3594 *Inorg. Chem.* **2010**, *49*, 3594–3601
DOI: 10.1021/ic9015383

Inorganic Chemistry
Forum Article

Activation of Molecular Oxygen, Polyoxometalates, and Liquid-Phase Catalytic Oxidation

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Received August 3, 2009

In this Forum Article, we discuss the use of dioxygen (O_2) in oxidations catalyzed by polyoxometalates. One- and two-electron-transfer oxidation of organic substrates is catalyzed by $H_5PV_2Mo_{10}O_{40}$ and often occurs via an outer-sphere mechanism. The reduced polyoxometalate is reoxidized in a separate step by O_2 with the formation of water. $H_5PV_2Mo_{10}O_{40}$ also catalyzes electron transfer−oxygen transfer reactions. Here, in contrast to the paradigm that high-valent oxo species are often stronger oxygen-transfer species than lower-valent species, the opposite occurs. Thus, oxygen transfer from the catalyst is preceded by electron transfer from the organic substrate. The monooxygenase-type reduction of O_2 with polyoxometalates is also discussed based on the formation of a stable iron(III) hydroperoxide compound that may have implications for the oxidation of other lower-valent polyoxometalates such as vanadium(IV)- and ruthenium(II)-substituted polyoxometalates. Finally, the formation of hybrid compounds through the attachment of electron-accepting polyoxometalates to coordination compounds can modify the reactivity of the latter by making higher-valent oxidation states more accessible.

Introduction

Our interest over the last 20 years in the activation of molecular oxygen has been curiosity driven by a desire to understand the mechanistic complexities of the utilization of ground-state dioxygen (O_2) together with a more goal-oriented approach that is needed to invent and develop new practical and sustainable catalytic oxidation reactions. The motivation for using inorganic catalysts, such as polyoxometalates, originally also had its applicative appeal because a priori it seemed logical that for eventual efficient catalytic processes inherently stable catalysts that would not be prone to self-oxidation would be needed. However, as will be shown, polyoxometalates by virtue of their high anionic charge, solubility, redox properties, and diversity of structure have enabled the realization of alternative oxidation mechanisms that can be translated into novel reactivity.

In the context of this Forum, it seems appropriate to comment on how we view the molecular oxygen activation "problem". Thus, from a thermodynamic standpoint, organic compounds tend to combust or overoxidize, finally leading to CO_2 and H_2O. On the other hand, despite the favorable free energy of reaction for hydrocarbon oxidation with O_2, the kinetic activation barrier is high. In the literature, this barrier has been attributed to factors such as the triplet nature of ground-state O_2 that needs to react with singlet organic substrates, the high homolytic and heterolytic disassociation energies of the O−O bond, and the reality that the one electron transfer of O_2 to superoxide has a positive free energy. These thermodynamic and kinetic limitations lead to the ubiquitous autoxidation of organic compounds that is initiated through the thermal or catalytic formation of organic free radicals and typically ends in nonselective product formation.[1] These autoxidation reactions are also mechanistically very complex, involving the interplay of many reactions steps, some still under dispute, with significant rate variability of the various reaction steps as a function of the different reaction parameters.

Because autoxidation reactions tend to be nonselective and free radicals are believed to be toxic and damaging to biological tissue, it is compelling to observe how nature has circumvented the autoxidation "problem" through the development of mostly monooxygenase enzymes for hydrocarbon oxidation.[2] The unifying mechanistic theme of these enzymes is the reductive (two electron−two proton) activation of

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molecular oxygen to yield water and the reactive oxygen-donating species. The use of reducing agents to activate O_2 is therefore energy-intensive and thus also produces waste. Furthermore, the need for reducing agents to attain sufficiently reactive intermediates also highlights the somewhat paradoxical observation that reduced oxygen-containing species such as peroxides (O_2^{2-}) and monooxygen donors and oxo intermediates (O^{2-}) are typically more reactive and selective compared to the more oxidized O_2. Bringing this train of thought further, one may note that, in fact, the key oxidizing species in the propagation of an autoxidation reaction is also the peroxo intermediate $R-O-O^{\bullet}$ formed by the reaction of O_2 with an initially formed radical, $R^{\bullet}$. Against this backdrop of the prevalence of autoxidation, on the one hand, and the need for additional reducing agents for monoxygenase-type reactivity, on the other hand, we have looked to alternative approaches for O_2 activation based on electron transfer, electron transfer−oxygen transfer (ET−OT) oxidation, and other mechanisms to be discussed below.

Although the area of polyoxometalate chemistry can be defined by a large diversity of structural types, including Keggin, Wells−Dawson, Lindqvist, Anderson, and various "sandwich" structures among many others,[3] surprisingly few compounds have been utilized in oxidation catalysis and even fewer in oxidation with O_2. In fact, if one does not consider reactions with O_2 that proceed by autoxidation, only very few polyoxometalates, to be discussed below, have been used for such oxidation reactions.

$H_5PV_2Mo_{10}O_{40}$ Polyoxometalate and Electron-Transfer Oxidations

The one- or two-electron-transfer oxidation of organic substrates, also called catalytic oxidase or alternatively catalytic dehydrogenation reactions, is synthetically useful for a variety of transformations. Oxidase-type catalysis[4] can also be mediated by polyoxometalates. About 25−30 years ago, a team of researchers headed by Matveev and Kozhevnikov demonstrated that $H_{3+x}PV_xMo_{12-x}O_{40}$ (x = 1−6) phosphovanadomolybdate Keggin-type compounds could be used as cocatalysts in place of copper salts in palladium-catalyzed oxidations.[5] Since then, the most often used polyoxometalate for catalytic electron-transfer oxidation has been based on the acidic polyanion containing two vanadium atoms, $H_5PV_2Mo_{10}O_{40}$. $H_5PV_2Mo_{10}O_{40}$ has the α-Keggin structure,[6] wherein a central phosphate moiety is surrounded by 12 molybdenum and vanadium addenda that are arranged as four M_3O_9 triads loosely connected to the four corners of the tetrahedral phosphate. In their orange-colored oxidized forms, all of the addenda metals have empty d orbitals and have tetragonally distorted octahedral coordination spheres. The inseparable five positional isomers of $H_5PV_2Mo_{10}O_{40}$ along with some bond lengths are presented in Figure 1.

