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Article

Unusual Oxidation of Phosphines Employing Water as the Oxygen Atom Source and Tris(benzene-1,2-dithiolate)molybdenum(VI) as the Oxidant. A Functional Molybdenum Hydroxylase Analogue System

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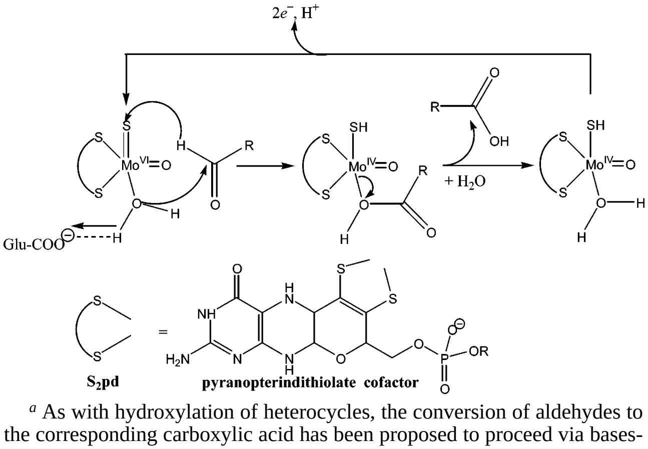
The kinetics of the reaction of $Mo^{VI}(S_2C_6H_4)_3$ with organic phosphines to produce the anionic Mo(V) complex, $Mo^V(S_2C_6H_4)_3^-$, and phosphine oxide have been investigated. Reaction rates, monitored by UV–vis stopped-flow spectrophotometry, were studied in THF/H_2O media as a function of the concentration of phosphine, molybdenum complex, pH, and water concentration. The reaction exhibits pH-dependent phosphine saturation kinetics and is first-order in complex concentration. The water concentration strongly enhances the reaction rate, which is consistent with the formation of $Mo^{VI}(S_2C_6H_4)_3(H_2O)$ adduct as a crucial intermediate. The observed pH dependence of the reaction rate would arise from the distribution between acid and basic forms of this adduct. Apparently, the electrophilic attack by the phosphine at the oxygen requires the coordinated water to be in the unprotonated hydroxide form, $Mo^{VI}(S_2C_6H_4)_3(HO)^-$. This is followed by the concerted abstraction of $2e^-$, H^+ by the Mo(VI) center to give $Mo^{IV}(S_2C_6H_4)_3^{2-}$, H^+, and the corresponding phosphine oxide. However, this Mo(IV) complex product is oxidized rapidly to $Mo^V(S_2C_6H_4)_3^-$ via comproportionation with unreacted $Mo^{VI}(S_2C_6H_4)_3$. The Mo(V) complex thus formed can be oxidized to the starting Mo(VI) complex upon admission of O_2. Consequently, $Mo^{VI}(S_2C_6H_4)_3$ is a catalyst for the autoxidation of phosphines in the presence of water. Additionally, there was a detectable variation in the reactivity for a series of tertiary phosphines. The rate of Mo(VI) complex reduction increases as does the phosphine basicity: $(p\text{-}CH_3C_6H_4)_3P > (C_6H_5)_3P > (p\text{-}ClC_6H_4)_3P$. Oxygen isotope tracing confirms that water rather than dioxygen is the source of the oxygen atom which is transferred to the phosphine. Such reactivity parallels oxidase activity of xanthine enzyme with phosphine as oxygen atom acceptor and $Mo^{VI}(S_2C_6H_4)_3$ as electron acceptor.

Introduction

Under the Hille classification of molybdenum enzymes,[1] the xanthine oxidase family is a group of enzymes that catalyze the transfer of an oxygen atom from water to substrates, purines, pyrimidines, and pterins, in addition to aldehydes, in reactions that involve the cleavage of a C−H and the formation of a C−OH bond. All these enzymes possess a structurally similar molybdopterin cofactor in the active site, which contains, in the oxidized Mo(VI) state, an oxo group, a sulfide group, a dithiolene side chain to a pterin, and a water or hydroxide ligand (Scheme 1).[2] The pterin-dithiolene ligand is an organic molecule which can have, in addition, a nucleotide molecule attached by a pyrophosphate link.[3] These proteins may also have other redox cofactors such as iron−sulfur centers, flavin, and hemes, which are assumed to be involved in electron-transfer processes.

Scheme 1. Reaction Mechanism for the Aldehyde Oxidase Group of Molybdenum Hydroxylases[a]



[a] As with hydroxylation of heterocycles, the conversion of aldehydes to the corresponding carboxylic acid has been proposed to proceed via bases-assisted nucleophilic attack of the Mo−OH on the substrate carbonyl, with concommitant hydride transfer to the Mo═S bond.

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10.1021/ic052161f CCC: $33.50

Mechanistic studies,[4] crystal structures of inhibited forms,[5] and X-ray absorption spectroscopy (XAS) as a structural probe of the active site of the enzymes indicate that the oxygen transferred to the substrate comes from the water/hydroxyl ligated to the Mo atom (Scheme 1). It appears that the pterin−dithiolene ligand does not participate directly in the chemistry of hydroxylation:[6] in all enzymes thus far characterized crystallographically, it is situated behind the molybdenum in the active site, on the opposite side of the metal from the water access channel and substrate binding site. Instead, the cofactor likely plays an indirect role in modulating the reduction potential and/or reactivity of the molybdenum center, in addition to having a role in electron-transfer either into or out of the metal center.[7−10] Romão et al.[11] have solved the crystal structure of aldehyde oxidoreductase from *D. gigas* (DgAOR). The proposed structure-based mechanism indicates that a water ligand is deprotonated by a nearby glutamate basic residue and thus primed to attack the carbonyl carbon atom of the substrate. This would trigger hydroxylation of the carbon center, causing an electron drift into the vacant Mo^{VI} d orbital and reduction to Mo^{IV} (Scheme 1). The overall reaction generates rather than consumes reducing equivalents, and the enzyme is subsequently reoxidized by NAD^+ or molecular oxygen in a reaction that occurs at the FAD (after electron transfer from the molybdenum center via the iron−sulfur centers).

While there has been progress in the generation of synthetic and functional analogue systems relevant to sulfite oxidase[7,8] and DMSO reductase molybdo-enzymes,[9] the dearth of oxo-thio species, $Mo^{VI}OS$, especially any with reactive aqua or hydroxo coligands, has provided little opportunity for the development of good chemical models for some characteristic reactions of xanthine oxidase class of enzymes. Recently, there has been some progress in the synthesis of monomeric *cis*-oxosulfido-Mo(VI) species which provide useful spectroscopic and reactivity information.[10]

Trisdithiolene complexes of transition metal have been much studied for several reasons including their trigonal prismatic structures and reversible electron transfer reactions which involve orbitals of mainly ligand character.[12] Initial results led to the recognition that many with the same metal and ligand may be interrelated by facile one-electron oxidation−reduction reactions during which the coordination remains intact. Complexes with varying overall charges of 0, −1, −2, $[M(S_2C_2R_2)_3]^{0/1-/2-}$ (M = Mo, W) with the metal in various oxidation states, may then be chemically or electrochemically formed which constitute members of electron transfer series. They obviously can act as sources (reduced complexes) or as sinks (oxidized complexes) of electrons and as such initiate or participate in many reactions.

