# Comparative Kinetics of Oxo Transfer to Substrate Mediated by Bis(dithiolene)dioxomolybdenum and -tungsten Complexes

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The recent discovery of enzymes containing tungsten has created a new imperative for examination of key features of the structure and reactivity of biologically related compounds of this element and their relation to the corresponding properties of analogous molybdenum complexes. We have examined the relative rates of oxygen atom (oxo) transfer to substrate in the second-order reactions $[MO_2(mnt)_2]^{2-} + (RO)_{3-n}R'_nP \rightarrow [MO(mnt)_2]^{2-} + (RO)_{3-n}R'_nPO$ in DMF solution (M = Mo, W; $n = 0$, R = Me; $n = 1$, R = Me, R′ = Ph; $n = 1$, R = Et, R′ = Me). At all temperatures examined, $k_{Mo} > k_W$; at 298 K, $k_{Mo}/k_W \approx 10^2-10^3$. For $(MeO)_2PhP$ as substrate, the activation parameters for M = Mo/W are $\Delta H^{\ddagger} = 8.2/11$ kcal/mol and $\Delta S^{\ddagger} = -33/-38$ eu. For $(MeO)_3P$, the values are $\Delta H^{\ddagger} = 10/14$ kcal/mol and $\Delta S^{\ddagger} = -32/-33$ eu. The rate differences arise primarily because of the activation enthalpy differences $\Delta H^{\ddagger}_W - \Delta H^{\ddagger}_{Mo} \approx 3-4$ kcal/mol. Using a recent theoretical treatment of molybdenum-mediated oxo transfer to substrate (Pietsch, M. A.; Hall, M. B. *Inorg. Chem.* **1996**, *35*, 1273), an energy profile for the preceding oxo transfer reactions is proposed. Factors contributing to the difference in barriers, whose individual values fall in or close to the $\Delta H^{\ddagger} = 10-20$ kcal/mol range for oxidation of tertiary phosphines by $Mo^{VI}O_2$ complexes, are considered. Reducibility of the metal center and the strength of M═O bonds are two factors that will tend to differentially increase the tungsten vs molybdenum barrier. Data from other systems are assembled to support this contention. The present results suggest that, more generally, $k_{Mo} > k_W$ for atom transfer or other processes involving reduction of the metal center and the reverse for oxidation. At present, this work provides the only comparative oxo transfer rates for molybdenum and tungsten compounds with common substrates.

## Introduction

The discovery of at least a dozen enzymes whose native catalytic sites contain tungsten[1,2] has created the subfield of tungsten bioinorganic chemistry. Such enzymes occur in thermophilic bacteria, where the same or related organisms may produce analogous molybdenum and tungsten enzymes. However, hyperthermophilic archaea grow obligately on tungsten and are unable to utilize molybdenum. The enzymes thus far isolated from these organisms are mainly members of the aldehyde oxidoreductase (AOR) family, catalyzing the overall reaction $RCHO + H_2O \rightarrow RCOOH + 2H^+ + 2e^-$ with broad substrate specificity. The crystal structure of the AOR ($\alpha_2$, 67 kDa/$\alpha$) from *Pyrococcus furiosus* (*Pf*) has been solved at 2.3-Å resolution.[3] The enzyme contains per subunit one $Fe_4S_4$ cluster and one tungsten atom at the catalytic site; the two subunits are bridged by a structural iron atom. The tungsten atom is coordinated in a distorted trigonal prismatic manner by two dithiolene chelate rings from two pterin cofactors and perhaps by two oxygenous ligands. The initial EXAFS study of dithionite-reduced *Pf* AOR, which predated the X-ray determination, indicated the presence of two W═O groups at 1.74 Å, about three W−S bonds at 2.41 Å, and a possible W−O/N bond at 1.97 Å.[4] A subsequent investigation has disclosed one W═O (1.75 Å) bond, four or five W−S (2.40 Å) bonds, and possibly one W−O/N (1.97 Å) bond,[2] in better agreement with the crystallographic results. All tungsten enzymes have pterin cofactors.[1,2]

Hille[5] has usefully classified the large group of mononuclear molybdenum enzymes that catalyze the general reaction $X + H_2O \rightarrow XO + 2H^+ + 2e^-$ into three families named for their prototypic members: xanthine oxidase, sulfite oxidase, and DMSO reductase. These enzymes may be broadly described as oxotransferases in that oxygen atom (oxo) transfer involves addition or removal of an oxygen atom to or from the molybdenum site. In two cases, milk xanthine oxidase[6a] and the DMSO reductase from *Rhodobacter sphaeroides*,[6b] this pathway has been proven by $^{18}O$-labeling experiments. The aldehyde oxidase reaction, catalyzed by both molybdenum and tungsten enzymes, is ostensibly one of oxo transfer, with a possible source of transferred oxygen being oxo or hydroxo ligands in the fully oxidized (M(VI)) forms of the enzymes. However, the active structures of AOR[3] and the molybdenum aldehyde oxidoreductase from *Desulfovibrio gigas*[9,10] are quite different. In the oxidized form, the latter contains an $Mo^{VI}OS$ group to which are coordinated a water molecule and the

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(5) Hille, R. *Chem. Rev.* **1996**, *96*, 2757.
(6) (a) Hille, R.; Sprecher, H. *J. Biol. Chem.* **1987**, *262*, 10914. (b) Schultz, B. E.; Hille, R.; Holm, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 827. Note that the reaction scheme presented in this reference has been revised[7] to take into account the subsequent finding by protein crystallography that the oxidized enzyme contains the monooxo $Mo^{VI}O$ group.[8]
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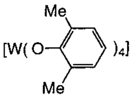
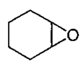
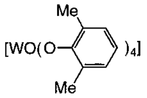
dithiolene ring from one pterin cofactor ligand. The water ligand, activated toward deprotonation by coordination, is considered a likely source of transferred oxygen in the product acid.[10] These two cases constitute the only available comparison between crystallographically characterized molybdenum and tungsten enzymes that catalyze the same overall reaction, there being no implication of similarities in mechanisms at this stage. In the Hille scheme, the *D. gigas* enzyme, with its $Mo^{VI}OS$ unit and one bound pterin cofactor ligand, is categorized in the xanthine oxidase family.

