction of vicinal diol moieties to alkenes and is catalyzed by polyoxo metal complexes. Catalytic turnover of DODH is typically achieved by removal of one equivalent of water and one "O atom" which can be accepted by a terminal reductant (Scheme 3). To this end, many solvents and oxo transfer agents have been explored as possible reductants to drive DODH.

The first evidence of vanadium dioxo-driven deoxydehydration (DODH) was provided by Nicholas and coworkers featuring $[VO_2(2,6\text{-dicarboxylatopyridine})]^-$ as the catalyst.[13] 1-phenyl-1,2-ethanediol was reduced to styrene in 95% yield using triphenylphosphine as the reductant.



Scheme 3. Possible mechanisms of DODH catalyzed by dioxo metal complexes.

Exchanging phosphine for sodium sulfite hampered the yield mildly, giving 87% styrene. The vanadium complex effectively catalyzes the deoxydehydration of aliphatic, electron deficient, and sterically encumbered diols. Conformationally locked *cis*-1,2-cyclohexanediol was the lowest yielding substrate, forming cyclohexene in only 15% yield, suggesting that substrate inflexibility significantly impacts reactivity. Other vanadium dioxo complexes were shown to be active catalysts for DODH by the Nicholas group.[14] Among the three new reported catalysts, one complex catalyzed the deoxydehydration of 1-phenyl-1,2-ethanediol, diethyl tartrate, and 1,2-hexanediol using carbon monoxide as a reductant.

While exploring the inhibition of reactivity by ring strain, Bryce and coworkers found that alkene yields were substantially lower in the absence of ambient light.[15] Intersystem crossing events and stepwise olefin extrusion have been previously explored and are supported by DFT[16] but explicit enhancement of yield by light are shown here. The yields of cyclic *cis* and *trans* diols were still low (<20%), but enhancements of up to 5x were observed for reactions performed in light versus dark conditions.

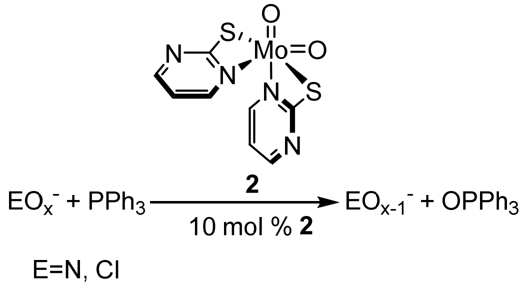
Molybdenum

Isoelectronic to vanadium dioxos, molybdenum dioxos exhibit the most diverse chemistry of all the reported dioxo complexes. Molybdenum dioxo complexes are also among the most well studied metal dioxos in the literature. Commercially available $MoO_2Cl_2(L)_2$ (L=DMF, DMSO, H_2O, etc.) alone is an extremely versatile catalyst for a variety of organic transformations.[17,18]

Oxygen Atom Transfer. The topic of molybdenum-catalyzed epoxidation of alkenes has been extensively investigated and is reviewed elsewhere.[19] Notably in recent years, epoxidation has been invoked as a critical initial step in the stereoselective anti dihydroxylation of alkenes utilizing commercially available molybdenum dioxo sources and chiral ligands.[20–22]

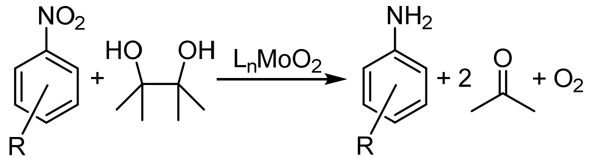
Oxygen atom transfer to and from sulfur atoms has been reported using a variety of terminal oxygen donors and acceptors and will not be discussed here.[23–45]

Isomers of a molybdenum dioxo complex bearing two pyrimidine-2-thiolate ligands (Scheme 4, complex 2) were found to reduce nitrate in the presence of triphenylphosphine.[46] While reactivity of this type is remarkable, low yields are believed to arise from insolubility of nitrate sources in organic solvents and catalyst deactivation by formation of an unreactive Mo(IV) nitrosyl complex. Complex 2 has also been shown to reduce perchlorate to chloride using four equivalents of triphenylphosphine.[47,48] Scandium and other Lewis acid additives have increased the turnover numbers in similar molybdenum dioxo complexes, affording yields surpassing 80%.[49] Molybdenum dioxo catalyzed nitrate reduction can be performed using thioethers as oxygen acceptors. In these cases, nitrate is converted to nitrite concomitant with oxidation of the thioether to sulfoxides. [50,51]



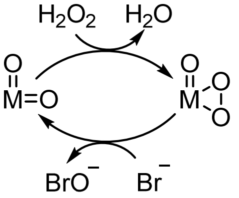
Scheme 4.