The existence of metal−dithiolene coordination in all known tungsten and molybdenum enzymes provokes an imperative for new reactivity investigations of the robust and chemically well-characterized trisdithiolene complexes of these elements that may be related to enzymatic active sites. The results of recent investigations[13,14] provide compelling evidence that trisdithiolene complexes of Mo(VI) and W(VI), $M^{VI}(S_2C_2R_2)_3$, can bind a hydroxide ion reversibly. In the $Mo^{VI}(S_2C_6H_4)_3$ case, the seven-coordinate $[Mo^{VI}(S_2C_6H_4)_3(OH)]^-$ adduct may attack at a solvent water molecule, generating a dihydrogen peroxide Mo(IV) intermediate that yields the reduced Mo(V) complex and O_2.[15] In this article, we describe the results of an extensive investigation of the oxidation of a subtract like tertiary phosphines. The present system allows fast oxidations of phosphines via a coupled electron−proton transfer reaction involving a water molecule coordinated to a trisdithiolene−Mo(VI) complex, and is the first system to do so. Preliminary aspects of this investigation and certain related reactivity results have been briefly communicated.[15]

Experimental Section

Materials. The preparation and purification of neutral tris(benzene-1,2-dithiolate)molybdenum(VI), $Mo^{VI}(S_2C_6H_4)_3$, has been previously reported.[16] Only recrystallized samples were used for kinetics measurements. Unless otherwise indicated, all reactions were conducted under Ar. Anhydrous THF was distilled from CaH_2, while water of low conductivity was doubly distilled prior to use. Both solvents were degassed by five freeze/pump/thaw cycles and infused with Ar. Only fresh distilled solvents were used to prepare solutions. Triphenylphosphine and its derivatives $(p\text{-}CH_3C_6H_4)_3P$ and $(p\text{-}ClC_6H_4)_3P$ were obtained from Merck, and Bu_4NClO_4, acetic acid, phosphoric acid, and sodium hydroxide were obtained from Fluka. They were purchased in the highest available purity (> 99%) and were used as received. Water (95 atom % $H_2{}^{18}O$) was purchased from Cambridge Isotope Laboratories.

Instruments. Stopped-Flow Spectrophotometer. Kinetic runs were carried out on a SF-300 Biokine stopped-flow multimixing spectrophotometer (dead time 3−4 ms) equipped with a millisecond visible diode-array (minimum acquisition time 0.8 ms) and a quartz microcell (pathlength 1 cm, volume 40 μL). Typical diode integration times ranged from 1 ms to 5 ms depending on the observed

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reaction. The instrument was equipped with an anaerobic gas-flushing kit, and the temperature in the mixing cell was maintained to ±0.1 °C.

The pH of solutions used for kinetics measurements was determined by using a Radiometer model 62 pH meter and a combined electrode after calibration with standard buffer solutions.

HPLC/GC-MS. Separation and analysis of the solution products was achieved by means of reverse-phase chromatography. Aliquots of 25 μL (typically $10^{-2}-10^{-4}$ M in PPh_3) were injected onto a Kromasil C-18 (150 × 4.6 mm) column (Scharlau) via an injector (Rheodyne) attached to a Waters 515 HPLC isocratic pump. The compounds were detected with a variable wavelength UV100 UV−vis detector at the maximum absorbance of PPh_3 (265 nm). Mass spectra studies were carried out with a Varian Star 3400 CX gas chromatograph equipped with a 30 m phenyl-methyl siloxane capillary column, attached to a Varian Saturn 3 MS detector.

Kinetic Measurements. Stopped-Flow Measurements. Phosphines react so quickly with $Mo(S_2C_6H_4)_3$ and water that reaction rates were investigated using the stopped-flow technique. Depending on the reaction rate, kinetics were followed scanning from 100 to 1000 spectra between 400 and 800 nm with a fast diode-array detector. Typical observation times ranged from 0.5 to 25 s.

In a typical experiment, stock solutions of $Mo(S_2C_6H_4)_3$ (1.5×10^{-4} M, solution A), and PPh_3 (2.50×10^{-2} M) in THF, and aqueous Bu_4NOH (0.1 M) were prepared. Aqueous buffer solutions of known pH were prepared by mixing the appropriate amount of Bu_4NOH, glacial acetic acid (0.2 M in acetic/acetate), and Bu_4NClO_4 (0.2 M in the tetrabutylammonium cation). These solutions were used to prepare buffered solutions of PPh_3 (by mixing 15 mL of the PPh_3 stock solution and 10 mL of buffer (solution B)), and auxiliary solutions (by mixing 10 mL of THF with 10 mL of buffer (solution C)) were used to dilute the PPh_3 solutions. The reaction mixtures were prepared in situ by mixing solutions A, B, and C in a volumetric ratio 3:x:10−x (x ranging from 1 to 7) making use of the automatized mixing facilities fitted up on the SF-300 Biokine stopped-flow multimixing spectrophotometer. The injected volume of A was constant, whereas variable amounts of excess phosphine, B, were injected. The sum of the volumes of B and C, the buffer and water amounts, was always the same. After mixing, the initial concentrations of reactants were as follows: 4.30×10^{-5} M in $Mo(S_2C_6H_4)_3$, 15.7 M in H_2O, and the PPh_3 concentration ranged from 10^{-2} M (x=7) to 1.5×10^{-3} M (x=1).

Catalytic Oxidation of Tertiary Phosphines. Catalytic oxidations of phosphines do occur under air but at much longer time-scales than those of the stopped-flow experiments, where just a net stoichiometric redox reaction of one phosphine molecule with two of $Mo(S_2C_6H_4)_3$ takes place. In a typical experiment, 3.0 mg (6.4×10^{-3} mmol) of $Mo(S_2C_6H_4)_3$ were dissolved with 50 mL of a solution prepared dissolving 40 mg (0.15 mmol) of PPh_3 in 100 mL of a THF/H_2O 4:1 v/v mixture. This reactive mixture was poured into a 100 mL round-bottom flask equipped with a magnetic stir bar and condenser. This mixture was heated to 35 °C and stirred at that temperature under air for 4−6 h.

The yield of oxidized phosphine was determined by HPLC analyses carried out on aliquots of 0.25 mL extracted from the reaction vessel every 30 min. The chromatographic peaks corresponding to PPh_3 an $OPPh_3$ species were resolved passing through the column a mobile phase of the same composition than that used to perform the reaction. Good separations were achieved under isocratic conditions at a flow rate of 1.0 mL/min. Elution times of the complex product, $Mo(S_2C_6H_4)_3^-$ (0.8 min), $OPPh_3$ (1.4 min), and PPh_3 (1.8 min) agreed with those of authentic samples under the same chromatographic conditions. The percentage of phosphine and phosphine oxide was determined by integration of both peaks

For the reaction of $Mo(S_2C_6H_4)_3$ with PPh_3 in $H_2{}^{18}O$/THF, PPh_3 and $OPPh_3$ were resolved making use of the following chromatograph settings: injector at 250 °C; MS-detector at 260 °C; transfer line at 250 °C; oven initially at 100 °C and then heated to 250 °C at 35 °C min^{-1} keeping this temperature balanced for 8 min ($t_r(OPPh_3)$=11.9 min, $t_r(PPh_3)$=9.05min). Helium was used as the carrier gas at the flow rate of 1 mL min^{-1}.