The foregoing differences notwithstanding, the emergence of tungsten enzymes at a time when the structural features of molybdenum oxotransferases are being established and mechanistic aspects further advanced inevitably directs attention to the fundamental chemistry of oxo−dithiolene complexes of these elements. The bis(dithiolene) complexes $[MO(bdt)_2]^{2-,1-}$ and $[MO_2(bdt)_2]^{2-}$ (M = Mo,[11,12] W[13]) and $[MO(mnt)_2]^{2-}$ and $[MO_2(mnt)_2]^{2-}$ (M = Mo,[14,15] W[16,17]) are pertinent in this respect. In the course of our current investigation of the synthesis and oxo transfer reactivity of molybdenum and tungsten dithiolenes, we have been aware of certain inadequacies in information requisite to an understanding of this type of reactivity. Two deserve mention here. First, the atom transfer chemistry of tungsten is poorly developed. In our 1987 treatment of oxo transfer,[18] no more than a half-dozen tungsten-mediated reactions could be documented. All oxo transfer reactions described since then and known to us are collected in Table 1.[19−24] About a dozen new reactions have emerged, of which two involve oxo−dithiolene complexes. Except for the system $[WO(bdt)_2]^{2-}/Me_3NO$, for which there is a rate constant at one temperature,[13] there are no kinetics parameters. In contrast, the oxo transfer chemistry of molybdenum is the most extensive of any metal in terms of both observed and kinetically defined reactions,[25−31] some of which are pertinent to the present work. Second, there are almost no data on *relative* reaction rates in systems differing only in the metal. The ratio of observed rate constants $k_{Mo}/k_W = 25$ is reported for the reaction systems at room temperature with $[MO(bdt)_2]^{2-}/Me_3NO$ in DMF at ambient temperature.[13] While the rate order W > Mo for oxo transfer from substrate (and Mo > W for the reverse reaction) is consistent with periodic properties and anticipated by other results (vide infra), a quantitative kinetics comparison including activation parameters is absent for any substrate. In this work, we address the relative kinetics of atom transfer from metal center to substrate in the systems containing $[MO_2(mnt)_2]^{2-}$ (M = Mo, W) with $(MeO)_3P$ and $(MeO)_2PhP$ as principal substrates.

**Table 1.** Tungsten-Mediated Oxo Transfer Reactions[a]

| species | reactants | product | ref. |
|---|---|---|---|
| | **W(II) → W(IV)** | | |
| $[WCl_2(PR_3)_4]$[b] | $N_2O$, $O_2$, $Me_2SO$, $CO_2$, $SO_2$ <br>  | $[WOCl_2(PR_3)_3]$[c] | 19 |
| | **W(IV) → W(VI)** | | |
|  |  |  | 20 |
| $[WO_5(OH_2)]$[d] | $Me_2SO$, $Ph_3AsO$ | $[W(O)O_5]$ | 21 |
| $[WO(bdt)_2]^{2-}$ | $Me_3NO$ | $[WO_2(bdt)_2]^{2-}$ | 13 |
| $[WO(mnt)_2]^{2-}$ | $HCO_3^-$ | $[WO_2(mnt)_2]^{2-}$[e] | 16 |
| | **W(VI) → W(IV)** | | |
| $[WO_2(S_2CNC_5H_{10})_2]$ | $(MeO)_3P$ | $[W_2O_3(S_2CNC_5H_{10})_4]$[f] | 22 |
| $[WO_2(S_2CN(CH_2Ph)_2)_2]$ | $Et_3P$ | $[WO(S_2CN(CH_2Ph)_2)_2(PEt_3)]$ | 23 |

[a] For the limited number of earlier examples, *cf.* ref. 18. [b] $R_3 = Me_3$, $Ph_2Me$. [c] Some products bind deoxygenated oxo source (CO, olefins). [d] Site in a heteropolytungstate. [e] $HCO_2^-$ reported as reduced substrate product. [f] W(V) product from a complete intermetal oxo transfer reaction[18]: $W^{IV}O + W^{VI}O_2 \rightarrow W^V{}_2O_3$.

## Experimental Section

**Materials.** The compounds $(Et_4N)_2[MO(mnt)_2]$ (M = Mo,[15a] W[17]), $(Bu_4N)_2[MoO_2(mnt)_2]$,[15a] and $(Ph_4P)_2[WO_2(mnt)_2]$[17] were prepared as described. Trimethyl phosphite (Aldrich, 99.999+%) and methyldiethoxyphosphine (99%, Strem) were used as received. Phenyldimethoxyphosphine (98%, Strem) was vacuum-distilled prior to use. $^{31}P$ NMR spectra indicated ≲1% impurities in these substrate compounds. DMF (anhydrous, 99.8%, Aldrich) was used as received. Acetonitrile was distilled from $CaH_2$, and THF, from sodium; both solvents were stored over 4 Å molecular sieves. All complexes, substrates, solutions, and solvents were stored under a pure dinitrogen atmosphere.