$MoO_2Cl_2(DMF)_2$ catalyzes OAT from sulfoxides and aryl nitro groups using pinacol as a reductant.[52] Mechanistic interrogations into the OAT from aryl nitro groups to pinacol utilizing a cis-dioxo Mo N-heterocyclic carbene (NHC) complex invoke a reduced Mo(IV) oxo accepting an oxygen directly from the coordinated nitro moiety.[53] The resulting aryl nitrosonium is posited to react with water to access the final aniline product. This strategy was later used to reduce nitroaromatic substrates that were then coupled to one equivalent of ketone formed from pinacol oxidation. Scheme 5 outlines the reduction of nitroaromatic substrates to anilines. Generally the mechanism for the reaction entails reduction of a Mo(VI) dioxo to a Mo(IV) oxo species. The ensuing oxo transfer from nitroaromatics to the molybdenum center affords a reduced aryl nitrosonium. Protonation of the nitrosonium by water leads to release of oxygen and formation of aniline. Intramolecular cyclization to form heterocyclic compounds after reduction of the nitroaniline has been demonstrated and often incorporates the oxidized reductant.[54–57] Notably, Pyridine-n-oxides are also catalytically deoxygenated by $MoO_2Cl_2(DMF)_2$ using pinacol as a reductant. [58] Aside from cyclization, new C-N bonds are formed when $MoO_2Cl_2(DMF)_2$ catalyzes the reduction of nitroaromatics by triphenylphosphine. Following reduction, the coordinated O-N-R fragment is attacked by the alkyl of a boronic ester forming a new C-N bond. [59]



Scheme 5.

The oxidation of bromide to hypobromite by hydrogen peroxide is catalyzed by the $[MoO_2]^{2+}$ moiety. Hypobromite formed *in situ* acts as a potent brominating agent of aromatic rings (Scheme 6). This strategy has been demonstrated with numerous molybdenum complexes bearing a variety of ligands.[60–72] However, despite the structural diversity of the molybdenum complexes, reactivity is presumed to always follow the general mechanism of formation of a metal oxo-peroxo species followed by attack of the metal peroxo by bromide to yield hypobromite. Reactions of this type do not easily fit the typical description of OAT from a metal dioxo as the metal oxygen double bond is not acting as the oxygen atom donor. Oxidation of bromide does provide another unique example of reactivity involving metal oxo peroxo complexes. There are fewer examples of vanadium dioxos catalyzing similar transformations.[73,74]



Scheme 6.

A notable example of nonclassical OAT has been reported by Brown and coworkers.[75] They find oxygen atom transfer from triethylamine-N-oxide to a six-coordinate Mo(VI) center yields an eight-coordinate Mo(VI) *trans* dioxo complex. This eight-coordinate species performs OAT to phosphines. However, reduction is observed at the redox non-innocent ligand instead of at the metal center. In this example of nonclassical OAT, molybdenum functions as an atom donor and acceptor without changing oxidation state.

Following OAT, molybdenum dioxos have been shown to be competent single electron transfer agents. These single electron transfers result in a Mo(V) oxo species. A molybdenum dioxo complex was reduced via OAT to a phosphine.[76] Treatment of the resulting Mo(IV) complex with ferricenium yields a stable Mo(V) oxo complex that is coordinately unsaturated. Later work by the same group incorporates two ferrocenium moieties into the ligand backbone.[77] When the complex is exposed to excess phosphine, superstoichiometric amounts of phosphine oxide (relative to Mo) are observed. To account for this excess oxidized phosphine, the authors posit OAT is followed by association of a water molecule to give a Mo(IV) oxo aquo complex. Intramolecular charge transfer from the reduced Mo(IV) center to the Fe(III) on the ligand backbone and loss of two protons regenerates the initial Mo(VI) dioxo complex that can further participate in OAT.

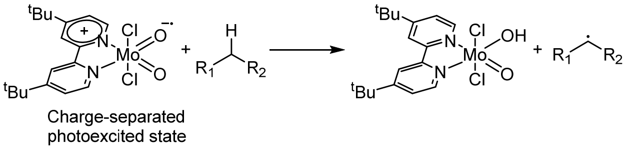
Similar reactivity is realized by incorporation of ruthenium polypyridyl into the molybdenum dioxo ligand backbone.[78,79] In these cases, rates of OAT from DMSO to triphenylphosphine may be accelerated under visible light irradiation.

