kcal/mol)[25] by ~45 kcal/mol, as is silane (372.2 kcal/mol)[21] than methane (416.8 kcal/mol).[21] This trend reflects the greater ability of the silicon radical to stabilize the negative charge, as is indicated by the 31 kcal/mol higher electron affinities of $CH_2{=}SiH$ (46.4 ± 0.2 kcal/mol) than $CH_2{=}CH$ (15.4 ± 0.6 kcal/mol)[25] and of SiH_3 (32.4 ± 0.3 kcal/mol)[6,9] than CH_3 (1.8 ± 0.7 kcal/mol).[26]

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A Single Model Displaying All the Important Centers and Processes Involved in Catalysis by Molybdoenzymes Containing $[Mo^{VI}O_2]^{2+}$ Active Sites

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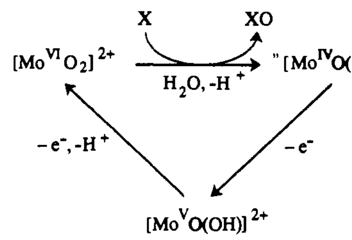
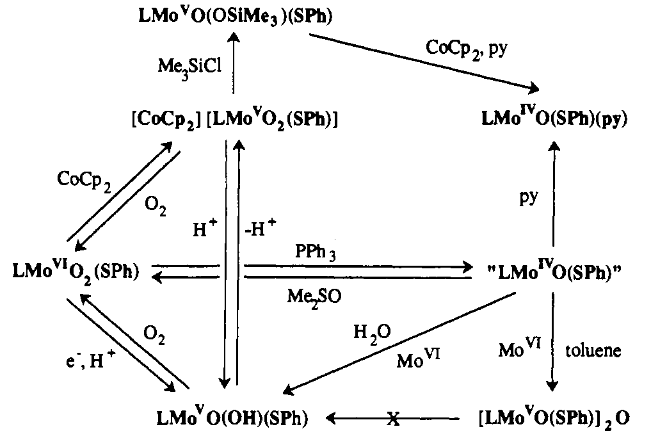
The molybdopterin enzymes catalyze a variety of two-electron redox reactions involving net exchange of an oxygen atom between substrate and water.[1-4] EPR studies[3] support the regeneration of the active site by two one-electron processes, the first of which produces transient Mo^V states. Many of these enzymes feature $[Mo^{VI}O_2]^{2+}$ resting centers, and Scheme I presents a minimal catalytic cycle, based upon current physical and chemical evidence, for an enzyme such as sulfite oxidase.[1-4] In this and similar systems, transfer of the oxygen atom from Mo to substrate and its replacement from water appear to occur in the Mo^{VI} to Mo^{IV} transformation.[4-6]

Scheme I



Scheme II



No single model system which incorporates all of the species and processes shown in Scheme I has been described. Oxygen-atom-transfer reactions which interconvert $[Mo^{VI}O_2]^{2+}$ and $[Mo^{IV}O]^{2+}$ centers are well-established.[4,7,8] In contrast, the regeneration of a $[Mo^{VI}O_2]^{2+}$ center by two *one-electron* processes initiated on a $[Mo^{IV}O(X)]^{n+}$ (X = OH^- or H_2O from water) center has not been demonstrated. Progress in ligand design has been able to inhibit the condensation of mononuclear Mo^V ($4d^1$) species[7-12] and has allowed characterization of the enzymatically relevant $[Mo^VO_2]^+$ and $[Mo^VO(OH)]^{2+}$ centers in solution.[11,12] However, a combination of redox potentials and reaction rates which allows observation of the full cycle has not been found to date. This communication reports that a model based upon $LMo^{VI}O_2(SPh)$ [L = hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion] has that necessary combination: observed reactions are outlined in Scheme II. The facially tridentate pyrazolylborate ligand inhibits dinucleation and restricts chemistry to the remaining facial sites; an accurate model of the crucial oxo–ligand based chemistry taking place at the enzyme active site is thereby facilitated. In addition, a $[Mo^VO_2]^+$ center has been isolated in substance for the first time.