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**Table 2.** Kinetics Data for the Reaction $[MO_2(mnt)_2]^{2-} + X \rightarrow [MO(mnt)_2]^{2-} + XO$ in DMF Solutions (M = Mo, W)

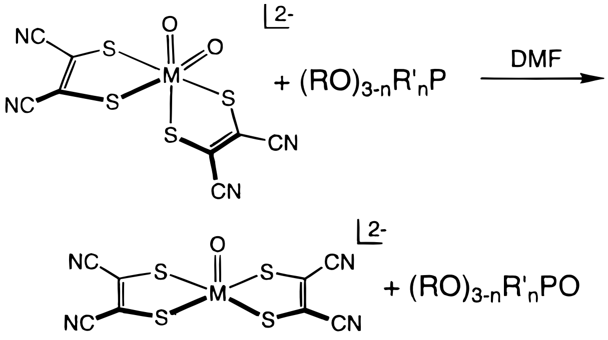
| M | X | *T* (K) | *k* ($M^{-1}\,s^{-1}$) | $\Delta H^‡$ (kcal/mol) | $\Delta S^‡$ (eu) |
|---|---|---|---|---|---|
| Mo | $(MeO)_2PhP$ | 278 | 0.14(1) | 8.2(4) | −33(1) |
| | | 288 | 0.27(1) | | |
| | | 298 | 0.45(2) | | |
| | | 303 | 0.64(1) | | |
| | | 308 | 0.74(3) | | |
| | | 313 | 0.85(2) | | |
| | | 318 | 1.1(1) | | |
| W | $(MeO)_2PhP$ | 288 | $2.9(2) \times 10^{-4}$ | 11(1) | −38(2) |
| | | 298 | $4.5(2) \times 10^{-4}$ | | |
| | | 313 | $1.2(1) \times 10^{-3}$ | | |
| | | 318 | $1.7(1) \times 10^{-3}$ | | |
| | | 328 | $3.1(2) \times 10^{-3}$ | | |
| Mo | $(MeO)_3P$ | 288 | $1.3(1) \times 10^{-2}$ | 10(1) | −32(1) |
| | | 293 | $1.7(1) \times 10^{-2}$ | | |
| | | 298 | $2.5(1) \times 10^{-2}$ | | |
| | | 308 | $4.2(1) \times 10^{-2}$ | | |
| | | 313 | $5.5(1) \times 10^{-2}$ | | |
| | | 318 | $7.8(2) \times 10^{-2}$ | | |
| | | 323 | $9.5(5) \times 10^{-2}$ | | |
| | | 328 | $1.3(1) \times 10^{-1}$ | | |
| W | $(MeO)_3P$ | 313 | $2.5(2) \times 10^{-5}$ | 14(1) | −33(2) |
| | | 318 | $4.7(1) \times 10^{-5}$ | | |
| | | 328 | $9.4(4) \times 10^{-5}$ | | |
| | | 338 | $1.4(1) \times 10^{-4}$ | | |
| | | 348 | $3.1(4) \times 10^{-4}$ | | |
| | | 353 | $4.8(3) \times 10^{-4}$ | | |

**Kinetics Measurements.** Reactions were performed under anaerobic conditions in DMF solutions, except for several ambient-temperature measurements in acetonitrile and THF. Reactions were monitored using a Cary 3 spectrophotometer equipped with a cell compartment thermostated to ±0.5 °C and a multicell changer. Thermal equilibrium was reached by placing quartz cells (1 mm, NSG Glass) charged with 0.2 mL of $[MO_2(mnt)_2]^{2-}$ solution into the cell compartment 15−20 min prior to reaction initiation. Reactions were started by the injection of a DMF solution of the substrate (principally $(MeO)_3P$ or $(MeO)_2PhP$) through the septum cap of the quartz cell using gastight syringes (Hamilton) fitted with 21 gauge stainless steel needles.

Substrate oxidations were monitored by following the decrease in intensity of the 425 nm band of $[MoO_2(mnt)_2]^{2-}$ or of the 382 nm band of $[WO_2(mnt)_2]^{2-}$. Reaction systems had the initial oxidant concentrations $[MoO_2(mnt)_2{}^{2-}]_0 = (1.0-2.6) \times 10^{-3}$ M, with 10−110 equiv of substrate, and $[WO_2(mnt)_2{}^{2-}]_0 = 9.4 \times 10^{-4}-1.7 \times 10^{-3}$ M, with 250−4000 equiv of substrate, depending on reaction rates. For each substrate, reactions were conducted at a minimum of five temperatures in the ranges in Table 2. At each temperature, at least four independent runs were performed under pseudo-first-order conditions. Plots of $\ln[(A - A_\infty)/(A_0 - A_\infty)]$ vs time were linear over at least 3 half-lives. Plots of $k_{obs}$ vs substrate concentration were linear and yielded second-order rate constants, from which activation parameters were determined from plots of the Eyring equation $k = (k_BT/h)[\exp(\Delta S^‡/R - \Delta H^‡/RT)]$.

## Results and Discussion

**Selection of Reaction Systems.** In assessing the kinetics of oxo transfer in molybdenum and tungsten systems, we chose to utilize bis(dithiolene) complexes because of the relationship to the two pterin cofactor ligands in members of the DMSO reductase family.[5] A number of bis(dithiolene) $M^{IV}O$ and $M^{VI}O_2$ complexes of these elements have been prepared.[31,32] Preliminary screening of some of the $Mo^{IV}O$ and $Mo^{VI}O_2$ species indicated that the mnt complexes were the most stable by spectrophotometric examination under the time and temperature conditions used in kinetics runs.[33] Consequently, reaction



(1)

system 1 ($n = 0, 1$) in DMF was selected for study. It involves oxo transfer to substrate in a second-order process and structural conversion from distorted trigonal prismatic $[MO_2(mnt)_2]^{2-}$ [15a,17] to square pyramidal $[MO(mnt)_2]^{2-}$.[15b,17] Structural differences between complexes in the same oxidation state are negligible. The principal substrates, $(MeO)_3P$ and $(MeO)_2PhP$, were selected because they afforded clean reactions at experimentally convenient rates for both metals. These are obviously not biological substrates. However, we have demonstrated that the oxidized form ($Mo^{VI}O$) of DMSO reductase from *R. sphaeriodes* can oxidize a water-soluble tertiary phosphine to the phosphine oxide with transfer of the $^{18}O$ label.[6b] Oxo transfer processes of the complexes in reaction 1 are not complicated by the reaction $Mo^{IV}O + Mo^{VI}O_2 \rightarrow OM^{V}{-}O{-}M^{V}O$,[15a,17] common to many molybdenum oxo transfer systems,[18,25] presumably because both complexes are anionic. Note that the reaction systems of eq 1 differ only in the metal.