Bond Making. The utility of both commercially available and synthetically unique molybdenum dioxo complexes as catalysts to make various new bonds continues to be developed. Analogous to the vanadium dioxo systems reported by Nicholas, lignin-derived benzylic alcohols undergo addition to the molybdenum-oxygen bond before C-O bond homolysis generates benzyl radicals which undergo radical coupling.[80] $MoO_2Cl_2(DMF)_2$ catalyzed the reductive coupling of aryl alcohols to an alkyl or aryl fluoroborate coupling partner using several reductants including alcohols.[81] Commercially available MoO_2Cl_2 catalyzed the formation of a carbon phosphorus bond between an imine and diethylphosphite to give alpha-aminophosphonates.[82]

Several other reductive bond-making reactions have been reported using molybdenum dioxo complexes as precatalysts. Thorough mechanistic investigations into these systems have not yet been reported for these reactions; however, these transformations remain noteworthy.[83–86]

In a unique subset of reactions to form new O-O bonds, commercially available $MoO_2(acac)_2$ served as a precatalyst for the hydroperoxidation of ketals, ketones, epoxides, and allylic alcohols.[87,88]

Bond Breaking. Chambers and coworkers demonstrated a rare instance of $[MoO_2]^{2+}$-mediated photochemical C-H activation by $MoO_2Cl_2(^{t}Bu_2\text{-bpy})$.[89] This exciting work demonstrates the oxidation of alkyl and allylic C-H bonds (Scheme 7). In the case of allylic 1,4-cyclobutadiene, quantitative conversion to benzene is observed. Allylic C-H activation in cyclohexene gives high yields of dimerized radical and minor chlorinated products. Stronger alkyl bonds can be activated and converted to oxygenated products. Strong evidence for turnover is supported by the breakdown of the inactive Mo(V/V) dimer back to the active $[MoO_2]^{2+}$ species by oxygen atom transfer agents such as pyridine-N-oxide and DMSO. Efforts to interrogate the characteristics of the excited states in $MoO_2X_2(^{t}Bu_2\text{-bpy})$ demonstrate that photoexcitation and subsequent reactivity with C-H bonds is extremely sensitive to identity of the X ligand.[90]



Scheme 7.

Another instance of single electron transfer to a $[MoO_2]^{2+}$ moiety has been recently reported. Reaction of $[MoO_2]^{2+}$ with trisperfluorophenyl borane affords a reactive frustrated Lewis pair (FLP). The FLP reacts with phenyl silane to give the transient molybdenum oxo siloxide. This siloxide serves as a single electron oxidant of a second equivalent of silane to generate reactive silyl radicals. [91]

Condensation and C-C bond cleavage in $MoO_2Cl_2(DMSO)_2$ is believed to yield a reduced Mo(IV) oxo complex. [92] DMSO serves as an oxo donor to regenerate the catalyst.

Reductive depolymerization of ester-based plastics was catalyzed by MoO_2Cl_2 using silanes as reductants.[93] Presumably ester cleavage proceeds as previously reported[94] with use of excess aryl silane. Long reaction times afford further reduction of silyl ethers by excess silanes. Reductive depolymerization of ester-containing polymers can also be realized using boranes as reductants.[95]

Deoxygenation. A notable deoxygenation reaction catalyzed by the precatalysts $MoO_2Cl_2(H_2O)_2$ and $MoO_2(acac)_2$ converts aryl ketones into alkenes.[96] Deoxygenation likely occurs by reduction of the ketones to alcohols before a final dehydration to the alkene products. Support for this mechanism is backed by reduction of independently synthesized secondary alcohols. Further reduction of aryl ketones to alkanes can be achieved using nonpolar solvents like toluene.[97]

Various commercially available molybdenum dioxo complexes catalyzed the reduction of lactic acid to a mixture of reduced products.[98] In addition to propionic acid from the direct deoxygenation of lactic acid, the gaseous products carbon dioxide, carbon monoxide, and methane were detected, indicating operant bond cleavage pathways. Other side products include polymeric and dimeric species of propionic acid and condensation products from the reaction of lactic acid with gaseous byproducts.

Dehydration catalyzed by another family of commercially available molybdenum dioxo complexes converted 1-phenylethanol to styrene with low yields. The same complexes were screened for dehydration reactivity towards a broad substrate scope.[99]

Deoxygenation of epoxides has been achieved by molybdenum dioxo complexes to yield alkenes. Multiple mechanisms are likely active during catalysis, as evidenced by the retention, inversion, and scrambling of stereochemistry from optically pure epoxides. [100–102]

Among the multitude of deoxygenation reactions reported in the literature, one attractive route to biomass up-conversion is the deoxydehydration of diols and polyols (*vide supra*, Scheme 3). Molybdenum dioxo complexes have been investigated in recent years due to their low cost and low toxicity, making them attractive alternatives to canonical Re complexes (Chart 1). Our group has recently published an in-depth review of DODH, here we provide an update for work published in recent years.[103]