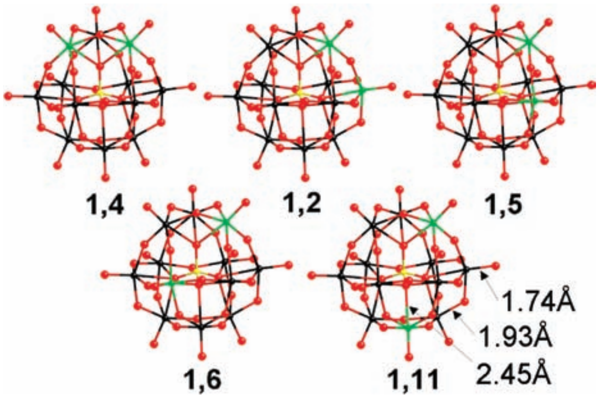

Figure 1. Isomers of $H_5PV_2Mo_{10}O_{40}$ with key bond lengths.

Scheme 1. Redox Transformation of Substrates by $H_5PV_2Mo_{10}O_{40}$

$$SH_2 + [PV^{V}{}_2Mo_{10}O_{40}]^{5-} \longrightarrow S + 2\,H+ + [PV^{IV}{}_2Mo_{10}O_{40}]^{7-}$$

$$2\,H^+ + [PV^{IV}{}_2Mo_{10}O_{40}]^{7-} + 1/2\ O_2 \longrightarrow [PV^{V}{}_2Mo_{10}O_{40}]^{5-} + H_2O$$

The earlier research and the more synthetic applications carried out in our laboratory connected with $H_5PV_2Mo_{10}O_{40}$-catalyzed reactions have been discussed in previous reviews.[7] Here, we only discuss the more mechanistically important observations and conclusions. The basic unifying scheme for these reactions is a two-stage redox reaction (Scheme 1) where in the first step a substrate, generically written as SH_2, reacts with the oxidized polyoxometalate $H_5PV^{V}{}_2Mo_{10}O_{40}$ to yield an oxidized product, S, and a reduced polyoxometalate, $H_6PV^{IV}V^{V}Mo_{10}O_{40}$ or $H_7PV^{IV}{}_2Mo_{10}O_{40}$, through proton-coupled, one or two electron transfers. In the second step, the reduced polyoxometalate, which has a signature green to blue color depending on the degree of reduction, is reoxidized by O_2 to yield water.

The oxidation potential of $H_5PV^{V}{}_2Mo_{10}O_{40}$ is 0.7 V vs normal hydrogen electrode (NHE) so it was not surprising that for the oxidative dimerization of a series of phenols to selectively yield diphenoquinones was linearly correlated with the oxidation potential of the substrate pointing to an electron-transfer rate-determining step in the reaction (Chart 1).[8]

Similarly, $H_5PV_2Mo_{10}O_{40}$ catalyzed the oxidative dimerization of a series of alkylated anisole substrates. The observed reactivity was 4-ethylanisole > 4-isopropylanisole > 4-methylanisole.[9] This is in line with the expected relative reaction rates (2° > 1° > 3° or 2° > 3° > 1°), whereas for hydrogen-atom-transfer reactions, it is always found that the relative rate of reactivity is 3° > 2° > 1°, which is a function of the C−H bond dissociation energy.[10]

A more definitive early study was carried out on the oxidative dehydrogenation of α-terpinene to *p*-cymene.[11]

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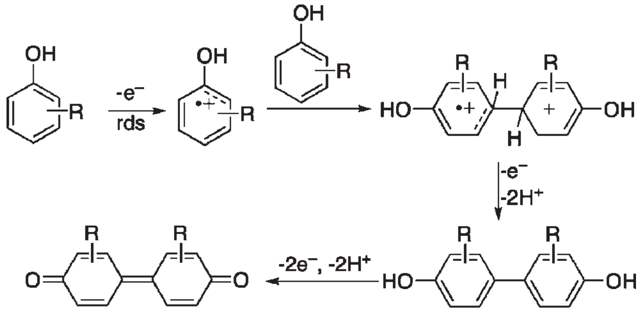
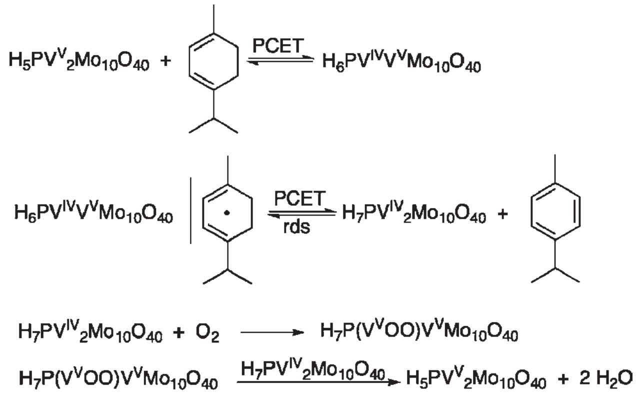
Chart 1. Proposed Pathway for Oxidative Dimerization



Substrate	Conversion,mol%	Oxidation Potential, V
3,5-dimethyl	~0	0.86
2,5-dimethyl	50	0.82
2,6-dimethyl	80	0.76
2,6-di-t-butyl	~100	0.69

Scheme 2. Mechanism for the Aerobic Oxydehydrogenation of α-Terpinene Catalyzed by $H_5PV_2Mo_{10}O_{40}$



Using UV−vis spectrometry, it was shown that the reaction between α-terpinene and $H_5PV^V{}_2Mo_{10}O_{40}$ was an equilibrium redox reaction that yielded an α-terpinene radical−$[PV^{IV}V^VMo_{10}O_{40}]^{6-}$ ion pair intermediate through a proton-coupled electron transfer (PCET) reaction that was observable by electron paramagnetic resonance (EPR) spectroscopy. In this case, as supported by kinetic measurements, the rate-determining step involved an additional PCET reaction to yield the *p*-cymene product and reduced $H_7PV^{IV}{}_2Mo_{10}O_{40}$. In the catalyst reoxidation step, the reaction was second-order in the polyoxometalate and first-order in O_2. This, together with some IR evidence indicating the formation of a peroxo intermediate, led to the proposal that one molecule of O_2 reacted with two molecules of reduced $H_7PV^{IV}{}_2Mo_{10}O_{40}$ to yield two molecules of water and the reoxidized catalyst $H_5PV^V{}_2Mo_{10}O_{40}$ in a *four*-electron oxidation. There was no evidence of the formation of hydrogen peroxide from oxygen in a possible two-electron oxidation. The mechanism proposed at the time is summarized in Scheme 2.