**Kinetics of Oxo Transfer.** Kinetics of reactions 2−5 were followed spectrophotometrically at different temperatures. A time course of reaction 2 at 298 K is illustrated in Figure 1.

$$[MoO_2(mnt)_2]^{2-} + (MeO)_2PhP \rightarrow [MoO(mnt)_2]^{2-} + (MeO)_2PhPO \quad (2)$$

$$[WO_2(mnt)_2]^{2-} + (MeO)_2PhP \rightarrow [WO(mnt)_2]^{2-} + (MeO)_2PhPO \quad (3)$$

$$[MoO_2(mnt)_2]^{2-} + (MeO)_3P \rightarrow [MoO(mnt)_2]^{2-} + (MeO)_3PO \quad (4)$$

$$[WO_2(mnt)_2]^{2-} + (MeO)_3P \rightarrow [WO(mnt)_2]^{2-} + (MeO)_3PO \quad (5)$$

The bands of $[MoO_2(mnt)_2]^{2-}$ at 425 and 525 nm decrease in intensity with time while a feature at 368 nm due to $[MoO(mnt)_2]^{2-}$ grows in. Tight isosbestic points are observed at 357 and 378 nm. The final spectrum is the same as that of $[MoO(mnt)_2]^{2-}$ measured separately. A corresponding depiction of reaction 3 is provided in Figure 2. Here the 382 and 455 features of $[WO_2(mnt)_2]^{2-}$ decrease in intensity as the reaction proceeds while the 355 nm band of $[WO(mnt)_2]^{2-}$ becomes

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[33] We encountered some difficulty in devising other reaction systems for both molybdenum and tungsten with the same ligands that allowed quantitive kinetics measurements in the absence of complex instability or other undesired reactions. For example, we were unable to obtain a well-behaved kinetics description of the system $[MoO(bdt)_2]^{2-}/Me_3NO$ in acetonitrile examined by others.[31]

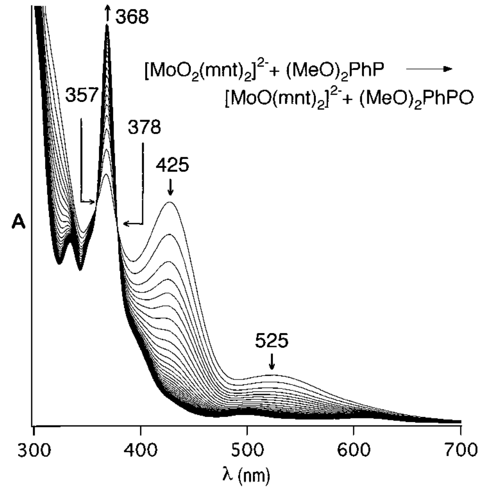

**Figure 1.** Spectrophotometric monitoring of the reaction system $[\mathrm{MoO_2(mnt)_2}]^{2-}$ (3.30 mM) + $\mathrm{(MeO)_2PhP}$ (1.8 equiv) in DMF solution at 298 K. These quantities were selected to provide small incremental changes in spectra recorded every 2 min for a period of 64 min. Band maxima and isosbestic points (nm) are indicated.

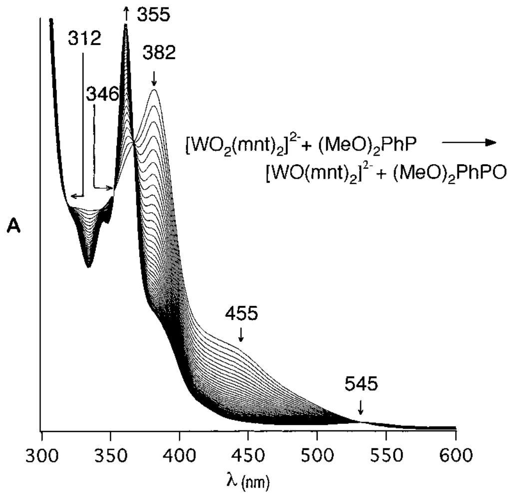

**Figure 2.** Spectrophotometric monitoring of the reaction system $[\mathrm{WO_2(mnt)_2}]^{2-}$ (1.7 mM) + $\mathrm{(MeO)_2PhP}$ (600 equiv) in DMF solution at 298 K. These quantities were selected to provide small incremental changes in spectra recorded every 2 min for a period of 78 min. Band maxima and isosbestic points (nm) are indicated. The unlabeled isosbestic point occurs at 366 nm.

more intense. Well-defined isosbestic points occur at 312, 346, 366, and 545 nm. The final spectrum is the same as that of $[\mathrm{WO(mnt)_2}]^{2-}$ measured separately. In the case of reactions 4 and 5, $^{31}$P NMR confirmed the formation of trimethyl phosphate. The same UV−visible spectral changes were observed in reactions 4 and 5 and with other substrates (vide infra).