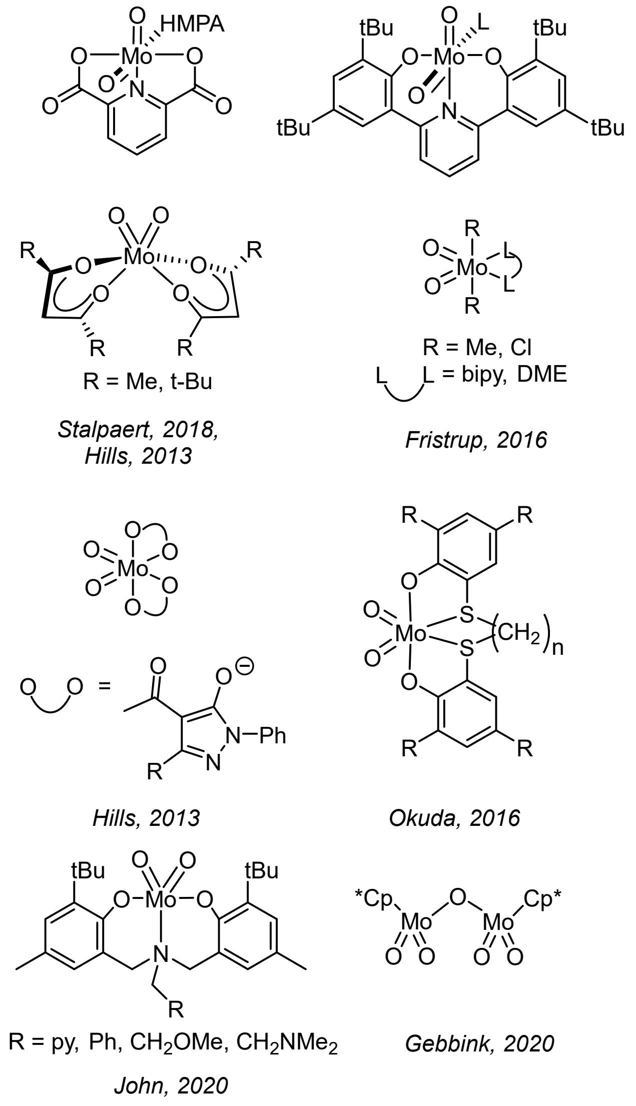


Chart 1. MoO_2-based DODH catalysts

As described above DODH can function via many mechanisms. Mo-based DODH catalysts exhibit this diversity of mechanisms possible. Employing $MoO_2Me_2(bpy)$ as a catalyst, Fristrup and coworkers screened a variety of polar protic, aprotic, and nonpolar solvents for their abilities to act as both a solvent and reductant.[104] They found isopropanol to be the most suitable choice for solvent/reductant given its ability to readily reduce the molybdenum dioxo complexes. DODH of 1,2-hexanediol was achieved at 250 °C with greater than 98% conversion of diol and 42% selectivity for alkene. Dominant side reactions include oxidation of the diol to carbonyl products, which may further react to give acetal formation. Notably, alkene yields never surpass 50%, implying oxidation of substrate may be a dominant reduction mechanism. The resulting carbonyl products may undergo secondary reactions.

Aiming for commercial accessibility of DODH systems, $MoO_2(acac)_2$ has been explored as a possible catalyst.[105] Under microwave irradiation in toluene and using triphenyl phosphine as a terminal reductant, 1-phenyl-1,2-ethanediol was converted to styrene at 170 °C in 40 minutes. Reductions of more challenging aliphatic diols were also realized in anisole. 1,2-hexanediol was reduced to hexene with 40% yield at 220 °C in 40 minutes. 1,2-decanediol was reduced to decene with 53% yield at 230 °C in 40 minutes. All the reported catalytic reactions gave high (99%) conversions of diol with low (<10%) yields of oxidized substrate. The authors conclude that the high conversion at high temperatures may be due in part to thermal instability of the substrate.

Bulkier acetylacetonate ligands, dubbed β-diketones, were explored for the DODH reaction as alternatives to the commercially available $MoO_2(acac)_2$.[106] The steric and electronic effects of these ligands are easily tuned by substituting the β-diketone. Mild enhancements in the DODH of 1,2-hexanediol to hexene were afforded by increasing the electron donation of the ligand but significant increases in yield were found when more sterically demanding β-diketones were employed. The best results utilized the mildly electron donating and very sterically crowded 2,2,6,6-tetramethylhemptate,3,5-dione as a ligand. Steric crowding at the catalyst is posited to inhibit extensive oligomerization, which would effectively decrease sites for catalysis. A survey of the substrate and reductant scope gave excellent yields of hexene, cyclohexene, and diethyl fumarate when triphenylphosphine was used as a reductant in mesitylene.