Results and Discussion

General Features. Consistent with a prior literature report,[17] we find that neutral tris(benzene-1,2-dithiolate)-molybdenum(VI), $Mo^{VI}(S_2C_6H_4)_3$, is not detectably reduced by triphenylphosphine in neat THF, and hence its electronic spectrum is unchanged by the presence of PPh_3 (up to 0.1 M). Noticeably, we have observed that if water is added, a quantitative and very rapid reduction of $Mo^{VI}(S_2C_6H_4)_3$ to $Mo^V(S_2C_6H_4)_3^-$ monoanion occurs. The neutral $Mo^{VI}(S_2C_6H_4)_3$ complex is therefore inert to PPh_3 in the absence of water, and an observable and rapid reaction takes place only in the presence of all three components. Both $Mo^{VI}(S_2C_6H_4)_3$ and $Mo^V(S_2C_6H_4)_3^-$ complexes have been thoroughly characterized elsewhere.[16] The characterization consisted of solid and solution electronic spectra, solid structures, polarographic and CV potentials, and the ESR spectrum of Mo(V).

HPLC and ^{31}P NMR spectroscopy were used for a quantitative determination of the triphenylphosphine-derived product of the reaction with $Mo^{VI}(S_2C_6H_4)_3$ and water. Both techniques confirmed that triphenylphosphine oxide was formed in the yield of $[Mo^{VI}(S_2C_6H_4)_3)]_0/[OPPh_3] = 2$. In view of the quantitative conversion of $Mo^{VI}(S_2C_6H_4)_3$ to $Mo^V(S_2C_6H_4)_3^-$ and the yield of $OPPh_3$, it is evident that the reaction stoichiometry can be described by eqs 1 and 2 occurring in parallel

$$Mo^{VI}(S_2C_6H_4)_3 + H_2O + PPh_3 \rightarrow Mo^{IV}(S_2C_6H_4)_3{}^{2-} + 2H^+ + OPPh_3 \quad (1)$$

$$Mo^{IV}(S_2C_6H_4)_3{}^{2-} + Mo^{VI}(S_2C_6H_4)_3 \rightarrow 2Mo^V(S_2C_6H_4)_3{}^- \quad (2)$$

The overall process is described by reaction 3, the reduction of $Mo^{VI}(S_2C_6H_4)_3$ to $Mo^V(S_2C_6H_4)_3^-$, which represents a redox interaction that is accompanied by a drop in pH. Upon complete reduction of a 10^{-4} M solution of $Mo^{VI}(S_2C_6H_4)_3$ in THF/water (11.2 M) by PPh_3 (10−20 equiv) the pH decreases in fact (from about 6.8 to 5.5).

$$2Mo^{VI}(S_2C_6H_4)_3 + H_2O + PPh_3 \rightarrow 2Mo^V(S_2C_6H_4)_3{}^- + 2H^+ + OPPh_3 \quad (3)$$

Equation 3 parallels a process currently achieved only in nature by most pterin enzymes which mediate formal oxygen

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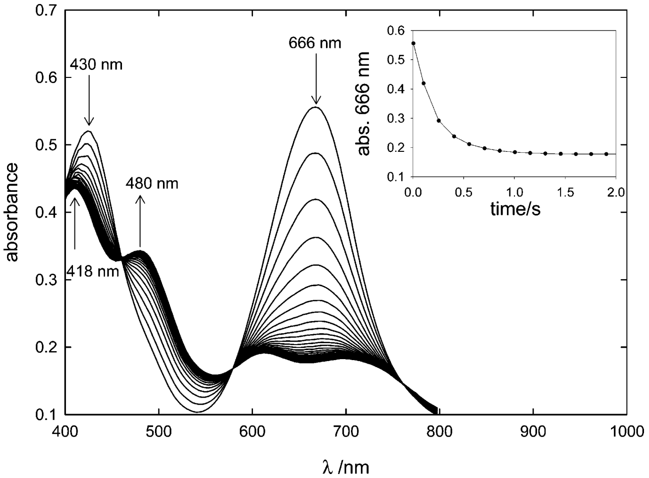

Figure 1. UV-vis/time traces monitoring the conversion from $Mo^{VI}(S_2C_6H_4)_3$ (1.25×10^{-5} M) ($\lambda_{max} = 666$ and 430 nm) to $Mo^{V}(S_2C_6H_4)_3^-$ ($\lambda_{max} = 480$ and 418 nm) at 23 °C in THF/water (15.4 M) in the presence of 1.07×10^{-2} M PPh_3 and acetic acid/tetrabutylammonium acetate buffer (pH=6.40). First spectrum taken after 5 ms, showed every 50 ms. The inset shows the absorbance trace at 666 nm fitted to a single-exponential function of the type $a+be^{-kt}$ (solid line).

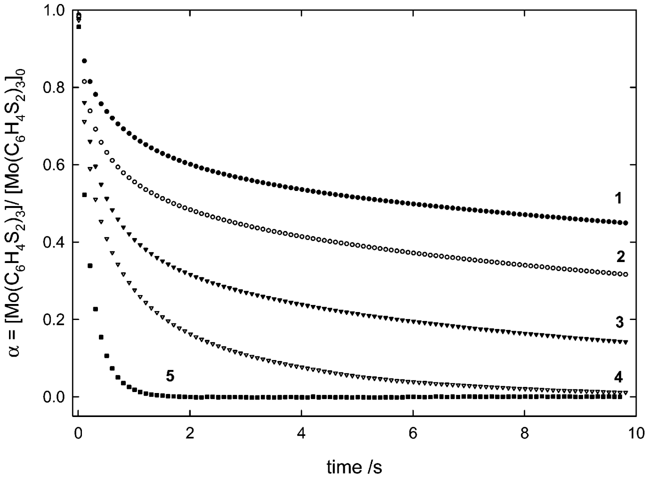

Figure 2. Plots of the molar fraction of the neutral molybdenum complex, $\alpha = [Mo^{VI}(S_2C_6H_4)_3]/[Mo^{VI}(S_2C_6H_4)_3]_0$, vs time for different initial concentrations of $Mo^{VI}(S_2C_6H_4)_3$: (**1**) 6.25×10^{-4} M; (**2**) 3.75×10^{-4} M; (**3**) 3.13×10^{-4} M; (**4**) 2.50×10^{-4} M; (**5**) 1.25×10^{-4} M. The α values were obtained from absorbance-time traces at 666 nm, $\alpha = (A_\infty - A_t)/(A_\infty - A_0)$, on reactions with PPh_3 (5.1×10^{-2} M) at 25 °C in THF/water (6.93 M) solutions.

atom exchange between substrate X and water, e.g.: $X + H_2O \rightleftarrows XO + 2H^+ + 2e^-$.[1]

Kinetics

We designate $Mo^{VI}(S_2C_6H_4)_3$, $Mo^{V}(S_2C_6H_4)_3^-$, and $Mo^{IV}(S_2C_6H_4)_3^{2-}$ as Mo(VI), Mo(V), and Mo(IV), respectively, and $[Mo(VI)]_0$ as the initial concentration of Mo(VI). All of the kinetic experiments described below were conducted with a large excess of PPh_3 in the range $[PPh_3]_0 = 0.001-0.01$ M in deoxygenated THF/water solutions, 0.056 M ionic strength (maintained with n-Bu_4NClO_4) at several concentrations of water.

Rate Law. Because reaction 3 was complete in a very short time, it was monitored by stopped-flow spectrophotometry. Figure 1 illustrates the time course of a representative reaction system. The absorption bands of the initial complex, Mo(VI), at 666 and 430 nm diminish in intensity as the reaction proceeds, and features at 480 and 418 nm emerge. Three tight isosbestic points at 462, 579, and 770 nm were observed, indicating no significant accumulation of an intermediate. The final spectrum is identical with that of Mo(V) measured separately. Thus, Figure 1 shows the total transformation of Mo(VI) into Mo(V) within the 0.5 s observing time of this experiment. To determine the parameters affecting the rate of this reaction, it has been performed under many varying conditions. Below, the independent effects of pH, concentration of various components, temperature, and phosphine substituents are discussed.