Reactions 2−5 are second-order with the rate law (6). Rate constants at different temperatures and activation parameters evaluated from the Eyring equation are collected in Table 2.

$$-\mathrm{d}[(\mathrm{MO_2(mnt)_2})^{2-}]/\mathrm{d}t = k[(\mathrm{MO_2(mnt)_2})^{2-}][(\mathrm{RO})_{3-n}\mathrm{R'}_n\mathrm{P}] \quad (6)$$

Eyring plots for reactions 2 and 3 are displayed in Figure 3. Linear plots were observed in all cases. It is immediately evident that large substantial differences exist for analogous molybdenum- and tungsten-mediated reactions. For the rate constants at 298 K given in Table 3, $k_{\mathrm{Mo}}/k_{\mathrm{W}}$ = 2600, 1000, 320 in the order of substrates listed. Thus, in these systems rate acceleration by molybdenum vs tungsten is in the $10^2$−$10^3$ range. Activation entropies are large and negative, consistent with a second-order process. The observed range, −32 to −38 eu, is narrow and consistent with a common associative mechanism for the two metals. Although the database is not extensive, values of $\Delta S^{\ddagger}$ occur in the range −10 to −37 eu for the oxidation of tertiary phosphines by $\mathrm{Mo^{VI}O_2}$ complexes in aprotic solvents.[18,27,28,30] All but one of these values is less than −20 eu. Because $\Delta S^{\ddagger}$ is more negative for reaction 3 than for reaction 2 by −5 eu, the predicted ratio $k_{\mathrm{Mo}}/k_{\mathrm{W}}$ = 12 for the two reactions at constant $\Delta H^{\ddagger}$, a value small compared to the experimental $10^3$ at 298 K. For reactions 4 and 5, the values of $\Delta S^{\ddagger}$ are experimentally indistinguishable. The main source of the relative rates of the two metals must lie principally in differences in $\Delta H^{\ddagger}$ values, which are larger by 2.8 and 4 kcal for the tungsten complexes in reactions 2/3 and 4/5, respectively.

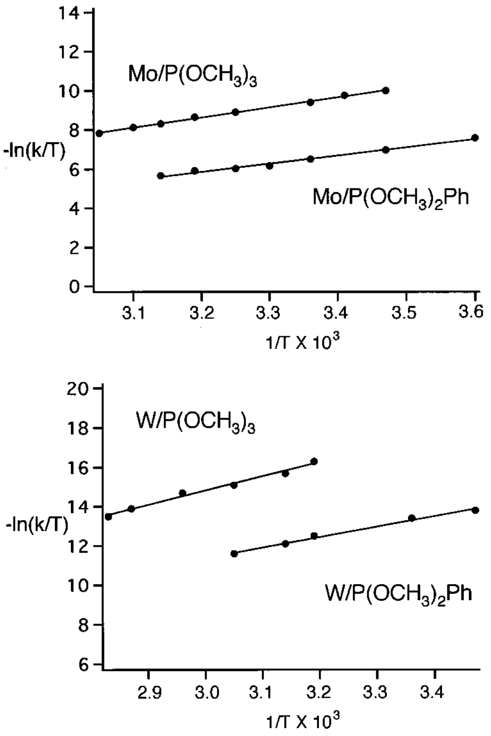

**Figure 3.** Eyring plots for reactions 2 and 4 (upper) and reactions 3 and 5 (lower) in DMF solutions.

**Table 3.** Rate Constants for Substrate Oxidation by $[\mathrm{MO_2(mnt)_2}]^{2-}$ in DMF Solutions at 298 K

| M | X | $k$ ($\mathrm{M^{-1}\,s^{-1}}$) | M | X | $k$ ($\mathrm{M^{-1}\,s^{-1}}$) |
|---|---|---|---|---|---|
| Mo | $\mathrm{(MeO)_3P}$ | $2.5 \times 10^{-2}$ | W | $\mathrm{(MeO)_3P}$ | $9.7 \times 10^{-6}$ [a] |
| Mo | $\mathrm{(MeO)_2PhP}$ | 0.45 | W | $\mathrm{(MeO)_2PhP}$ | $4.5 \times 10^{-4}$ |
| Mo | $\mathrm{(EtO)_2MeP}$ | 1.1 | W | $\mathrm{(EtO)_2MeP}$ | $3.4 \times 10^{-3}$ |

[a] Calculated from the Eyring equation.

**Reaction Profiles.** In seeking the source of the larger rates with molybdenum than with tungsten complexes, we have considered the theoretical analysis by Pietsch and Hall (PH),[34] who calculated a reaction pathway for the substrate oxidation system (7) in water. While the reactant complex was simplified

$$[\mathrm{Mo^{VI}O_2(SH)_2(NH_3)_2}] + \mathrm{Me_3P} + \mathrm{H_2O} \rightarrow [\mathrm{Mo^{IV}O(SH)_2(NH_3)_2(OH_2)}] + \mathrm{Me_3PO} \quad (7)$$

for calculational purposes and the geometries of all molybdenum

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(34) Pietsch, M. A.; Hall, M. B. *Inorg. Chem.* **1996**, *35*, 1273.