Further efforts to stabilize the molybdenum dioxo center for the DODH reaction have employed multidentate ligand frameworks. Okuda and coworkers synthesized a series of OSSO- and ONNO-coordinating tetradentate ligands and evaluated their ability to deoxydehydrate anhydroerythritol using 3-octanol as reductant.[107] The best yields of 2,5-dihydrofuran were achieved using the OSSO ligand, giving 57% yield of alkene at 200 °C. Catalytic runs using the ONNO ligand gave low conversions and yields.

ONO pincer ligands featuring a chelating pendant arm to stabilize the molybdenum dioxo centers and their use in DODH were explored by John and coworkers.[108] Modifications in the chelating pendant arm were unsuccessful in improving the deoxydehydration of 1-phenyl-1,2-ethanediol. Only when the pendant arm was modified to a noncoordinating benzyl group was catalytic activity enhanced. In this case, 34% styrene was observed using triphenylphosphine as a reductant. Removal of one half of the ONO ligand to give a dimeric molybdenum species gave nearly identical reactivity to the ONO-benzyl system, perhaps suggesting a catalytically competent bimetallic species.

Pincer ligands have also been used to stabilize Mo centers in the DODH reaction. Tran and Kilyanek synthesized a bulky bis-phenolate ONO ligand to inhibit dimerization of the reduced Mo species thought to neutralize catalytic activity.[109] The complex was capable of reducing aliphatic and aromatic diols with homogeneous and heterogeneous reductants. 1,2-hexane diol was reduced to hexene at 59% yield using triphenylphosphine as reductant with low yields of oxidized substrate. Showing promising results for scalability and facile product separation, carbon was employed as a heterogeneous reductant and 1-phenyl-1,2-ethanediol was reduced to styrene in 37% yield. Attempts to deoxydehydrate *trans*-stilbene often leads to complete substrate oxidation; however, increased propensity for DODH was observed when triphenylphosphine and the ONO complex catalyzed reduction. Interrogation into the initial reduction by triphenylphosphine suggests dimerization may still inhibit catalysis, despite the steric bulk of the ligand. Further evidence that catalytic efficiency is sensitive to coordination environment is supported by decreased reactivity when reactions are spiked with exogeneous triphenylphoshine oxide. Together, these results suggest catalysis likely requires coordinative unsaturation and is thereby inhibited by oligomerization and other strongly coordinating reaction byproducts.

A less bulky ONO coordination environment was also explored by the same group using 2,6-pyridinedicarboxylate as a ligand.[110] 1-phenyl-1,2-ethanediol was chosen as a model substrate and an extensive scope of reductants was performed. The commercially attractive secondary alcohols 2-propanol and 3-octanol were found to give styrene yields of 30% and 14%, respectively. Heterogenous reductants carbon and zinc gave modest yields of 31% and 33%, respectively. The highest performing reductant was triphenyl phosphine, which gave maximum yields of 61%; however, styrene was found to be consumed by formation of polystyrene at reaction times greater than one hour. Addition of hydroquinone as an inhibitor of polystyrene formation increased yields to 69% after 6 hours of reaction. Kinetic analysis of the triphenylphosphine/1-phenyl-1,2-ethanediol system was conducted using *in situ* IR spectroscopy to monitor the formation of triphenylphosphine oxide. The results are consistent with a mechanism involving initial rapid reduction of the metal dioxo center followed by slow catalyst turnover to afford alkene. DFT studies support rapid reduction by phosphine, but the largest energetic span in the catalytic cycle[111] involved proton transfer during the condensation between substrate and the metal oxo bond.

In addition to a broad range of deoxygenation reactions (*vide supra*), a molybdenum dioxo supported by two acylpyrazolonate ligands was found to catalyze the deoxydehydration of 1-phenyl-1,2-ethanediol.[100] Deoxydehydration of 1,2-cyclooctanediol using triphenylphosphine as the reductant gave yields of up to 55%. The authors note that the disparity between triphenylphosphine oxide formation and alkene implies additional side reactions of the substrate, inflating the observed consumption.