Quite a few salient properties of $H_5PV_2Mo_{10}O_{40}$ need to be emphasized that are specifically very relevant to these electron-transfer reactions.

$H_5PV_2Mo_{10}O_{40}$ is a strong Brønsted acid, and therefore acid cocatalysis needs to be considered where applicable. The acidic form of $[PV_2Mo_{10}O_{40}]^{5-}$ is a considerably stronger oxidant compared to when the cation is a quaternary ammonium salt, alkali metal, or others. The presence of a proton as a countercation is critical also for the oxidation of $H_7PV^{IV}{}_2Mo_{10}O_{40}$ with O_2 to water (Scheme 1). Under nonacidic conditions, this oxidation is very sluggish.[12] In cases where nonacidic catalysts have been used, for example, in the oxidation of benzylic alcohols and primary amines by $Na_5PV_2Mo_{10}O_{40}$ supported on carbon,[13] it was later discovered that the carbon support was not innocent and acted in concert with the polyoxometalate in the oxidation reaction likely through the formation of semiquinone−polyoxometalate species that were the active oxidizing agents.[14]

The $H_5PV_2Mo_{10}O_{40}$ polyoxometalate is uniquely reactive compared to the $H_4PVMo_{11}O_{40}$ compound and especially compared to $H_3PMo_{12}O_{40}$ even though the latter have similar oxidation potentials. This is mostly associated with the much faster reoxidation of reduced $H_7PV^{IV}{}_2Mo_{10}O_{40}$ with O_2. $H_6PV_3Mo_9O_{40}$ and more highly vanadium-substituted analogues are also excellent electron-transfer oxidants; however, they are significantly less stable, making $H_5PV_2Mo_{10}O_{40}$ the practical catalyst of choice. Computation has shown that free-energy one-electron reduction of $[PV_2Mo_{10}O_{40}]^{5-}$ to $[PV_2Mo_{10}O_{40}]^{6-}$ is equivalent for all isomers, whereas for two-electron reduction to $[PV_2Mo_{10}O_{40}]^{7-}$, there are differences between distal vanadium isomers (1,6 and 1,11) and vicinal isomers (1,2, 1,4, and 1,5).[15] The computations also show that the structure of the polyoxometalate remains unchanged upon reduction. Some preliminary experimental work described below, however, suggests a more complicated situation that still will need to be investigated.

Under temperate conditions, $H_5PV_2Mo_{10}O_{40}$ typically acts as an antioxidant by either electron-transfer oxidation of radicals to form cations (see also below) or prevention of the propagation cycle of autoxidation. Thus, organic radicals formed via PCET and observable as stable intermediates, for example, the α-terpinene radical mentioned above, do not react with O_2 to yield oxygenated products but rather are dehydrogenated via a further PCET reaction.[11] Similarly, compounds very susceptible to autoxidation with reactive benzylic C−H bonds, for example, tetralin and xanthene, do not undergo autoxidation in the presence of $H_5PV_2Mo_{10}O_{40}$. This antioxidant property of $H_5PV_2Mo_{10}O_{40}$ has been utilized also in the high-temperature epoxidation of alkenes.[16] Thus, it is known that silver supported on alumina is an effective catalyst for the high-temperature aerobic epoxidation of alkenes without allylic C−H bonds, such as ethane, but when used for the epoxidation of propene, selectivity to the epoxide product is very low. Stabilization of silver and also ruthenium colloids with $H_5PV_2Mo_{10}O_{40}$ and then their support on alumina yielded catalysts that were highly selective for epoxidation of terminal alkenes such as 1-octene but also cyclic alkenes such as 1-methylcyclohexene. Over time, however, at the high temperatures used, autoxidation became a side reaction.

As noted above, the oxidation potential of $H_5PV_2Mo_{10}O_{40}$ is about 0.7 V vs NHE as measured by cyclic voltammetry.

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This raises the question, how is it thermodynamically possible for $H_5PV_2Mo_{10}O_{40}$ to oxidize substrates by electron transfer such as α-terpinene and others that have an oxidation potential that is higher than 1.3 V? The difference between the oxidation potentials of $H_5PV_2Mo_{10}O_{40}$ and the organic substrates excludes the possibility of an inner-sphere electron transfer. Correction of the free energy, ΔG°, under prevailing reaction conditions using the Marcus theory[17] can give the corrected free-energy value, $\Delta G^{\circ\prime}$:

$$\Delta G^{\circ\prime} = \Delta G^\circ + \frac{331.2B}{r_{12}D}(Z_1 - Z_2 - 1) \quad \text{where } B = 10^{-21.9 r_{12}\sqrt{\mu/DT}}$$

At a null ion strength, $\mu = 0$, $B = 1$, and thus $\Delta G^{\circ\prime}$ is a function of (i) the radius $r_{12} = 7.3$ Å derived from $r_1 + r_2 = 5.6$ Å ($H_5PV_2Mo_{10}O_{40}$)+1.7 Å (assuming side-on interaction between the polyoxometalate and the aromatic ring), (ii) the dielectric constant, D, of the solvent (for acetonitrile $D = 35$, and, most importantly, (iii) the charge of the polyoxometalate oxidant ($Z_1 = -5$) and substrate or reductant ($Z_2 = 0$). The calculations show the very strong positive influence of the negative charge of the polyoxometalate on $\Delta G^{\circ\prime}$. Therefore, the inherent anionic nature of the polyoxometalates is advantageous to their activity as electron-transfer oxidants.