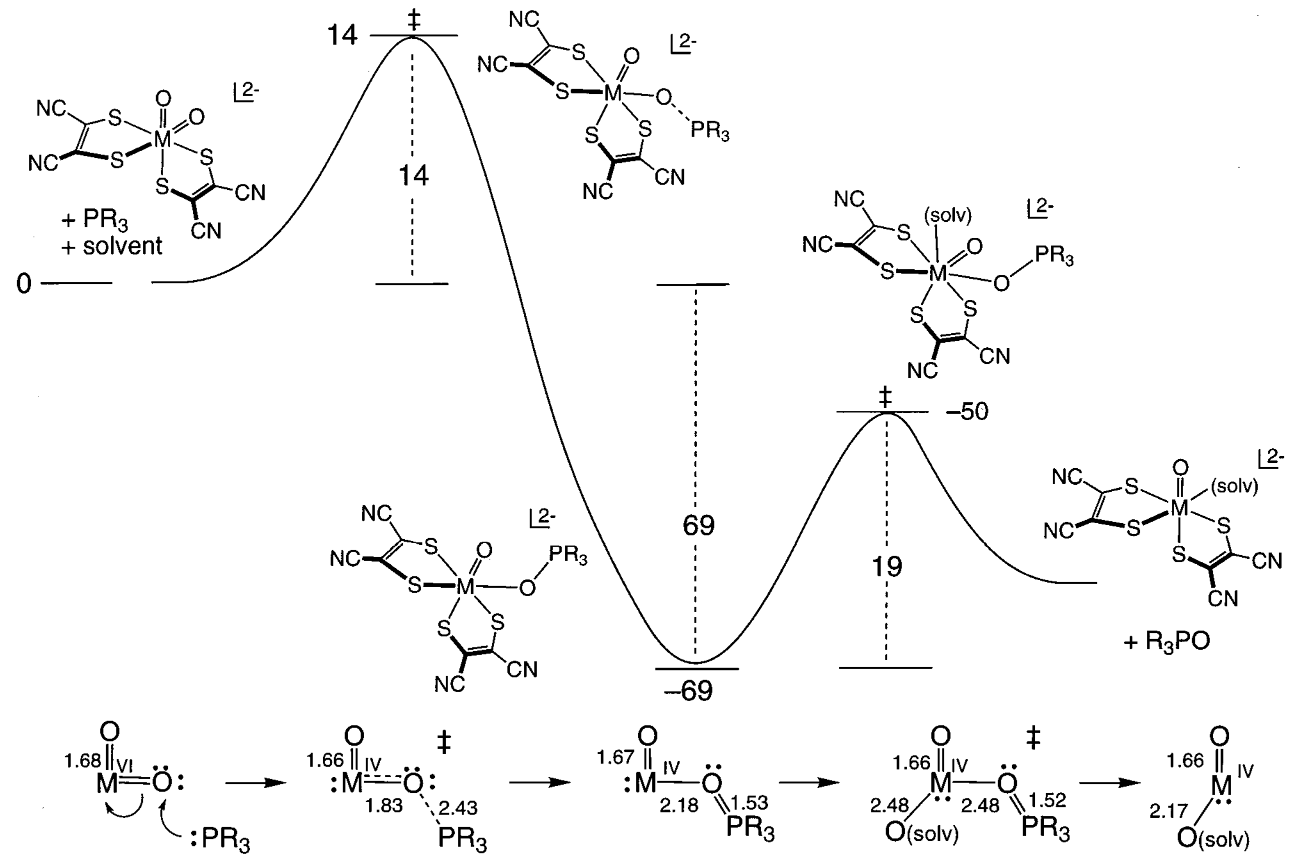

**Figure 4.** Proposed energy profile for reaction 1 with a generalized $PR_3$ substrate, adapted from the work of Pietsch and Hall[34] for reaction 7. Energies (kcal/mol) are relative to the reactants, and bond lengths are optimized values; both refer to transition states and intermediates in reaction 7. Depictions of M = Mo and W species simulate theoretical descriptions. The order of events in reaction 7 is taken as the same for M = Mo and W systems of reaction 1.

species along the reaction pathway were theoretically optimized, the donor atom sets and atom charges (but not all Mo bond angles and lengths) are the same as,[28,35] or similar to,[36] those of functional atom transfer systems. The $Mo^{VI}O_2$ reactant has $C_{2v}$ symmetry with a standard Mo−O bond distance (1.68 Å). The energy profile in Figure 4 is adapted from the results of PH. The energies of the possible transition states and intermediates relative to the reactants have been retained in order to convey the calculated energy changes in the steps of reaction 7. Mo−O and P−O bond distances are displayed along the bottom of the diagram. There is no implication that these values or the energies apply to reaction 1. However, we conclude that the sequence of events, recognized but for the most part set out less exactly in various papers on molybdenum-mediated oxo transfer, is the same as for the reactions of molybdenum and tungsten studied here. A similar theoretical treatment for tungsten-mediated oxo transfer is not available.

The initial event is the nucleophilic attack on one oxo atom by the phosphine, causing an electron drift into the vacant Mo $d_{xy}$ orbital. This event generates the first transition state. One Mo−O bond, involving a "spectator" oxo atom in the sense of Rappé and Goddard,[37] is slightly shortened, the bond subject to attack is greatly lengthened, and a weak P···O interaction is developed. In reaction 7, generation of this transition state requires an activation energy of 14 kcal/mol. An intermediate is developed upon formation of a $Mo^{IV}$−O single bond involving the atom to be transferred to the $R_3P$ substrate and creation of a short P−O bond typically found in phosphine oxides and phosphate triesters. In reaction 7, the first intermediate ($C_1$ symmetry) is some 69 kcal/mol more stable than the uncombined reactants. The structure of this intermediate, which is an $R_3PO$ adduct of a $Mo^{IV}O$ complex, is chemically reasonable, although we are unaware of any such complexes having been directly detected in a molybdenum or tungsten oxo transfer system. In the aqueous system (7), the next event is reckoned to be formation of a seven-coordinate monosolvated entity, an associative transition state. At this stage, a water molecule resides on the molybdenum atom at a distance of 2.48 Å, the $Mo-OPR_3$ bond is near the dissociation limit, and the P−O and spectator Mo−O bond lengths are essentially unchanged. Next, the $R_3PO$ ligand dissociates, and water occupies the vacated site at an Mo−O distance of 2.17 Å, affording $[Mo^{IV}O(SH)_2(NH_3)_2(OH_2)]$ in a process that is predicted by PH to be concerted in nature. In succeeding steps, this species is converted by coupled proton−electron transfer to the initial $Mo^{VI}O_2$ complex. In the nonaqueous system (1), we have no direct evidence for a solvated transition state or a (weakly solvated) final product $[M^{IV}O(mnt)_2(DMF)]^{2-}$, so neither can be ruled out. While we did not investigate the matter in detail, the room-temperature rate constants for reaction 2 are somewhat solvent-sensitive, with the extreme values varying by a factor of 6 for the solvents tested (THF, 0.21; DMF, 0.45; MeCN, 1.2 $M^{-1}\ s^{-1}$). The depictions of the various dithiolene species in Figure 4 (including the solvated transition state and product) simulate the PH theoretical predictions for reaction 7. Our brief