A final example of molybdenum catalyzed DODH that cannot be overlooked is the report by Gebbink and coworkers drawing a direct corollary between the $CpReO_3$ system and its molybdenum counterpart, $[CpMoO_2]_2O$.[112]

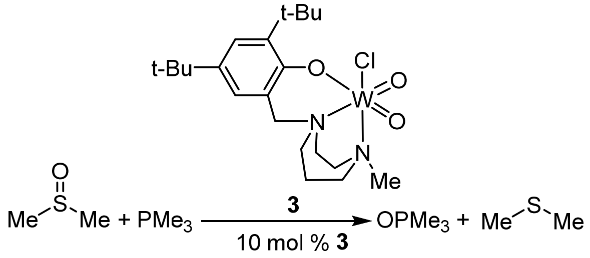
Tungsten

Reports on tungsten dioxo complexes since 2010 are sparse, and the reactivity of these complexes mainly centers on epoxidation.[113–118] One standout addition to the literature is

$WO_2(acac)_2$ functioning as a precatalyst in the asymmetric epoxidation of alkenes in the presence of a chiral ligand.[119]

Cp*WO_2R where R is a silyl alkane inserts oxygen atoms into the metal-carbon bond to give quantitative amounts of alcohol using three unique pathways.[120] Salen-type ligands supported a luminescent $[WO_2]^{2+}$ metal center active in the photocatalytic cyanation of tertiary amines and the oxidative hydroxylation of aryl boronic acids.[121]

A tungsten dioxo complex catalyzed the OAT between DMSO and trimethylphosphine with rates exceeding the molybdenum analogue (Scheme 8).[122] A pyridine-thiolate-supported biomimetic tungsten dioxo was found to transfer oxygen from DMSO to trimethyl and triphenyl phosphine faster than its molybdenum analogue.[123] The same compound also catalyzes the oxidation of triphenylphosphine using oxygen as the terminal oxidant.[124]



Scheme 8.

Oxidative bromination analogous to the cases involving molybdenum dioxo complexes (*vide supra*, Scheme 6) have been reported for a few tungsten dioxo complexes.[125]

Chromium

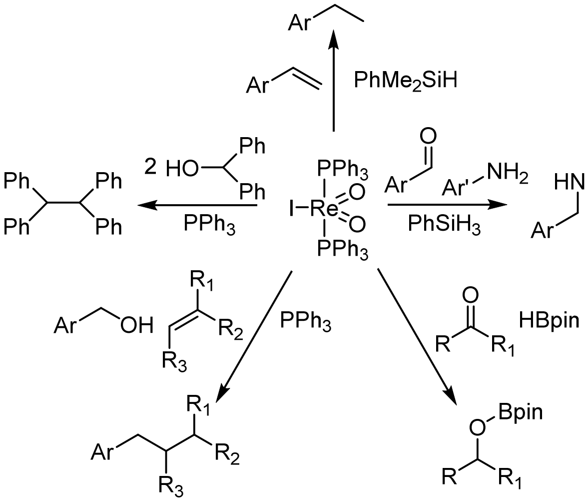
Recent reports of chromium dioxo complexes are sparse but the historic contribution of chromyl chloride ($Cr_2O_2Cl_2$) warrants attention within the context of reactivity in metal dioxo complexes. Chromyl chloride oxidations of hydrocarbons dates to the 19th century reports by Étard.[126] For an overview of reactivity involving chromyl chloride, we point readers to the publication of Limberg.[127] The mechanism of chromyl chloride oxidation of hydrocarbons was elucidated by Mayer and Cook.[128,129] In their report of chromyl chlorides oxidation of cyclohexane, they demonstrated oxidation was initiated by initial hydrogen atom abstraction evidenced by a kinetic isotope effect of 2.2. The rate of hydrogen atom transfer to chromyl chloride was related to the strength of the resulting CrO-H bond, not the radical character in the parent chromyl chloride complex. Further evidence for reaction rates dependance on the strength of bonds formed and bonds broken came from reactions of chromyl chloride with toluene, isobutane, and cyclooctane. The weaker C-H bonds of toluene, isobutane, and cyclooctane accelerated the rate of oxidation by chromyl chloride (compared to cyclohexane). These observations undoubtedly helped create the foundation for a generalized theory of proton-coupled electron transfer wherein reactivity is dominated by the thermodynamics of the bonds being broken and formed.[130]

Rhenium

In contrast to the systems discussed above, rhenium dioxos are commonly found as Re(V) d^2. The unique electronic state in addition to the dioxo moiety affords catalytic reactivities not observed for other d^0 metal dioxos. The largest disparity in reported reactivity between Re(V) complexes and other d^0 metal dioxos is the ability to form Re hydrides. The Re hydride is a critical intermediate in many bond forming and reductive processes, accessed through an initial addition across the rhenium oxo bond. d^0 metals are unable to access hydrides in one step, instead requiring initial reduction.

Bond Making. Among the most common rhenium dioxo catalyst is the commercially available $ReIO_2(PPh_3)_2$. Scheme 9 summarizes the bond-making reactions catalyzed by this complex.

$ReIO_2(PPh_3)_2$ catalyzes the reduction of imines to form C-N bonds in high yields for primary amines and in moderate yields for secondary amines using phenylsilane as a reductant.[131] Mechanistic interrogation used dimethylphenylsilane-*d* as a reductant. Selective deuterium-carbon bond formation in the reduced imine implies a rhenium hydride forms during catalysis before hydride attack on the N-coordinated imine. A silylated intermediate is formed by elimination and is subseqeuntly undergoes hydration to give the final product and silanol byproducts.