In general, the free-energy values, both ΔG° and $\Delta G^{\circ\prime}$ vs $\Delta G^\ddagger$, appear to support an outer-sphere electron transfer, as opposed to an inner-sphere process, for activation of hydrocarbons by $H_5PV_2Mo_{10}O_{40}$. It should be pointed out that the kinetic analysis of the reaction of polyoxometalates with electron donors may be complicated by the effects of the ionic strength, ion pairing between the polyoxometalate and any cations in the solution, and formation of stable complexes between the polyoxometalate and the electron donor (hydrocarbon). In fact, further analysis based on the Marcus theory would indicate that there is preassociation between the polyoxometalate and the hydrocarbon substrate prior to electron transfer.[9]

It should be noted also that the oxidation potential of O_2 to water is 1.23 V, sufficient to reoxidize reduced $H_7PV^{IV}{}_2Mo_{10}O_{40}$ to $H_5PV_2Mo_{10}O_{40}$ to water by either an inner-sphere or outer-sphere mechanism. In this context, it is telling that as yet we have not found a polyoxometalate of higher oxidation potential that is capable of oxidizing more demanding substrates, on the one hand, and still be reoxidized by O_2 under temperate conditions.

ET−OT Reactions

As noted in the Introduction, monooxygenase-type activation of O_2, for example, with iron-based enzymes, takes places in the presence of reducing equivalents. The general paradigm in these and also many other systems (dioxygenases, copper-based enzymes, and so forth) is that the more reactive species are higher-valent metal−oxygen species. This mechanistic paradigm is summarized in a very simplified form in Scheme 3.

Because such transformations require the addition of wasteful reducing reagents, we are interested in the development of an alternative monooxygenase approach, summarized in Scheme 4. In such a reaction scheme, there are three steps. In the first step, electron transfer or PCET events from the substrate to the catalyst supply the eventual reducing equivalents and protons needed for the eventual reductive activation of O_2 to yield a higher-valent metal−oxygen species and water (step 3). Critically, however, in step 2, the *more reduced* metal−oxygen species is the reactive oxygen-transfer intermediate rather than the higher-valent analogue. As such, these types of mechanisms can be described as an ET−OT mechanism or in certain cases also as a PCET−oxygen transfer (PCET−OT) mechanism. Such types of oxidation can be typically relevant for oxidations involving C−H bond activation, e.g., hydroxylation, but probably not reactions such as the epoxidation of alkenes.

Scheme 3. Reductive Activation of O_2 and Oxygen Transfer via Higher-Valent Metal−Oxygen Species

$$M + O_2 + 2e^- + 2H^+ \longrightarrow M^{2+}{=}O + H_2O$$

$$M^{2+}{=}O + R \longrightarrow M + RO$$

Scheme 4. ET−OT Mechanism for O_2 Activation and Substrate Oxygenation

$$RH_2 + M{=}O \longrightarrow R + 2H^+ + M^{2-}{=}O$$

$$M^{2-}{=}O + R \longrightarrow M^{2-} + RO$$

$$M^{2-} + O_2 + 2H^+ \longrightarrow M{=}O + H_2O$$

In the oxidation literature, such ET−OT mechanisms have been known for many years in (very) high-temperature gas-phase oxidation reactions heterogeneously catalyzed by mixed-metal transition- and main-metal oxides.[18] Some of the most important examples of such reactions that occur via what is also called the Mars−van Krevelen mechanism are the oxidation of propene to acrolein, the oxidation of butane or benzene to maleic anhydride, and the oxidation of *o*-xylene or naphthalene to phthalic anhydride. To the best of our knowledge, such mechanisms had not been described for liquid-phase, low-temperature oxidation reactions. Motivated also by our desire to expand the scope of reactivity of $H_5PV_2Mo_{10}O_{40}$ from oxidative dehydrogenation reactions to oxygenation reactions, we set out to see if $H_5PV_2Mo_{10}O_{40}$ could be applied in ET−OT reactions.

As summarized in Scheme 4, the oxygenation reaction should be initiated by electron transfer or PCET from a reactive substrate to $H_5PV_2Mo_{10}O_{40}$. This requirement led to the use of relatively reactive, that is, lower oxidation potential, substrates such as xanthene (IP = 7.65 eV, OP = 1.45 V vs NHE), anthracene (IP = 7.44 eV, OP = 1.39 V vs NHE), and the like in this research.[9] Notably, xanthene and anthracene have very different C−H bond dissociation energies (75−80 vs ~100 kcal mol^{-1}). When the electron-transfer oxidation of the substrate by $H_5PV_2Mo_{10}O_{40}$ was measured separately, there was a clear correlation of the electron-transfer rate as a function of the ionization potential of the substrate, while there was no such correlation to the C−H bond dissociation energy, providing evidence that the reaction is indeed initiated by electron transfer. In the case of

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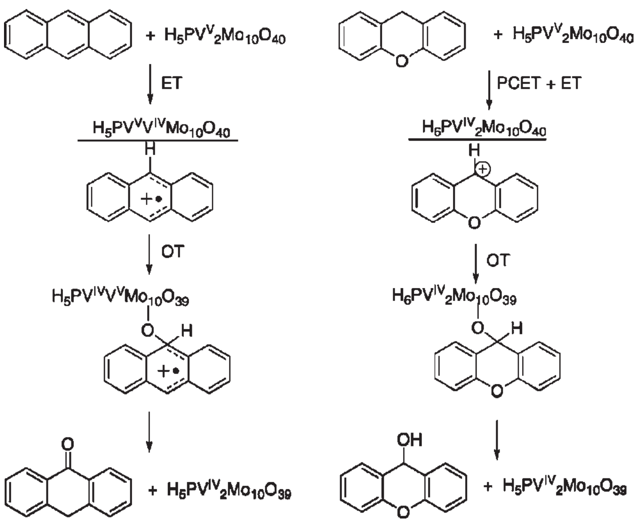
anthracene, the proton-transfer step is slow so that the ion pair $H_5PV^VV^{IV}Mo_{10}O_{40}$–anthracene cation radical may be observed directly by EPR spectrometry including simulation of the spectrum of the anthracene cation radical. On the other hand, in the case of xanthene, the initial electron transfer is coupled to a fast proton transfer and an additional fast electron transfer to yield a $H_5PV^{IV}{}_2Mo_{10}O_{40}$–xanthenyl cation ion pair, which one can directly observe by ^1H NMR because of the stabilization of the xanthenyl cation by the lone pairs of the oxygen in xanthene.