Brown $LMo^{VI}O_2(SPh)$ is produced conveniently from the reaction of $LMoO_2Br$, HSPh, and NEt_3 in dichloromethane.[13] In DMF or MeCN, oxygen atom abstraction by PPh_3[8] leads to an intermediate which behaves as if it were coordinatively-unsaturated $LMo^{IV}O(SPh)$ or weakly solvated $LMo^{IV}O(SPh)(solvent)$. It can be trapped as $LMo^{IV}O(SPh)(py)$ in pyridine (85% yield) or, oxidatively, as mononuclear $LMo^VOCl(SPh)$ in CH_2Cl_2 (52% yield) or as binuclear $[LMo^VO(SPh)]_2O$ in dry toluene (13% yield). Unreacted $LMo^{VI}O_2(SPh)$ is the source of oxidizing equivalents in the latter case:

$$\text{“}LMo^{IV}O(SPh)\text{”} + LMo^{VI}O_2(SPh) \rightarrow [LMo^VO(SPh)]_2O$$

Addition of Me_2SO to the Mo^{IV} complexes above regenerates $LMoO_2(SPh)$ in greater than 90% isolable yield.

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(13) A solution of $LMoO_2Br$ (0.5 g, 1.0 mmol) in dry, deoxygenated dichloromethane (30 mL) was treated with a solution of HSPh (0.22 mL, 2.0 mmol) and NEt_3 (0.55 mL) in toluene (2 mL), and the mixture was stirred for 2 h. After reducing the volume of solvent, the mixture was column chromatographed (silica/dichloromethane), and the first brown band was collected and evaporated to dryness. The residue was recrystallized from dichloromethane/methanol to give $LMoO_2(SPh)$ (yield 0.48 g, 91%) with spectroscopic properties identical to those previously reported.[8]

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However, in wet tetrahydrofuran or toluene, the reaction takes a different course: $\mathrm{LMo^{V}O(OH)(SPh)}$ is detected directly via its EPR spectrum (g, 1.953; $a(^{95,97}\mathrm{Mo})$, 43.3×10^{-4} cm^{-1}; $a(^{1}\mathrm{H})$, 13.1×10^{-4} cm^{-1} in toluene; cf. refs 11 and 12). This species cannot be generated from preformed $\mathrm{[LMo^{V}O(SPh)]_2O}$ under the same conditions, and the reaction would appear to involve an intermediate aquo–Mo(IV) complex:

$$\mathrm{LMo^{IV}O(OH_2)(SPh) + LMo^{VI}O_2(SPh) \rightarrow 2LMo^{V}O(OH)(SPh)}$$

Certainly, $\mathrm{LMo^{V}O(OH)(SPh)}$ can be trapped oxidatively as $\mathrm{LMo^{VI}O_2(SPh)}$ with $\mathrm{O_2}$ in 85% isolated yield. Water, not dioxygen, is the source of the oxo ligand: use of $\mathrm{H_2{}^{18}O}$ (95 atom % ^{18}O) under anaerobic conditions with a prolonged incubation at the $\mathrm{Mo^{V}}$ level followed by admission of $^{16}\mathrm{O_2}$ provides material enriched with 80 atom % ^{18}O.[14] Use of $\mathrm{H_2{}^{17}O}$ (51.5 atom % ^{17}O) leads to clearly resolved ^{17}O structure in the EPR spectrum of the $\mathrm{LMo^{V}O(OH)(SPh)}$ intermediate ($a(^{17}\mathrm{O})$, ca. 7×10^{-4} cm^{-1}; cf. ref 15). The two-electron $\mathrm{Mo^{VI}}$ to $\mathrm{Mo^{IV}}$ step is slower than the one-electron $\mathrm{Mo^{IV}}$ to $\mathrm{Mo^{V}}$ step preventing direct access to the putative $\mathrm{LMo^{IV}O(OH_2)(SPh)}$ intermediate. In the presence of dioxygen and an excess of $\mathrm{PPh_3}$, production of $\mathrm{OPPh_3}$ is catalytic in Mo. Initial experiments indicate that at least 100 turnovers are possible with 98% isolated yields of $\mathrm{OPPh_3}$.[16]