Figure 2 illustrates the variation of the molar fraction of Mo(VI), $\alpha = [[Mo(VI)]/[Mo(VI)]_0$, vs time for several initial concentrations of Mo(VI). This type of plots should be exponential if the reaction obeys first-order kinetics. Notably, the reaction is quite slow at high $[Mo(VI)]_0$ concentrations and yields intractable kinetics, whereas at low $[Mo(VI)]_0$ the reaction is much faster and deviates only slightly from pseudo-first-order behavior. Such dependence on $[Mo(VI)]_0$ appears to be a general proton effect because H_3O^+ concentration, the cation associated with the formed complex anion Mo(V), depends on $[Mo(VI)]_0$ (eq 2).

The participation of H_3O^+ as a moderator becomes evident by analyzing the role of pH on the reaction rate. Selected buffers (acetate and phosphate) at the 0.056 M concentration were employed to determine this dependence over the pH range of 7.0−3.5 in 14.5 M water at 0.056 M ionic strength. To prevent possible complications caused by the direct interaction of Mo(VI) with OH^- at a high pH,[13] no reaction was performed at pH > 7.0. At any given pH, the reaction is first order in Mo(VI) concentration as shown by the linearity of plots of $\ln(A-A_\infty)$ vs time in experiments with greater than 10 equiv of PPh_3. The slopes of these lines, the pseudo-first-order constant, k_{obs}, markedly increased with the initial PPh_3 concentration (Figure 3).

As shown in Figure 4, plots of k_{obs} vs $[PPh_3]_0$ at different pHs are nonlinear, showing saturation kinetics at high phosphine concentrations. The data are well-fitted to Michaelis−Menten eq 4; double reciprocal plots generate straight lines which afford k_B/k_A (the x axes intercept) and $1/k_A$ as the slope. The logarithms of the slopes are plotted vs pH in the inset of Figure 4, where an inverse dependence is obtained ($k_A = k_C/[H_3O^+]$).

All together, the empirical rate, r, for Mo(VI) reduction by triphenylphosphine in the presence of buffer can be expressed by eq 4

$$r = -\frac{d[Mo(VI)]}{dt} = k_{obs}[Mo(VI)] = \frac{(k_C[H_3O^+]^{-1})[PPh_3]}{1 + k_B[PPh_3]}[Mo(VI)] \quad (4)$$

Because of the acid−base properties of a water molecule potentially bound to Mo(VI), the observed pH-dependence of the reaction rate suggests that $Mo^{VI}(S_2C_6H_4)_3$ reacts with

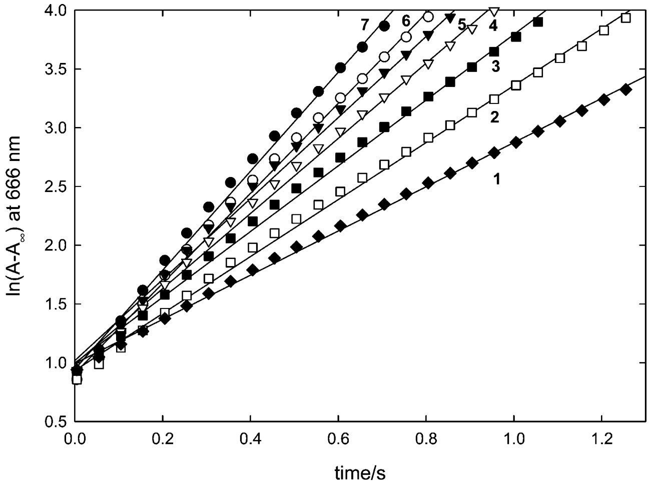

Figure 3. Logarithmic variation of absorbance at 666 nm vs time corresponding to the loss of $Mo^{VI}(S_2C_6H_4)_3$ (initial concentration 4.57×10^{-5} M) on reaction with PPh_3 (initial concentrations: (**1**) 1.53×10^{-3} M; (**2**) 3.07×10^{-3} M; (**3**) 4.60×10^{-3} M; (**4**) 6.13×10^{-3} M; (**5**) 7.67×10^{-3} M; (**6**) 9.21×10^{-3} M; (**7**) 1.07×10^{-2} M). The solvent THF/water, 14.5 M in water, contained acetic acid/tetrabutylammonium acetate buffer to maintain the pH at 6.4, and Bu_4NClO_4 to control the ionic strength at 0.056 M (T=23 °C). First-order rate constants k_{obs} are directly obtained from the slope of the linear plots.

H_2O to form an addition complex intermediate. To probe such interaction, the kinetics of the reaction between Mo(VI) and PPh_3 were studied in different THF/H_2O solvent mixtures covering a significant range of water concentrations, from 3 to 20 M, at controlled ionic strength of 0.04 M. The buffer was removed to avoid rate variations attributable to changes in pH owed to the dependence of the acidic constant of the buffer (K_{HB}) on water concentration.

In each THF/H_2O mixture, the absorption spectrum of Mo(VI) and Mo(V) remained quantitatively the same with only very slight shifts (<5 nm) of band maxima. Isosbestic points in Figure 1 were maintained, but the first-order rate dependence upon Mo(VI) concentration was lost as the reaction advanced due to variations in the pH. Because of this limitation, the reaction kinetics was studied by means of an initial rate method. Initial rates were evaluated from absorbance vs time curves, monitored at 666 nm, by extrapolation at $t = 0$, according to equation $r_0 = 1/(\epsilon_{Mo(VI)} - \epsilon_{Mo(V)}) \times (dA/dt)_{t=0}$, where $\epsilon_{Mo(VI)}$ and $\epsilon_{Mo(V)}$ are the optical densities of Mo(VI) and Mo(V) complexes, respectively.

Significant increases in the values of the initial rate (r_0) are obtained as the water concentration is increased. This is made particularly evident in Figure 5, where the observed values of r_0 are represented vs water concentration. The trace indicates that r_0 is small and varies quadratically at low water concentrations (<5 M), whereas at higher water concentrations (>8 M) a linear dependence with the slope of 1.0 is observed. Although such dependence of r_0 on water concentration appears to be quite complex, the rate data give an excellent fit to eq 5, which will be justified on a mechanistic basis later on.

$$\frac{r_0}{[\mathrm{Mo(VI)}]_0} = \frac{k_D[\mathrm{H_2O}]^2}{1 + k_E[\mathrm{H_2O}]} \qquad (5)$$