The critical verification of the ET–OT mechanism was by separately probing the oxygen-transfer step from ^{18}O-labeled $H_5PV_2Mo_{10}O_{40}$ by both IR spectroscopy of $H_5PV_2Mo_{10}O_{40}$ and mass spectroscopy of the product formed. The direct oxidation of the substrates by O_2 was also discounted by use of $^{18}O_2$. Kinetic experiments supported also by deuterium-isotope-labeling experiments showed that the oxygen-transfer step is also the rate-determining step in these reactions. The initial products in the oxidation of anthracene and xanthene are anthrone and xanthenol. However, because these products are 100-fold more reactive that anthracene and xanthene, they are not accumulated in significant amounts. The mechanistic pathways for anthracene and xanthene ET–OT oxidation are summarized in Scheme 5.

An additional example of an ET–OT mechanism is the oxidative C–C bond cleavage of primary alcohols catalyzed by $H_5PV_2Mo_{10}O_{40}$.[19] For example, in the oxidation of 1-butanol under anaerobic conditions and as predicted by the Marcus theory analysis of electron transfer between $H_5PV_2Mo_{10}O_{40}$ and an organic substrate discussed above, an association complex between the polyoxometalate and 1-butanol prior to electron transfer was observed as evidenced by ^{13}C NMR. In this reaction, the electron-transfer step was deduced from the reduction of $H_5PV_2Mo_{10}O_{40}$ and the subsequent oxygen transfer was proven by isotope incorporation into the products from ^{18}O-labeled $H_5PV_2Mo_{10}O_{40}$. Kinetic experiments yielded a low $\Delta S_{338}^{\ddagger} = -47.2$ cal mol^{-1} K^{-1} indicative of a highly ordered transition state in the rate-determining step. Reaction also with deuterium-labeled 1-butanol and the α and β positions showed that C–H bond cleavage was not involved in the rate-determining step either. The data assembled led to a mechanistic proposition, as presented in Scheme 6. It should be emphasized that the initial aldehyde formed in these reactions is not observed. Instead, under the acidic conditions used, it has been surmised that hemiacetals or perhaps acetals are formed through the reaction of the aldehyde product and the alcohol substrate that are oxidized in situ to the corresponding esters. Therefore, for example, for 1-butanol, butyl propionate and butyl formate were formed in 1:1 ratios at high yields.

It should be emphasized here that the ET–OT mechanism, apparently unique to $H_5PV_2Mo_{10}O_{40}$-catalyzed reactions, leads to an atypical oxidation of primary alcohols involving C–C bond cleavage rather than the usual oxidation at the α carbon to yield the corresponding aldehyde and then carboxylic acid. It is also notable that vicinal diols react in an identical manner.[18] Thus, C–C bond cleavage of 1,2-ethanediol leads to the formation of formaldehyde, which then reacts with excess 1,2-ethanediol to yield 1,3-dioxolane and 2-hydroxyethyl formate.

Scheme 5. Oxidation of Anthracene (Left) and Xanthene (Right) by ET–OT Mechanisms



Another example of a ET–OT mechanism catalyzed by $H_5PV_2Mo_{10}O_{40}$ is the oxidation of CO in the presence of a palladium(0) cocatalyst to yield CO_2.[20] As described above, the electron-transfer and oxygen-transfer stages can be appreciated by the reduction of the polyoxometalate and the formation of labeled CO_2 from labeled substrates. As noted in Schemes 5 and 6, information on the properties of the complexes between the polyoxometalate and the organic substrate can be gained via EPR and NMR spectroscopy. However, these methods do not lead to a direct observation of the key intermediate that leads to the critical oxygen-transfer step. When continuous-wave EPR (CW-EPR) and HYSCORE (hyperfine sublevel correlation) were utilized, X-band EPR measurements allowed the direct spectroscopic observation of two species upon the reduction of $H_5PV_2Mo_{10}O_{40}$ with ^{13}CO in the presence of palladium(0). The major species was determined to be similar to a vanadyl cation that is supported on the polyoxometalate and showed a bonding interaction with ^{13}CO. The data led to the formulation of a proposed pre-oxygen-transfer complex, as shown in Scheme 7.

These EPR techniques also allowed us to differentiate between the structures of the various isomers of $H_5PV_2Mo_{10}O_{40}$ after reduction (Figure 1). In the $H_5PV_2Mo_{10}O_{40}$ isomers that are vicinal, the reduced vanadium center is removed from, but supported on, the polyoxometalate structure, whereas for isomers with vanadium sites in distal positions, the reduced vanadium atom remains incorporated, but somewhat distanced, from the heteroatom (phosphate) core. At least with CO as the substrate, the indication is that oxygen transfer is more likely to occur in reactions catalyzed by $H_5PV_2Mo_{10}O_{40}$ isomers, where the vanadium atoms are nearest neighbors.

In the analysis presented so far, we have not discussed the mechanism of the reaction that completes the catalytic cycle, that is, the reoxidation of the reduced and oxygen-deficient polyoxometalate (Scheme 4, step 3). In principle, several inner-sphere scenarios are possible (Scheme 8).

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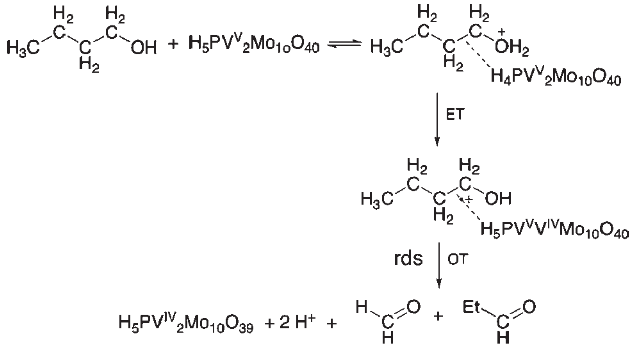
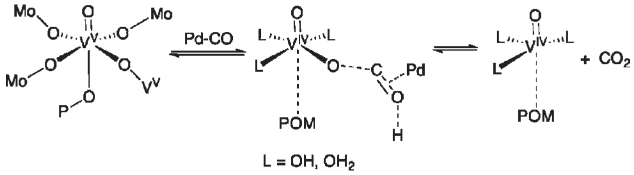
(20) Goldberg, H.; Kaminker, I.; Goldfarb, D.; Neumann, R. *Inorg. Chem.*, in press (http://dx.doi.org/10.1021/ic900868t).