Scheme 9.

Hydroboration of aldehydes was catalyzed by $ReIO_2(PPh_3)_2$ to give the corresponding borate.[132] Hydroboration of quinolines was also reported. Reactivity is believed to proceed through formation of an initial rhenium hydride, forming the metal borate in the process.

Carbon-carbon bond formation from the reductive coupling of alcohols is catalyzed by $ReIO_2(PPh_3)_2$.[133] Benzylic and allylic alcohols were reductively coupled using triphenylphosphine as the terminal reductant. Reactivity is believed to proceed through condensation between two equivalents of alcohol and catalyst to yield a bis alkoxide intermediate. In contrast to the radical recombination seen in vanadium systems (*vide supra*), C-O bond homolysis is followed by direct radical attack of the adjacent metal alkoxide, affording C-C bond formation. [134] Lack of reaction with HAT donors further supports this mechanism. Carbon monoxide was also found to be an efficient reductant in the reductive coupling of benzhydrol. In an analogous fashion, alkenes function as competent coupling partners for aryl radical homolyzed by reduced rhenium alkoxides. [135]

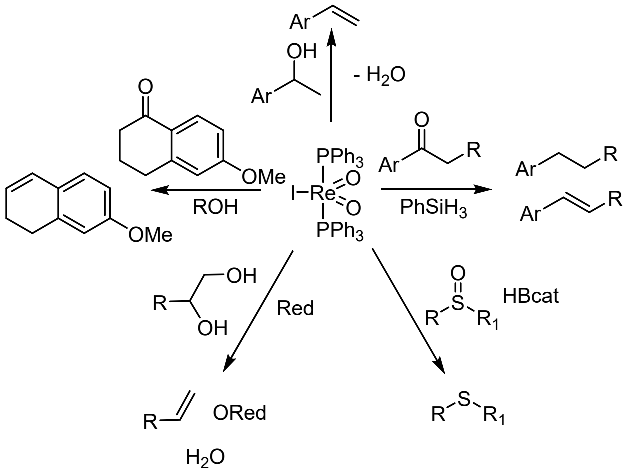
Catalytic hydrosilation of carbon dioxide was catalyzed by a PNN-bound rhenium dioxo complex under high pressures at room temperature.[136] Initial addition of the silane generates a purported rhenium hydride siloxide followed by CO_2 insertion into the hydride generating bound formate. Elimination of the silyl formate regenerates the catalyst. Further reaction with excess silane further reduces the silyl formate to silyl methanol.

$ReIO_2(PPh_3)_2$ catalyzes the reduction of alkenes in the presence of excess silane reductant. [137] Presumably, rhenium hydride is formed from the addition of the silane and the metal oxo bond. Insertion into the hydride yields a metal alkyl complex that can oxidatively eliminate silyl ethers. σ-bond metathesis with excess silane possibly yields alkane and a new silicon-silicon bond.

Bond Breaking. Methyltrioxorhenium (MTO) is among the most used organometallic metal oxo compounds. MTO has found numerous applications, including as an oxygen-transfer catalyst, in DODH, and in other deoxygenation chemistries. Methyldioxorhenium(V) (MDO) is commonly invoked as a catalytically competent species in the DODH reaction.[138,139] MTO catalyzed deoxygenation reactions of biomass and biomass-surrogate molecules are extremely important, especially in the work of Toste[140,141], Nicholas[142] and others and has been extensively reviewed elsewhere.[143–148]

One specific instance where MDO's reactivity has been implicated is in the cleavage of lignin model compounds. MTO is converted to the active catalyst MDO *in situ* via hydrogen transfer and is active for the cleavage of the β-O-4 linkages in the lignin model compounds.[149] The resulting phenolic and aldehyde products provide promising results towards sustainable chemical feedstocks using biomass upconversion.

Che and coworkers present a rare case of an octahedral, d^2 *cis*-dioxo Re(V) complex.[150] Electrochemical single-electron oxidation affords a Re(VI) complex that is active towards the oxidation of weak C-H bonds via hydrogen atom transfer.



Scheme 10.

Deoxygenation. Analogous to the molybdenum dioxo catalyzed deoxygenation reactions, $ReIO_2(PPh_2)_2$ performs similar reactions including dehydration of benzylic alcohols[151], dehydration of alpha-terpineol[152], reduction of sulfoxides using boranes[153], deoxygenation of aryl ketones to alkanes[154] or alkenes[155], and DODH[156]. These reactions are summarized in Scheme 10.