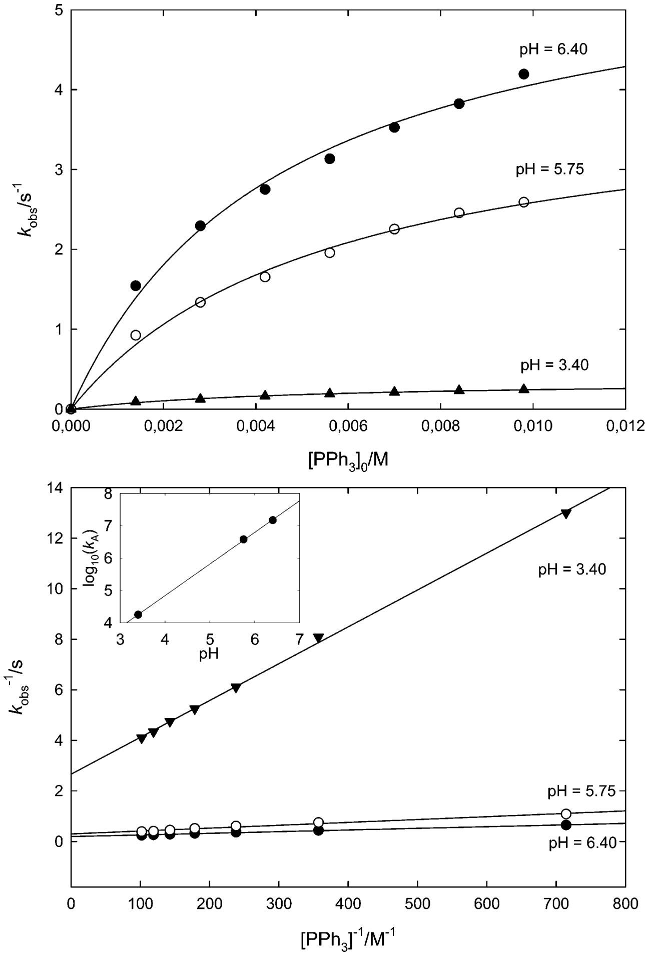

Figure 4. Upper: dependence of the pseudo-first-order rate constants k_{obs} on the phosphine concentration in buffered THF/H_2O (14.5 M) solutions at 23 °C. Lower: plots of $1/k_{obs}$ vs $1/[PPh_3]$ for the reactions in the upper figure. Inset shows the logarithmic variation of the slopes vs pH, which is a line of slope 1.0_2. The initial concentration of $Mo^{VI}(S_2C_6H_4)_3$ 4.57×10^{-5} M.

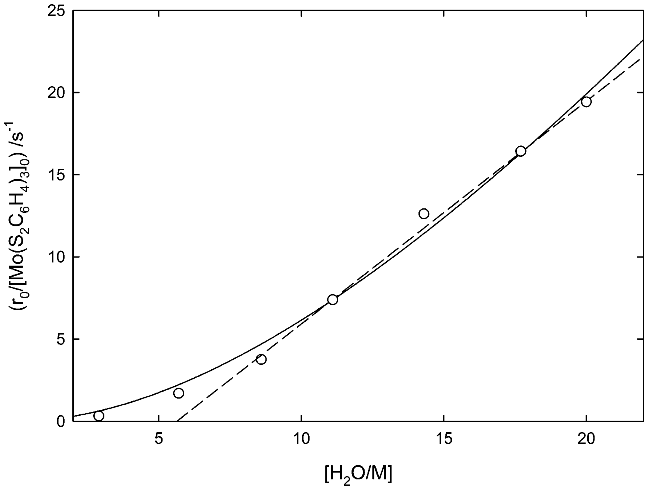

Figure 5. Plot of $r_0/[Mo(VI)]_0$ vs $[H_2O]_0$ at low complex concentration. The initial concentrations of $Mo^{VI}(S_2C_6H_4)_3$ and PPh_3 are 3.8×10^{-5} M and 8.9×10^{-3} M, respectively, in THF with the ionic strength controlled at 0.04 M by tetrabutylammonium perchlorate. T = 22.7 °C. The solid line shows the fit to eq 5. Dashed line illustrates the linear dependence of the initial rate on water concentration at $[H_2O] > 8$ M (slope=1.0).

Phosphine Substituent Effects. Electron withdrawing substituents (X=Cl) in $(p\text{-}XC_6H_4)_3P$ remove electron density

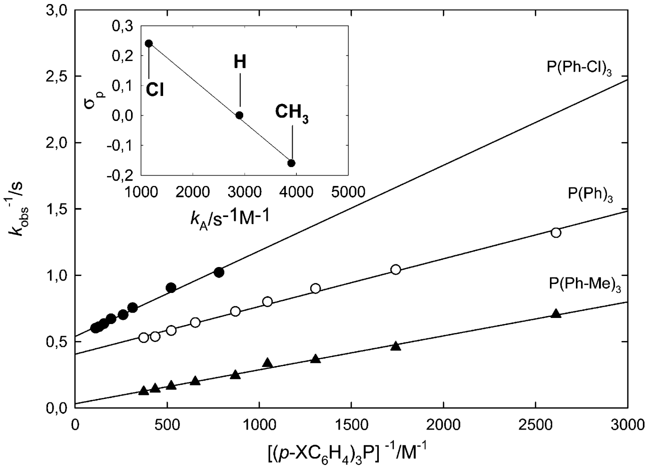

Figure 6. Variation of k_{obs}^{-1} with $[p\text{-}(XC_6H_4)_3P]^{-1}$ (X=Cl, H, CH_3). Experimental conditions: $[Mo^{VI}(S_2C_6H_4)_3] = 3.5 \times 10^{-5}$ M; solvent THF/water; $[H_2O]$ =15 M; acetic/tetrabutylammonium acetate buffer with the ionic strength controlled at 0.056 M by tetrabutylammonium perchlorate at pH 7.4; T = 25 °C. From the slope of these lines the following values of k_A were obtained: X = CH_3, k_A = 3900 s^{-1} M^{-1}; X = H, k_A = 2900 s^{-1} M^{-1}; X = Cl, k_A = 1150 s^{-1} M^{-1}. Inset: plot of Hammett σ_p vs k_A for $(p\text{-}XC_6H_4)_3P$.

from the phosphorus atom, making the phosphine more electrophilic, whereas the opposite effect occurs for electron donating substituents (X=CH_3).

This difference in the electrophilic character of the phosphine is manifested in the systematic variation of the specific rate constants, k_A, that is obtained for the reaction with Mo(VI) at a fixed pH and water concentration. With the data shown in Figure 6 there is a linear dependence of k_A versus the Hammett σ_p parameter[18] for the X substituent. The phosphine contains substituents that span the range from electron withdrawing (X=Cl) to electron donating (X=CH_3), and the rate constant for X=Cl is approximately a factor of 5 larger than that found for X=CH_3. These results clearly demonstrate that the changes in the k_A value are controlled by the various substituents that are found in the phosphine.

Comparison with Dioxo-Mo(VI) ($Mo^{VI}O_2$) Complexes

Triphenylphosphine is a common substrate in nonbiological oxygen atom transfer reactions, which simulates nucleophiles such as sulfite that are proposed to attack $Mo^{VI}=O$ groups in substrate oxidations. Reactions with dioxo and monooxo Mo(VI) complexes are generally second-order, first-order in both complex and phosphine, with rate constants in the range $10^{-6}-10^{-2}$ M^{-1} s^{-1}, depending on the nature of the coligands.[19] The bimolecular reaction of $MoO_2(S_2CNEt_2)_2$ and PPh_3 in 1,2-dichloroethane is the fastest for which kinetic data are available (k_2=7.1 × 10^{-2} M^{-1} s^{-1}; T=25 °C).[20] According to eq 4, the values of the above rate constant k_A, which depend on proton and water concentrations, are strictly comparable to this second-order rate constant. This is graphically illustrated in Figure 7. The conclusion is inescapable that, in terms of second-order rate constants, the rate for PPh_3 oxidation by $MoO_2(S_2CNEt_2)_2$ is several orders of magnitude lower. According to Figure 7, at pH = 6.4 and in THF/water 15 M, the rate constant k_A is ca. 10^5 times larger.