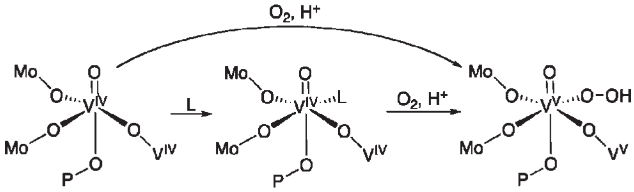
Scheme 6. Mechanistic Pathway for the ET−OT Oxidation of Primary Alcohols That Involves C−C Bond Cleavage in the Rate-Determining Step



Scheme 7. Suggested Pathway for the Activation of CO on $H_5PV_2Mo_{10}O_{40}$ Mediated by Palladium(0)



Scheme 8. Possible Reoxidation Pathways of Reduced $H_5PV^{IV}_2Mo_{10}O_4$



Ligation of water or other solvents at the oxygen-deficient site followed by two-electron oxidation of coordinated O_2 or, alternatively, coordination of O_2 at the oxygen-deficient site and its reduction is shown. Although, to date, hydrogen peroxide has not been observed in such reactions, its formation followed by fast disproportionation is possible. Alternatively, in the presence of an additional reduced polyoxometalate, the intermediate peroxo species could lead to a four-electron oxidation of O_2. Outer-sphere electron-transfer reduction of O_2 is also possible but not considered here.

O_2 Reduction with Transition-Metal-Substituted Polyoxometalates

As stated in the Introduction and the section above, the reaction of O_2 with reduced complexes is a key step in the activation of O_2 and an integral part of catalytic aerobic oxidation cycles. Recently, we have been able to isolate a stable hydroperoxide species through the complexation of O_2 to a multi-iron(II)-substituted polyoxometalate.[21] Thus, the reaction of a brown-black "sandwich"-type polyoxometalate with six iron(II) atoms, $Na_{16}[Fe_4(H_2O)_2(FeW_9O_{34})_2]\cdot 46H_2O$, with O_2 yielded a yellow all-iron(III) polyoxometalate, $Na_{12}[Fe_4(O_2)_2(FeW_9O_{34})_2]\cdot 52H_2O$ of C_{2h} idealized symmetry, with two coordinated and reduced O_2 entities (Figure 2).

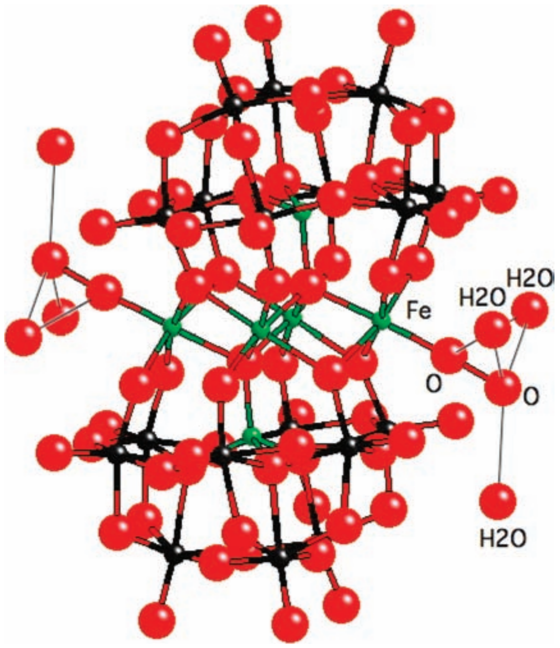


Figure 2. Reductive activation of O_2 with a hexairon-substituted polyoxometalate to yield a hydroperoxide species stabilized by a H_2O hydrogen-bonding network. The crystal was monoclinic ($P2_1/n$).

To the best of our knowledge, this is the first example of an "end-on" iron hydroperoxo species crystallized in a synthetic compound from O_2. These reductively activated O_2 species, described as bound hydroperoxide moieties, are surprisingly highly stable in aqueous solutions at neutral pH. $Na_{12}[Fe_4(O_2)_2(FeW_9O_{34})_2]\cdot 52H_2O$ was accessible because the initial $Na_{16}[Fe_4(H_2O)_2(FeW_9O_{34})_2]\cdot 46H_2O$ is a potential six-electron reducing agent, four of which are required for the reduction of the two-coordinated O_2 moieties to the corresponding hydroperoxides. The key bond characteristics of the two Fe−O−O units, which are the same by symmetry, show standard Fe−O bond lengths of 1.920(5) Å, long O−O bond lengths of 1.612(9) Å, and nearly linear Fe−O−O bond angles of 175.3(4)°. Importantly, from Figure 2, one may observe that the coordinated O_2 is stabilized by a network of hydrogen-bonded water molecules.

It is valuable to note that such hydrogen-bonding stabilization of O_2 complexes is also observed at active sites of enzymes. Although hydroperoxo species, which typically have bond lengths of 1.45−1.55 Å, show longer bond lengths in this case, we proposed that the multiple hydrogen-bonding interactions with water, the high negative charge on the polyoxometalate, and the strong electron-acceptor properties of polyoxometalates all combine to lead to the O−O bond lengths observed. The almost linear Fe−O−O bond angle is unique and is likely also to be a result of the hydrogen-bonding mode that was observed and also repulsive interactions due to the high negative charge of the polyoxometalate. Beyond being stable in water, the hydroperoxoiron(III) polyoxometalate was neither active in oxygen-transfer or electron-transfer oxidation reactions. Instead, it was able to efficiently reduce benzoquinone to hydroquinone with the release of the bound O_2. There is as yet no certain explanation for this observation; however, as we have seen above, polyoxometalates do have a propensity to participate in electron-transfer redox processes, and therefore it is possible that the oxidation potential of benzoquinone is

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(21) Barats, D.; Leitus, G.; Popovitz-Biro, R.; Shimon, L. J. W.; Neumann, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 9908–9912.

sufficient to reduce the hydroperoxoiron(III) polyoxometalate back to an iron(II) species with the release of O_2.