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**Table 4.** Differences of Redox Potentials of Pairs of Mononuclear Molybdenum and Tungsten Complexes

| couple[a] | oxidn states | $E_{Mo} - E_W$ (V) | ref |
|---|---|---|---|
| $[MF_6]^{0/1-}$, $[MF_6]^{1-/2-}$ | 6+/5+, 5+/4+ | 1.01, 0.98[b] | 38 |
| $[MCl_6]^{2-/3-}$ | 4+/3+ | 0.87 | 39, 40 |
| $[M([9]ane(NMe)_3)Cl_3]^{1+/0}$ | 4+/3+ | 0.84 | 41 |
| $[M(HB(Me_2pz)_3)Cl_3]^{0/1-}$ | 4+/3+ | 0.82 | 42a |
| $[MOCl_5]^{1-/2-}$, $[MOCl_5]^{2-/3-}$ | 6+/5+, 5+/4+ | 0.75, 0.75 | 40 |
| $[MNCl_4]^{1-/2-}$ | 6+/5+ | 0.68 | 40 |
| $[MCl_6]^{1-/2-}$ | 5+/4+ | 0.65 | 39, 40 |
| $[MO([9]ane(NMe)_3)Cl_2]^{1+/0}$ | 5+/4+ | 0.62 | 41 |
| $[MCl_6]^{0/1-}$ | 6+/5+ | 0.61 | 39, 40 |
| $[MO_2(HB(Me_2pz)_3)L]$[e] | 6+/5+ | 0.56−0.61 | 42b |
| $[MO(bdt)_2]^{1-/2-}$ | 5+/4+ | 0.28 | 13 |
| $[MO(SR)_4]^{0/1-}$, $[MO(SR)_4]^{1-/2-}$ | 6+/5+, 5+/4+ | 0.27, 0.27[c] | 43 |
| $[M(CN)_8]^{3-/4-}$ | 5+/4+ | 0.27 | 44 |
| $[M(mnt)_3]^{2-/3}$ | 4+/3+ (?) | 0.27, 0.37 | 14b, 45 |
| $[M([9]ane(NMe)_3)(CO)_3]^{1+/0}$ | 1+/0 | 0.09 | 41 |
| $[M(tfd)_3]^{0/1-}$, $[M(tfd)_3]^{1-/2-}$ | *d* | 0.07, 0.04 | 46 |

[a] Abbreviations: $[9]ane(NMe)_3$ = *N,N′,N″*-trimethyl-1,3,5-triazacyclononane; bdt = benzene-1,2-dithiolate(2−); $HB(Me_2pz)_3$ = tris(3,5-dimethylpyrazolyl)borate(1−); mnt = maleonitriledithiolate(2−); tfd = 1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate(2−). [b] W potential at 293 K; Mo potential at 273 K. [c] R = 2,4,6-$C_6H_2(^iPr)_3$. [d] Oxidation states uncertain. [e] Includes a set of six monoanionic ligands.

description of the energy profile for reaction 7 does not include certain orbital and structural changes; for these details the original treatment by PH must be consulted.

As PH have noted, and as is the case here, the theoretical activation barrier of 14 kcal/mol is comparable to measured values of $\Delta H^{\ddagger}$, all of which are in the 10−20 kcal/mol range in aprotic solvents.[18,27,28,30] These values include whatever solvation effects factor into creation of the transition states, whereas the PH energies do not. This unresolved matter notwithstanding, the apparent conformity of theoretical and experimental energies to a narrow interval suggests that some validity may be extended to the theoretical description of rate-limiting transition state formation. At least two properties, inherent to the metals, appear important in this respect: the reducibility of the metal center and the strength of terminal metal−oxo bonds. In terms of achieving the transition state, these factors can only be assessed by appeal to experimental data for other systems.

Whether the formation of the first transition state involves partial electron transfer to Mo(VI) or full transfer of an electron pair to give Mo(IV), the process is one of reduction. The relative tendencies of molybdenum and tungsten to be reduced follow from redox potential differences at parity of ligation and under otherwise identical conditions. There being no such database previously presented, we have collected in Table 4 potentials of chemically reversible mononuclear redox couples that appear to fulfill these criteria.[38−46] We note in particular the valuable work of Moock, Heath, Sharpe, and their coworkers,[39,40] who have provided potentials for a number of redox couples differing only in the metal. With innocent, weakly polarizable ligands, values of $E_{Mo} - E_W$ are largest and maximize at ca. 1 V for the hexafluoride couples. There is a notable separation of ca. 0.3 V between the $[MCl_6]^{0/1-}$ couple and those that contain anionic sulfur ligands or $\pi$-acid ligands. Three of these (mnt, bdt, tfd) are of the dithiolene type. For the couples $[MO(mnt)_2]^{1-/2-}$ in dichloromethane, $E_{Mo} - E_W$ = 0.17 V. Ligands in the lower part of the table are just those expected to form the more covalent bonds, whose effect would attenuate intrinsic electronic and reactivity differences between the metals. In the $[MO(mnt)_2]^{1-/2-}$ couple, for example, the M(V) state is well-defined by EPR;[15a,17] consequently, the ligand in the monoanion and dianion is reasonably formulated as a dithiolate dianion. The decreased potential difference is due to bond covalency, as in $[MO(SR)_4]^{1-/2-}$, whose ligands are innocent and whose difference is the same as that of $[MO(bdt)_2]^{1-/2-}$. Indeed, the smallest differences in potential are found with the highly oxidized $[M(tfd)_3]^z$ complexes, in which the metal and (noninnocent) ligand oxidation states are not certain owing to electron delocalization. The most important conclusion from the data in Table 4 is that, ligand effects on redox potentials notwithstanding, there are no exceptions to the potential order $E_{Mo} > E_W$. One should, therefore, expect that any event that increases the electron density at the two metal centers would require an incrementally larger energy for tungsten than molybdenum, other factors being constant as with the outer-sphere redox couples of Table 4.