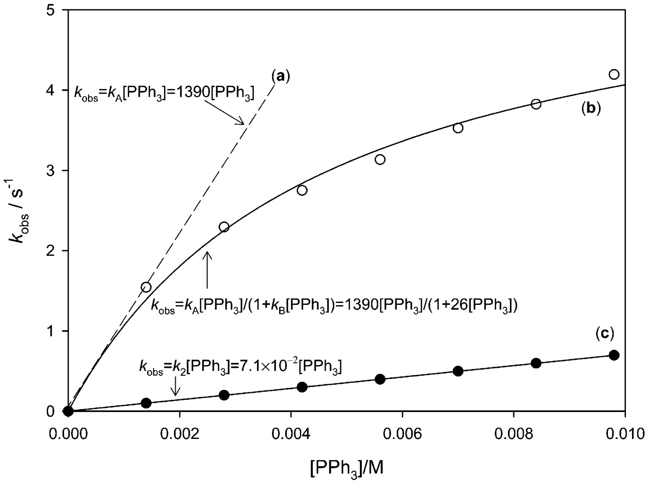

Figure 7. (a) Plot of k_{obs} when $[PPh_3]_0$ tends to 0; (b) experimental data fitted to eq 4 (pH=6.4; THF/water (15 M); and (c) pseudo-first-order rate constants obtained from the second-order rate constant for the reaction of $MoO_2(S_2CNEt_2)_2$ and PPh_3 in 1,2-dichloroethane (k_2=0.071 s^{-1} M^{-1};[20] the represented k_{obs} values have been multiplied by a factor f=1000).

In the $Mo^{VI}O_2/PR_3$[21] and $Mo^{VI}O/PR_3$[22] systems, the intermediates $Mo^{IV}O(OPR_3)$ and $Mo^{IV}(OPR_3)$, respectively, have been detected by mass spectrometry, which explains that reactions are second order and proceed through associative transition states: nucleophilic attack by the organophosphine lone pair on a π^* Mo=O orbital producing the oxo(phosphoryl)molybdenum(IV) intermediate that rapidly transforms into product.[23] Further, oxo(phosphine oxide)-molybdenum(IV) complexes have been isolated and structurally characterized from the reaction of the complexes *cis*-$Tp^{iPr}MoO_2(OAr)$ (Tp^{iPr} = hydrotris(3-isopropylpyrazol-1-yl)borate, ^-OAr = phenolate or naphtholate derivative) with PEt_3.[24]

Obviously, this mechanism cannot be operative in a system having no π^* Mo=O orbitals, and for the present one an oxygen lone pair of a coordinated water (or OH^-) molecule can conceivably be used to interact with a vacant orbital of phosphorus atom in the phosphine. Such interaction would lead to a Mo(VI) rather than a Mo(IV) complex intermediate, $Mo^{VI}(S_2C_6H_4)_3(OPPh_3)^{2-}$, which results unstable with respect to disproportionation into $Mo^{IV}(S_2C_6H_4)_3^{2-}$ and $OPPh_3$, as shown below in Scheme 2. The nature of this complex intermediate, as deduced from the current kinetics data, as well as the relevance of reaction 3 to enzymes will be considered in the following section. However, the large value found for the observed rate contant (low activation energy)

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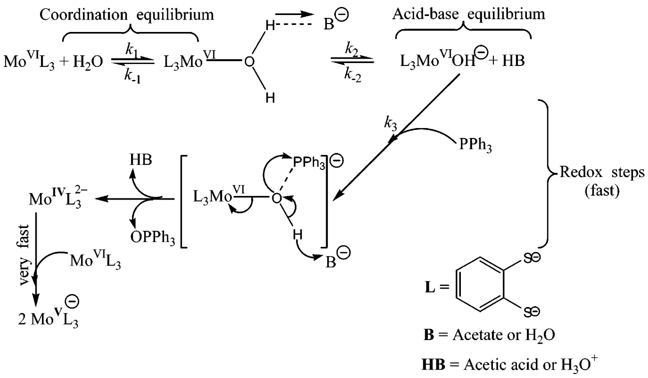
Scheme 2



is consistent with a mechanism which does not involve the break of a $Mo^{VI}{=}O$ bond.

Reaction Mechanism

A plausible initiation mechanism would parallel that reported for the reductive half-cycle of xanthine oxidase (Scheme 1), where a direct and specific interaction between the solvent water and the Mo(VI) center occurs. Accordingly, we propose the sequence illustrated in Scheme 2, whereby initial attack of water on $Mo^{VI}(S_2C_6H_4)_3$ results in the mononuclear seven-coordinated aqua trisdithiolene species $Mo^{VI}(S_2C_6H_4)_3(H_2O)$. In this context we note that the interaction of water molecules through the metal (additional coordination) has been reported as a possible explanation for the broadening of the dithiolenic hydrogen in tris(1,2-dithiolenes) complexes of Mo(VI) and W(VI) when monitored by ^{1}H NMR spectroscopy in acetone/water mixtures.[25]

Water must be weakly coordinated to the Mo(VI) atom in this seven-coordinated molybdenum complex since the equilibrium constant K_1 $(=k_1/k_{-1})$ for the formation of this adduct is apparently very low ($k_1 \ll k_{-1}$ in Scheme 2). In fact, we failed to observe any adduct formation by NMR or electronic spectroscopy in an acidic THF solution of Mo(VI) containing a high concentration of water ca. THF/water 40:60 v/v (ambient conditions).

The coordination to molybdenum would increase the acidity of the water molecule,[26] and coordination must be followed by a deprotonation equilibrium whose extent is dependent upon the pH and ionic strength of the medium. This proton transfer from the coordinated water to solvent water would give the hydroxide complex intermediate, $Mo^{VI}(S_2C_6H_4)_3(HO)^-$, which would be also a seven-coordinate Mo(VI) species. The above observed pH dependence of reaction rate provides a clear indication that the concentration of this last species limits the overall rate of reduction of Mo(VI). As in the case of the xanthine oxidase enzyme, the nucleophilic attack on substrate apparently requires the coordinated water molecule to be in the unprotonated hydroxide form, which results much more reactive than the protonated water form. So, the redox step of the mechanism would then involve nucleophilic attack of the Mo−OH group on the phosphorus atom of PPh_3, generating the $OPPh_3$ molecule and one solvated proton. A simultaneous two-electron shift from the Mo−OH bond to the Mo(VI) center leads to the reduction to Mo(IV). However, the stable complex product is the Mo(V) complex, which indicates that the Mo(IV) complex interacts subsequently with unreacted Mo(VI) to form the Mo(V) complex. This is a very common reaction in the chemistry of Mo(IV) complexes,[23] and, for the case of trisdithiolene complexes, such reaction of comproportionation could be constrained to occur by an outer-sphere mechanism at or near the diffusion-controlled limit:

$$Mo^{IV}(S_2C_6H_4)_3{}^{2-} + Mo^{VI}(S_2C_6H_4)_3 \rightarrow 2Mo^{V}(S_2C_6H_4)_3{}^{-} \tag{6}$$

In an attempt to support better the fast character of reaction 6, a brief study of the rate was carried out in neat THF by stopped-flow spectrophotometric technique. First, the absorbance of Mo(VI) and Mo(IV) complexes decayed to produce Mo(V). Second, both complexes react so quickly that total formation of Mo(V) was observed after the mixing time (3 ms) of stoichiometric amounts of the Mo(IV) and Mo(VI) complexes. This means a lower limit for the rate constant for reaction 6 of $k > 3 \times 10^6\ s^{-1}\ M^{-1}$, and an extensive kinetics study was prohibited by the extremely rapid rate of this reaction.