There remains an interesting question on if and how the reaction of O_2 with the iron(II)-substituted polyoxometalate relates to the reaction of O_2 with reduced $H_7PV^{IV}{}_2Mo_{10}O_{40}$ or $H_5PV^{IV}{}_2Mo_{10}O_{39}$. Our present working hypothesis still to be verified is that the O_2 chemistry should be similar. The presence of two electrons is sufficient for O_2 reduction to a peroxo species, and such species may have been observed by IR spectroscopy in the past. However, the reaction conditions used in $H_5PV_2Mo_{10}O_{40}$-catalyzed reactions are more acidic and thus lead to different eventual outcomes.

In the past, we have also investigated the interaction of a ruthenium-substituted "sandwich"-type polyoxometalate with molecular oxygen.[22] In the UV−vis spectrum, a peak at 295 nm, attributable to a ligand-to-metal charge-transfer (LMCT) peak, was observed. A similar peak at 326 nm was associated with the LMCT of the Fe−O−O group in the iron polyoxometalate complex described above. IR spectroscopy also suggested the complexation of O_2 and probable further reaction to yield peroxo species or oxo species, through a comparison of the spectra of complexes prepared from $^{16}O_2$ and $^{18}O_2$. Based also on the observations that (i) in aerobic catalytic oxidations adamantane yielded only 1-adamantanol and no 2-adamanatanol or 2-adamantanone, (ii) the reactions were not inhibited by free-radical inhibitors, (iii) the reaction stoichiometry was consistent with 2 equiv of 1-adamantanol per 1 equiv of O_2, (iv) aerobic oxidation of *trans*-cyclooctene yielded mainly *trans*-cyclooctene oxide, (v) no water formation was observed in the reaction, and (vi) stoichiometric reactions of the ruthenium polyoxometalate activated with O_2 yielded epoxides from alkenes, we proposed that the ruthenium-substituted polyoxometalate activates O_2 by a dioxygenase mechanism and that autoxidation was strongly or completely inhibited. In such a mechanism, the initial complexation of O_2 to a ruthenium(II) site leads to the formation of a Ru−O−O−Ru dimer followed by the eventual formation of two ruthenium(IV) oxo species active in oxygen transfer.

More recently, this work has been disputed, with the main statements that the authors were (a) unable to reproduce the polyoxometalate synthesis and (b) the ruthenium polyoxometalate compound obtained is an autoxidation catalyst.[23] These contradictory results have led us to begin to revisit our previous research. Although this research is only in its very earliest stages, we have again *reproduced* our ruthenium polyoxometalate synthesis. In order to generate new results and further understanding, we are presently studying aerobic oxidation reactions in α,α,α-trifluorotoluene as opposed to the 1,2-dichoroethane solvent used in the previous research by others and ourselves. We have observed that substrates such as cyclohexene and benzaldehyde that are normally very susceptible to autoxidation are stable *without any product formation* over a period of 18 h at 110 °C. On the other hand, a reaction of thioanisole that is not known to react by an autoxidation mechanism [thioanisole (85 μmol) and ruthenium polyoxometalate (0.85 μmol) in 1 mL of α,α,α-trifluorotoluene at 110 °C under 2 bar of O_2 for 18 h yielded the sulfoxide of thioanisole in a 2.6% yield; ∼3 turnovers). It is obviously too early to make any further mechanistic statements beyond what has been previously stated by us concerning the reactivity of the ruthenium polyoxometalate, but hopefully future research will resolve the conflicting reports.

Metallorganic−Polyoxometalate Hybrid Complexes for O_2 Activation

One of the limitations of low-temperature electron-transfer and ET−OT oxidations catalyzed by the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate is its perhaps limited range for aerobic oxidation. Thus, interesting and valuable transformations involving C−H bond activation such as alkane oxygenation and alkane dehydrogenation under temperate conditions remain beyond reach because the oxidation potential of $H_5PV_2Mo_{10}O_{40}$ is insufficient for electron-transfer oxidation. We have therefore reasoned that mostly the electron-accepting properties and perhaps also the steric bulk of the polyoxometalates may significantly affect the catalytic properties of a metallorganic center to which one attaches a polyoxometalate to form a hybrid metallorganic−polyoxometalate complex. More specifically, it was thought that higher oxidation states, normally inaccessible, might become so in the presence of a conjugate polyoxometalate. Moreover, because modification of polyoxometalates by organic entities has been known for quite some time and various synthetic aspects of the preparation of metallorganic−polyoxometalate binary compounds have been worked out,[24] we decided to test the aforementioned hypothesis that higher oxidation states of coordination compounds might be attainable in the presence of a conjugate polyoxometalate.[25] As proof of principle for the electronic effects of a polyoxometalate on a coordination compound, we covalently attached a Keggin-type polyoxometalate to a metallosalen center via two propyl spacers. NMR, EPR, UV−vis, and X-ray photoelectron spectroscopy measurements clearly showed that the metallosalen was in an oxidized state relative to the control, nonmodified metallosalen analogue. Thus, for example, instead of obtaining a usual Mn^{III}salen species, modification of the metallosalen with the polyoxometalate led to the formation of a more oxidized Mn^{IV}salen polyoxometalate or Mn^{III}salen cation-radical polyoxometalate compound. Similar more oxidized nickel, cobalt, and palladium salen compounds were obtained upon attachment of a polyoxometalate to the ligand.

An interesting goal in the area of alkane oxidation is the oxidation of methane to methanol. One of the interesting concepts in this area is the use of platinum(II) species to catalyze this reaction. Originally, Shilov and co-workers demonstrated such a methane oxidation using platinum(IV) as the stoichiometric oxidant.[26] Later on, it was shown that

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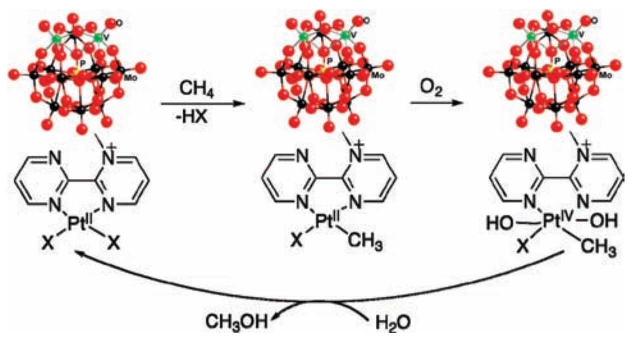
Scheme 9. Aerobic Oxidation of Methane to Methanol Catalyzed by a Platinum(II) Methylbipyridiminium−$H_5PV_2Mo_{10}O_{40}$ Compound