We have also achieved the first isolation of a dioxo–Mo(V) complex by the one-electron reduction of $\mathrm{LMoO_2(SPh)}$. Estimates of the relevant one-electron couples in MeCN suggested that the right-hand side is favored in the following equilibrium:

$$\mathrm{LMo^{VI}O_2(SPh) + CoCp_2 \Leftrightarrow [LMo^{V}O_2(SPh)]^- + [CoCp_2]^+} \qquad K,\ \text{ca. } 10^3$$

In acetonitrile, mixing of the reactants on the left-hand side leads to the rapid precipitation of green, microcrystalline, air-sensitive $\mathrm{[CoCp_2][LMo^{V}O_2(SPh)]}$ (Cp = η^5-$\mathrm{C_5H_5^-}$).[17] Isotope (^{18}O) labeling studies unambiguously identify a strong ν(MoO) band at 767 cm^{-1} in the anion and provide evidence for a second ν(MoO) band at 864 cm^{-1}, the assignment of which is complicated by interfering $\mathrm{[CoCp_2]^+}$ and $^{-}$SPh bands. These values are extremely low in energy relative to those observed in $\mathrm{LMo^{VI}O_2(SPh)}$ (922 and 889 cm^{-1}) and are consistent with the weakening of the Mo–O bonds expected due to population of the three-center π^* component of a *cis*-$\mathrm{MoO_2}$ bonding scheme. In MeCN, cyclic voltammetry reveals the separate and characteristic $\mathrm{Mo^{VI}O_2/Mo^{V}O_2}$ and $\mathrm{[CoCp_2]^+/CoCp_2}$ couples associated with the component ions.

Dissolution of $\mathrm{[CoCp_2][LMo^{V}O_2(SPh)]}$ in $\mathrm{CH_2Cl_2}$ at room temperature initially produces a broad EPR signal (g, 1.920; $a(^{95,97}\mathrm{Mo})$, 41×10^{-4} cm^{-1}; $W_{1/2}$, 1 mT) characteristic of $\mathrm{[Mo^{V}O_2]^+}$ centers.[11,12] Over time, the signal is replaced by that of the conjugate acid $\mathrm{LMo^{V}O(OH)(SPh)}$ via reaction with trace $\mathrm{H_2O}$. Upon freezing this solution at 77 K, the highly anisotropic spectrum of $\mathrm{[LMo^{V}O_2(SPh)]^-}$ (g values; 1.991, 1.931, 1.843) appears, presumably due to the equilibrium being shifted toward the conjugate base by freezing out of $\mathrm{H_2O}$.

Dioxygen rapidly and quantitatively oxidizes $\mathrm{[LMo^{V}O_2(SPh)]^-}$ to $\mathrm{LMo^{VI}O_2(SPh)}$. Reaction of $\mathrm{[LMo^{V}O_2(SPh)]^-}$ with $\mathrm{Me_3SiCl}$ produces $\mathrm{LMo^{V}O(OSiMe_3)(SPh)}$ in 92% isolated yield. When these reactions are performed on ^{18}O labeled anion *there is no significant loss of the label in the products*. The related $\mathrm{LMo^{V}O(OSiMe_3)(SCH_2Ph)}$ complex may be similarly produced and has been characterized by X-ray crystallography.[18] In turn, $\mathrm{LMoO(OSiMe_3)(SPh)}$ can be reduced to $\mathrm{LMo^{IV}O(SPh)(py)}$ (Scheme II) by reaction with $\mathrm{CoCp_2}$. Notably, we have been unable to observe any two-electron (i.e., oxygen atom transfer) chemistry with $\mathrm{[LMo^{V}O_2(SPh)]^-}$. This may be the reason that $\mathrm{[Mo^{V}O_2]^+}$ centers have never been detected during enzyme turnover.