On account for the observed rate law (eq 4), and to endow the rate coefficients in this equation with chemical meaning, the steady-state approximation was applied to the concentrations of $Mo^{VI}(S_2C_6H_4)_3(H_2O)$, $Mo^{VI}(S_2C_6H_4)_3(HO)^-$, and $Mo^{IV}(S_2C_6H_4)_3{}^{2-}$ intermediates in Scheme 2. Considering that $r = -d[Mo(VI)]/dt = d[Mo(V)]/dt$, the deduced rate equation is (see the Supporting Information)

$$r = \frac{(k_3K_1K_2K_{HB}[H_3O^+]^{-1})[H_2O][PPh_3]}{1 + \left\{\dfrac{k_3K_{HB}(k_{-1}[HB] + k_2)}{k_{-1}k_{-2}[H_3O^+]}\right\}[PPh_3]}[Mo(VI)] \tag{7}$$

where K_{HB} represents the buffer acid dissociation constant, and k_3, k_{-1}, k_{-2}, K_1, and K_2 are the rate constant and equilibrium constants indicated in Scheme 2. This rate law has the same form as the empirical rate law (eq 4), allowing k_C and k_B to be estimated:

$$k_C = (k_3K_1K_2K_{HB})[H_2O] \tag{8}$$

$$k_B = \frac{k_3K_{HB}(k_{-1}[HB] + k_2)}{k_{-1}k_{-2}[H_3O^+]} \tag{9}$$

If the reaction is conducted in the absence of buffer, the deduced rate equation takes the form of eq 10 (see the Supporting Information)

$$r = \frac{k_3k_2k_1[PPh_3][H_2O]^2}{k_{-1}k_{-2}[H_3O^+] + k_3(k_{-1} + k_2[H_2O])[PPh_3]}[Mo(VI)] \tag{10}$$

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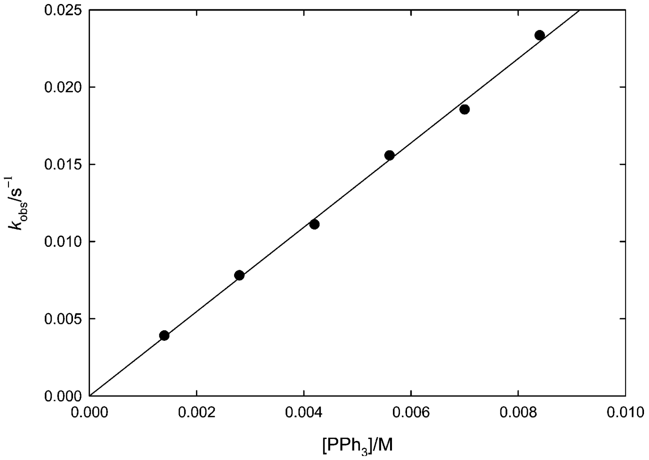

Figure 8. Dependence of k_{obs} on the [PPh_3] in perchloric acid media. [$Mo(S_2C_6H_4)_3$] = 4.8 × 10^{-5} M; [H_2O] = 15.4 M; [$HClO_4$] = 0.11 M (pH = 1.27); T = 24.3 °C. The slope of the line was $k = 2.7\ s^{-1}\ M^{-1}$.

An expression that can be rewritten as eq 11 at initial times is

$$\frac{r_0}{[\mathrm{Mo(VI)}]_0} = \frac{(k_2K_1)[\mathrm{H_2O}]^2}{1 + \left(\dfrac{k_1}{k_{-2}}\right)[\mathrm{H_2O}]} \tag{11}$$

Eq 11 is identical to that found empirically from the initial rate study (eq 5). Finally, eq 10 predicts that reactions conduced at very low pH ($k_{-1}k_{-2}[H_3O^+] \gg k_3(k_{-1} + k_2[H_2O])$) must exhibit a linear dependence of k_{obs} with regard to the PPh_3 concentration rather than a saturation kinetics (eq 12). Figure 8 illustrates the expected behavior in $HClO_4$ media.

$$r = \frac{(k_3K_2K_1[\mathrm{PPh_3}])[\mathrm{H_2O}]^2}{[\mathrm{H_3O^+}]}[\mathrm{Mo(VI)}] = k[\mathrm{PPh_3}][\mathrm{Mo(VI)}] \tag{12}$$

Autoxidation of the Reduced Mo(V) complex

Gray and co-workers[27] qualitatively first observed that olive-green solutions of $Mo^V(S_2C_6H_3CH_3)_3^-$ in 2-CH_3-THF are partially oxidized by air giving the neutral green complex $Mo^{VI}(S_2C_6H_3CH_3)_3$. To test this point, we have undertaken a study of the oxidation of $Mo^V(S_2C_6H_3CH_3)_3^-$ in oxygenated THF/water media at different pHs. A possible reaction sequence involves direct interaction with oxygen to yield O_2^-, followed by the disproportionation of HO_2 (eqs 14 and 15).

$$\mathrm{Mo^V(S_2C_6H_4)_3^-} + \mathrm{O_2} \rightarrow \mathrm{Mo^{VI}(S_2C_6H_4)_3} + \mathrm{O_2^-} \tag{14}$$

$$\mathrm{O_2^-} + \mathrm{H^+} \rightarrow 1/2\mathrm{H_2O_2} + 1/2\mathrm{O_2} \tag{15}$$

Accordingly, we found that although the tetrabutylammonium salt of $Mo^V(S_2C_6H_4)_3^-$ is not oxidized by O_2 in an air-saturated THF/water solution, the addition of excess acid ($HClO_4$ 0.01 M) results in the partial (~85%) oxidation of $Mo^V(S_2C_6H_4)_3^-$ to $Mo^{VI}(S_2C_6H_4)_3$. The reaction is a slow process that could be monitored by using conventional mixing spectrophotometric techniques. Specifically, at pH 1 and in aired solutions of THF/water 80:20 v/v, the reaction was first-order on Mo(V) complex concentration for ~70% of the reaction with $t_{1/2}$ ~ 20 s. Deviations at longer time were due to partial decomposition. However, a series of experiments showed that the radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol (BHT) is effective in producing good pseudo-first-order kinetics without grossly perturbing the reaction rates. Figure 9 shows the result when the reaction is conducted with 2 mM BHT; the loss of Mo(V) obeys excellent first-order kinetics, and the half-life is similar to that in the absence of BHT. Accordingly, we infer that BHT scavenges some minor reactive radicals that are short-chain carriers.

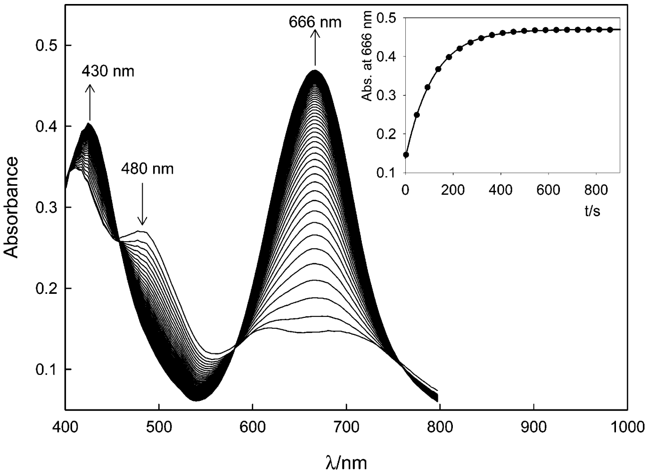

Figure 9. UV−vis/time traces monitoring the conversion from Mo^V-$(S_2C_6H_4)_3^-$ (3.14 × 10^{-5} M) (λ_{max} = 480 and 418 nm) to $Mo^{VI}(S_2C_6H_4)_3$ (λ_{max} = 666 and 430 nm) at 34.4 °C in THF/water (11 M) in the presence of 2.0 × 10^{-2} M BHT and [$HClO_4$] = 1.44 × 10^{-2} (pH=1.8). The inset shows the absorbance trace at 666 nm fitted to a single-exponential function of type a+b(1-e^{-kt}) (solid line).