**Table 5.** Metal−Oxo Bond Distances and Stretching Frequencies in $[M^{VI}O_2L_2]^{2-}$ Complexes (L = mnt, bdt)

| compound | M−O (Å) | $\nu_{Mo}$ ($cm^{-1}$) | ref |
|---|---|---|---|
| $(Bu_4P)_2[MoO_2(mnt)_2]$ | 1.69(1), 1.73(1) | 885, 850 | 15a |
| $(Ph_4P)_2[MoO_2(mnt)_2]\cdot 2MeOH$ | 1.721(6) | 885, 851 | 12b, 47 |
| $Q_2[WO_2(mnt)_2]$ | 1.701(6)[b] | 916, 874[a] | 17 |
| $Q_2[MoO_2(bdt)_2]$ | 1.724(2), 1.730(7)[b] | 858, 829[c] | 12b, 47 |
| $Q_2[WO_2(bdt)_2]$ | 1.727(9), 1.737(6)[b] | 885, 843[c] | 13, 47 |

[a] Q = $Bu_4N^+$. [b] Q = $Ph_4P^+$. [c] Q = $Et_4N^+$.

The formation of the first transition state involves the concerted processes of electron transfer to the metal center and lengthening of one M−O bond of the $M^{VI}O_2$ group. Therefore, the relative strengths of M−O bonds are relevant. Summarized in Table 5 are the $M^{VI}O_2$ stretching frequencies[15a,17,47] measured under the same conditions and $M^{VI}$−O bond lengths for pairs of mnt and bdt complexes. With the same ligand, $\nu_{WO} > \nu_{MoO}$, indicating stiffer bonds in the tungsten complexes. In $[WO_2(mnt)_2]^{2-}$, the bond distances are mildly suggestive of shorter bonds compared to the more accurate of the two $[MoO_2(mnt)_2]^{2-}$ structures, but the crystalline environments are different. These distances in the $[MO_2(bdt)_2]^{2-}$ pair are not distinguishable. Although no M−O bond is broken in the PH description or previous conceptions[25,27,28] of transition state formation, we consider briefly the actual strengths of such bonds. Collected in Table 6 are bond dissociation energy (BDE) differences for pairs of molybdenum and tungsten compounds ranging in oxidation state from M(II) to M(VI).[48−52] Unless

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**Table 6.** Molybdenum− and Tungsten−Oxo Bond Dissociation Energies

| compound | BDE (kcal/mol)<br>M = Mo | BDE (kcal/mol)<br>M = W | $BDE_W - DBE_{Mo}$ | ref |
|---|---|---|---|---|
| MO | 126, 133 | 161, 160 | 35, 27 | 48, 49 |
| $MO_2$ | 140 | 152 | 12 | 48 |
| $MOCl_4$ | 101 | 127 | 26 | 50 |
| | 150[a] | 169[a] | 19 | 51 |
| $MO_3$ | 141 | 142 | (1) | 50 |
| | 141 | 150 | 9 | 48 |
| $MO_2Cl_2$[a] | 158 | 179 | 21 | 52 |

[a] Theoretical estimates.

otherwise indicated, BDE's were calculated from thermochemical data. The values of $BDE_W - BDE_{Mo}$ for $MO_2Cl_2$ and $MOCl_4$ are perhaps the most pertinent and are in the 19−26 kcal/mol range. Taking these data as a rough guide, reaction 1 sacrifices one M═O bond of energy ca. 150 kcal/mol to form a P−O bond of energy 148 kcal/mol.[53] From Table 6, $BDE_W > BDE_{Mo}$, with the least certain case being $MO_3$, where the BDE difference calculated from heats of formation is essentially nil. Pyykkö[54] has argued that relativistic effects are responsible for these and other property trends of molybdenum and tungsten compounds. On the basis of the data in Table 6, the conclusion that more energy is required to deform a W−O than a Mo−O bond from its equilibrium value seems inescapable.

**Summary.** We have established that for three pairs of second-order oxo transfer reactions 1 using oxidants with bis(dithiolene) coordination, the rate order is $k_{Mo} > k_W$ in the direction M(VI) → M(IV) and the molybdenum rates are $10^2$−$10^3$ faster at room temperature. Two reactions were examined as a function of temperature in order to evaluate activation parameters. We conclude that the faster rates with molybdenum are the consequence of two intrinsic properties: *reducibility* as manifested by redox potentials and *bond length deformation* as reflected by stretching frequencies and BDE values. It is assumed that any differential solvation energy in attaining the transition state is small because the $[MO_2(mnt)_2]^{2-}$ complexes are isostructural with the same charge and were used at similar concentrations. Further, if the PH conception of the first transition state is correct, the structural change to reach it is rather small. We consider this likely in the present reactions. In any case, we have no basis for estimating any differential rearrangement energy. While it remains to be more generally established that for metal-centered reduction $k_{Mo} > k_W$ and the reverse for oxidation, several other redox reactions do follow these trends.[55] Larger differences in barriers may be anticipated for Mo/W reactant pairs with ligands less covalent than dithiolenes. Should a native molybdenum atom in an enzyme be replaceable by tungsten (or conversely) with retention of structure and activity, the present results indicate the expected direction of the rate change. In view of the monooxo centers present in the AOR (W) and DMSO reductase (Mo) families, considerable interest attends the oxo transfer propensities of dithiolene-coordinated monooxo M(VI) groups. We recently prepared components of the potential oxo transfer couple $[\text{nonoxo}-M^{IV}] + [O] \rightarrow [M^{VI}O]$ as bis(dithiolene) complexes with M = Mo and W. Their reactivity properties are currently under investigation.[56]

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