SO_3 in $>100\%$ H_2SO_4 could replace platinum(IV) as the oxidant to yield methyl sulfate as the product.[27] The previous use of platinum(IV) and SO_3 as oxidants highlights one of the difficulties in the platinum(II)-catalyzed oxidation of methane: the need for a strong oxidant to attain a platinum(IV) intermediate in the catalytic cycle. We hypothesized that perhaps the attachment of a polyoxometalate to a platinum(II) coordination compound could facilitate the formation of a platinum(IV) intermediate and thus lead to the aerobic oxidation of methane (Scheme 9).[28]

Indeed, a binary compound based on an electrostatic interaction between a platinum(II) complex of a methylbiypyrimidinium cationic ligand and the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate, which was supported on silica, did catalyze the aerobic oxidation in water of methane to methanol. In parallel, similar amounts of acetaldehyde were also formed via a C−C coupling reaction. In the formation of methanol, the use of isotope-labeling techniques and chloride nucleophiles showed that the catalytic cycle is consistent with an oxidative nucleophilic substitution of a platinum(IV) methyl intermediate as proposed in the literature. The study also indicated that acetaldehyde formation most likely occurred through the coupling of methane and formaldehyde. Over time, formaldehyde is accumulated and the oxidation of methane stops. Apparently, overoxidation to CO inhibits the catalyst, and, in fact, treating the catalyst with H_2 to reduce CO reactivates the catalyst. Support for the formation of a higher oxidation state platinum compound during the catalytic cycle is also clear from the observation that $H_5PV_2Mo_{10}O_{40}$ is reduced during the reaction and, as presented above, is reoxidized by O_2.

Just recently, we have introduced a new method for the preparation of metallorganic−polyoxometalate compounds by decorating a phenanthroline ligand with a crown ether moiety. In this way, the crown ether can be used to complex a polyoxometalate via induced dipole interactions between the crown ether and the hydronium or alkali-metal cation of a polyoxometalate. The first application of this methodology was the use of a palladium(II) phenanthroline−crown ether−$H_5PV_2Mo_{10}O_{40}$ hybrid complex for the Wacker oxidation of hydrophobic alkenes such as 1-octene to the corresponding methyl ketones.[29] It was shown that the hybrid catalyst was more effective than a mixture of palladium(II) phenanthroline and $H_5PV_2Mo_{10}O_{40}$ for aerobic oxidations; the advantage of the hybrid complex was much more pronounced using nitrous oxide as the oxidant. Also, here the oxidative role of the polyoxometalate was important in the completion of the catalytic cycle.

Conclusions

The principle that guides the use of the most studied phosphovandomolybdate, $H_5PV^{V}_2Mo_{10}O_{40}$, as an oxidation catalyst is that the two-electron-reduced forms, $H_7PV^{IV}_2Mo_{10}O_{40}$ or $H_5PV^{IV}_2Mo_{10}O_{39}$, can be reoxidized by O_2 with coformation of water. In this context, $H_5PV^{V}_2Mo_{10}O_{40}$ is a very versatile oxidation catalyst that can be utilized in electron-transfer oxidations that lead to the formation of dehydrogenation products, such as arenes from dienes, aldehydes from alcohols, and quinones from phenols. Typically, the electron-transfer oxidation of the organic substrate proceeds through an outer-sphere mechanism; the high negative charge of $[PV^{V}_2Mo_{10}O_{40}]^{5-}$ is thermodynamically advantageous in enabling the reaction. $H_5PV^{V}_2Mo_{10}O_{40}$ is also a unique ET−OT catalyst at low temperature and in the liquid phase. In such reactions, the reduction of $H_5PV^{V}_2Mo_{10}O_{40}$ by electron transfer from the organic substrate precedes oxygen transfer from the polyoxometalate to the substrate; the lower-oxidation-state vanadium(IV) oxo species is the potent oxygen-transfer agent, whereas the higher vanadium(V) species is inert. These ET−OT mechanisms lead to unusual reactivity such as the oxidation of primary alcohols by C−C bond cleavage rather than the typical oxidation via C−H bond activation.

$H_5PV^{V}_2Mo_{10}O_{40}$ as an electron acceptor can be further utilized through the formation of coordination compound−$H_5PV^{V}_2Mo_{10}O_{40}$ hybrid catalysts to access higher than "normal" oxidation states of the coordination compound. In this way, attachment by various strategies of $H_5PV_2Mo_{10}O_{40}$ to a coordination compound can lead to effective aerobic oxidations such as the platinum(II) methylbipyridium catalyzed oxidation of methane or the palladium(II) phenanthroline catalyzed ketonization of hydrophobic terminal alkenes to methyl ketones.

The reaction of O_2 with a hexairon(II)-substituted polyoxometalate allows the isolation of iron(III) hydroperoxo moieties stabilized in water by hydrogen bonding with uniquely long O−O bonds and a nearly linear Fe−O−O bond angle. Such a hydroperoxide species was not an effective oxidant but rather was reduced by electron transfer from an oxidant such as benzoquinone. It is surmised that a similar reaction of O_2 with a diruthenium(II)-substituted polyoxometalate can lead to a ruthenium(IV) oxo species via a dioxygenase mechanism.

Acknowledgment. This research has been supported over the years by the Israel Science Foundation, the German−Israeli Project Cooperation (DIP-G7.1), the Minerva Foundation, the European Community, and the Helen and Martin Kimmel Center for Molecular Design. The research described has been carried out by many including most notably Alexander M. Khenkin, Manfred Lissel, Helmut Jansen van de Wal, Michal Levin, Mazal Dahan, Inga Vigdergauz, Avi Rosenberger, Revital Ben-Daniel, Yan Wang, Itsik Bar Nahum, Galia Maayan, Hila Goldberg, Delina Barats, Jessica Ettedgui, Ronit Popovitz-Biro, Linda J. W. Shimon, Lev Weiner, Gregory Leitus, Hagai Cohen, and Leonid Konstantinovski. R.N. is the Rebecca and Israel Sieff Professor of Organic Chemistry.

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