In addition to the dioxo intermediates in MTO-catalyzed DODH, the *cis*-dioxo Re(V) complex reported first by Che (*vide supra)* and two structurally analogous complexes were tested for the DODH of diols.[157] Modest activity was observed for all complexes at temperatures below 180 °C. Presumably, the systems are functioning as precatalysts that thermally decompose near these temperatures to the active catalytic species.

A *trans* rhenium dioxo complex, $[Py_4ReO_2]^+$, functions as a prectalyst to reduce diols to alkenes.[158] Evidence for the direct involvement of the parent complex during catalysis is given by the stoichiometric reduction of 1,2-hexanediol in the absence of reductant. While involvement of the Re complex is unambiguous, the ability of a *trans* dioxo Re to catalyze DODH merits discussion. DODH may only occur when a stable *cis* dioxo configuration is available at the metal center. The lability of the pyridine ligands in $[Py_4ReO_2]^+$ suggests initial condensation of a diol and metal oxo bond displaces a pyridine ligand to yields a Re oxo diolate intermediate. A single turnover of this complex is believed to give the active catalyst species, $[Py_3ReO_3]^+$ which features the necessary *cis* dioxo geometry.

Conclusions and Future Outlook

Here we have described the recent literature involving reactivity of metal dioxo complexes. Over 40 years of research has diversified and progressed reactivities involving metal dioxo complexes and interest in these systems is expected to continue making broad impacts. Deoxygenation of biomass remains an attractive route to sustainable platform chemicals and metal dioxo complexes are a natural choice to catalyze these reactions. The reported reactivity of metal dioxos in catalyzing oxidative and reductive reactions exemplifies why they are an excellent candidate to drive the transformation of structurally diverse biomass derived substrates. We expect this to be an active area of research for many years to come.

The chemistry of metal dioxos as net hydrogen acceptors (two protons, two electrons) demonstrates the potential of a vast number of organic molecules to function as net hydrogen donors. The reactivity of metal dioxos diverges from late metal chemistry where hydrogen transfer generally leads to reactive metal hydride species. In contrast, metal dioxos generate a reduced metal and one equivalent of water. The resulting reduced metal oxo can be used to drive a variety of transformations including deoxygenations and dechalcogenations. Perhaps some of the most intriguing but currently underdeveloped chemistries involve the reduction of challenging substrates such as carbon dioxide. Reduction of carbon dioxide by two electrons and one proton to formate is precedented in enzymatic systems such as formate dehydrogenase containing high oxidation state Mo/W centers[159],[160]. Notably, hydrogen transfer to a metal dioxo accesses reduced oxidation states at the metal without forming metal hydride species, thus disfavoring hydrogen evolution which commonly competes with CO_2 reduction.

Oxygen atom transfer continues to be a powerful tool to achieve difficult reductions such as the reduction of nitrates, nitrites, and organic nitro functional groups. Reduced metal oxo species may be accessed from a variety of reductants and serve as potent oxo acceptors. The potential for reduction of N-O bonds has broad impacts, especially the remediation of drinking water.

Besides biomass conversion and deoxygenation reactions, metal dioxos are potent oxidants capable of activating small organic molecules. The intrinsic driving force provided by the high oxidation state metal, mildly basic terminal oxo, and tolerance to air and water make metal dioxo complexes a centerpiece in the development of organic oxidations, especially those involving the cleavage of C-H and O-H bonds. Oxidations of this type may also be driven electrochemically or photochemically, broadening the scope of possible terminal oxidants. Abstraction of a hydrogen atom from a C-H bond concomitant with reaction of the resultant carbon radical with a coordinated labile ligand is an intriguing strategy for net addition of a C-H bond to multiple sites on a metal dioxo complex. The reported redox noninnocence of some ligands supporting metal dioxos, e.g. the work of Brown and coworkers *vide supra*, lends credence to possible multisite reactivity. Additionally, photochemical excitation to generate charge separated radicals in metal dioxos may also yield similar multisite reactivity where long lived LMCTs may be quenched by carbon radical fragments from C-H bond homolysis.

Electrochemical methods may also find use in the reduction of metal dioxos which are otherwise readily reduced by chemical reductants that donate net hydrogen atoms. Achieving similar reductions electrochemically is theoretically possible with protons and electrons, presenting a viable route to electrochemically driven reduction reactions. Reductions of this type remain underdeveloped, and we expect reports of electrochemical routes to reduced metal oxos to grow as electrochemical techniques become more accessible.

The chemistry of metal dioxo species shows great promise going forward. The general modes of reactivity described here, oxygen atom transfer, addition across the metal oxo bond, or radical atom transfer, encompass a plethora of catalytic applications which will continue to bare fruit in the years to come.

Conflicts of interest

There are no conflicts to declare.

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