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(14) Under anaerobic conditions, tetrahydrofuran (10 mL) and $\mathrm{H_2{}^{18}O}$ (0.16 mL, 9.0 mmol, 95 atom % ^{18}O) were added to a mixture of $\mathrm{LMoO_2(SPh)}$ (0.240 g, 0.45 mmol) and $\mathrm{PPh_3}$ (0.062 g, 0.24 mmol). After stirring for 7 h, $^{16}\mathrm{O_2}$ was bubbled through the solution which rapidly turned from dark-green to dark-brown in color. Column chromatography (silica/toluene in air) yielded a major dark brown fraction, which was collected and evaporated to dryness. Recrystallization from $\mathrm{CH_2Cl_2/MeOH}$ gave a 76% yield of 80 atom % ^{18}O-enriched $\mathrm{LMoO_2(SPh)}$ (enrichment estimated by simulation of EI mass spectra). The infrared spectrum of the sample exhibited at least six bands and shoulders assignable to the $^{16}\mathrm{O}^{16}\mathrm{O}$, $^{18}\mathrm{O}^{16}\mathrm{O}$, and $^{18}\mathrm{O}^{18}\mathrm{O}$ isotopomers.

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(16) A mixture of $\mathrm{LMoO_2(SPh)}$ (0.05 g, 0.094 mmol) and $\mathrm{PPh_3}$ (2.45 g, 9.4 mmol) in tetrahydrofuran (20 mL) and water (0.34 mL, 20 mmol) was stirred at 40 °C while being continuously purged with oxygen. Thin-layer chromatography revealed the quantitative conversion of $\mathrm{PPh_3}$ to $\mathrm{OPPh_3}$ after 10 h; workup permitted the isolation of $\mathrm{OPPh_3}$ in 98% yield. The reaction does not occur in the absence of catalyst.

(17) A solution of cobaltocene (0.14 g, 0.74 mmol) in dry, deoxygenated MeCN (10 mL) was added to $\mathrm{LMoO_2(SPh)}$ (0.20 g, 0.37 mmol), and the mixture was stirred for 0.25 h. Green microcrystals were filtered off, washed with MeCN, and dried under vacuum. The yield of $\mathrm{[CoCp_2][LMoO_2(SPh)]}$ was 0.19 g, 70%. Anal. Calcd for $\mathrm{C_{31}H_{37}BCoMoN_6O_2S}$: C, 51.47; H, 5.16; N, 11.62; S, 4.43. Found: C, 51.23; H, 5.28; N, 11.90; S, 4.33. Cyclic voltammetry (MeCN, 0.1 M $\mathrm{Bu_4NPF_6}$). $E_{1/2}$ −1.05 ($\mathrm{Mo^{VI}/Mo^{V}}$), −1.23 ($\mathrm{CoCp_2{}^+/CoCp_2}$), −2.16 V vs $\mathrm{Ag/AgNO_3}$ (0.01 M).

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An Oxothio–Molybdenum(VI) Complex Stabilized by an Intramolecular Sulfur–Sulfur Interaction: Implications for the Active Site of Oxidized Xanthine Oxidase and Related Enzymes

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The oxothio–molybdenum(VI) active site proposed[1] for oxidized xanthine oxidase and related enzymes is supported by EXAFS studies[2] and, indirectly, by strong EPR evidence for $\mathrm{[Mo^{V}OS]^+}$ and $\mathrm{[Mo^{V}O(SH)]^{2+}}$ centers in enzyme[1,3d] and model systems.[3,4] However, $\mathrm{[MoOS]^{2+}}$ complexes are extremely rare and are generally quite unstable.[5] Thus, the synthesis of a model for the

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