Figure 9 demonstrates that the spectral variation with time for the Mo(V) oxidation by air is the reverse of that in Figure 1 (Mo(VI)→ Mo(V) transformation), with the 420 and 480 nm bands decreasing, and the 666 nm band increasing in intensity as the reaction proceeds. Mo(V) is completely consumed, and the final spectrum is consistent with a complete conversion to Mo(VI). Observed first-order constant values decreased as the pH increases, varying by 1 order of magnitude between 2 (8 × 10^{-3} s^{-1}) and pH 7 (5 × 10^{-4} s^{-1}). Additionaly, these rate constants are 10^2−10^3 lower than those noted above for the reactions of Mo(VI) with PPh_3 and water.

Autoxidation of Triphenylphosphine Catalyzed by $Mo^{VI}(S_2C_6H_4)_3$ and Water

Catalytic oxidations of phosphines[8] and thiols[28] involving *cis*-dioxo-Mo(VI) complexes with sulfur ligands but not dithiolenes are available in the literature. These systems appear to require O_2 and/or water for regeneration of $[Mo^{VI}O_2]^{2+}$ from $[Mo^{IV}O]^{2+}$ species formed via the oxygen

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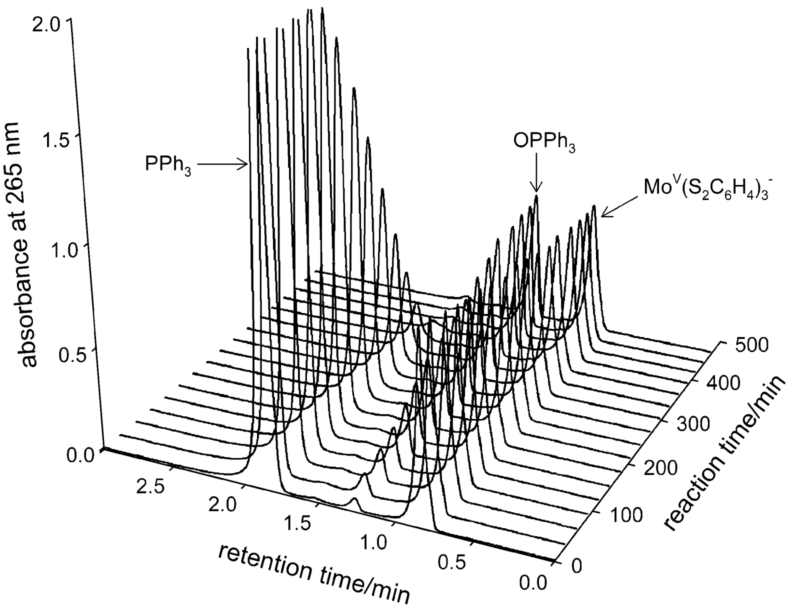

Figure 10. HPLC chromatograms obtained from a reactive mixture containing 6.4 × 10^{-3} mmol of $Mo^{VI}(S_2C_6H_4)_3$, 0.16 mmol of PPh_3 in 50 mL of THF/water 80:20 v/vs $t_r(Mo^{VI}(S_2C_6H_4)_3) = 0.86$ min, $t_r(OPPh_3) = 1.28$ min, $t_r(PPh_3) = 1.86$ min.

atom transfer (OAT) reaction from the $[Mo^{VI}O_2]^{2+}$ complex to the phosphine. Herein, the occurrence of reactions 3 and 14 led to the possibility of the two reactions being coupled to produce a catalytic cycle that is operative at room temperature. The overall reaction, which is the formation of $OPPh_3$ from O_2 and PPh_3, can be divided into two parts. First, two protons and $OPPh_3$ are simultaneously generated from water and PPh_3 (reaction 3). Second, reoxidation of Mo(V) to Mo(VI) by O_2 consumes protons and generates H_2O_2 (eqs 14 and 15), which oxidizes another equivalent of phosphine to its oxide.

When $Mo^{VI}(S_2C_6H_4)_3$ was dissolved in an open-air THF/water (80/20 v/v) solution containing up to 10 equiv of PPh_3, UV−vis spectral changes indicate that very rapid formation of $Mo^V(S_2C_6H_4)_3^-$ takes place. Thus, the final spectrum lacks the intense visible bands of the neutral Mo(VI) complex and reveals no features unattributable to the monoanionic Mo(V) complex, which remains unchanged until all PPh_3 is oxidized to $OPPh_3$. Apparently, as expected from the above kinetics results, reaction 3 is much more rapid than reaction 14 and leads to a fairly constant concentration of $Mo^V(S_2C_6H_4)_3^-$ throughout catalysis, which is approximately equal to $[Mo^{VI}(S_2C_6H_4)_3]_0$.

High-performance liquid chromatography (HPLC) was employed to analyze PPh_3 and $OPPh_3$ concentrations at various times. Chromatograms over a 6-h period are provided in Figure 10. It is immediately evident that the integrity of the catalyst system was retained throughout this multicycle experiment: (i) over this period, PPh_3 (t_r=1.8 min) is consumed and $OPPh_3$ (t_r=1.4 min) is progressively generated, (ii) the integrated intensity for the signal at t_r= 0.8 min corresponding to complex Mo(V) remained constant, (iii) the pH of the solution remained constant, and (iv) more than 100 equiv of PPh_3 per equivalent of catalyst Mo(VI) can be oxidized without loss of catalytic activity. Under identical conditions in the absence of the molybdenum complex catalyst, there is no significant phosphine oxidation.

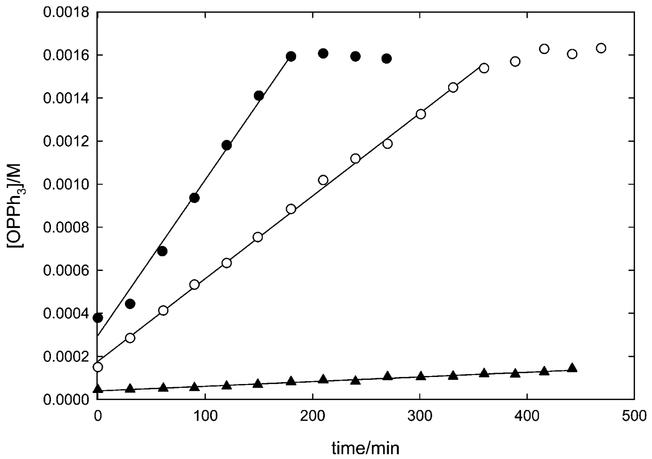

Figure 11. Variation of $[OPPh_3]$ with time for the catalytic cycle. Solvent THF/water 80:20 v/v; T = 34 °C; $[PPh_3] = 1.58 \times 10^{-3}$ M. (•) $[Mo(VI)] = 2.56 \times 10^{-4}$ M; (○) $[Mo(VI)] = 1.28 \times 10^{-4}$ M; (▲) $[Mo(VI)] = 0$, uncatalyzed reaction.

To determine the rate for catalysis, a series of runs containing different $[PPh_3]_0$ and $[Mo^{VI}(S_2C_6H_4)_3]_0$ concentrations were carried out. For each run, the plot of the $[OPPh_3]/[PPh_3]_0$ ratio vs time is linear over the entire period of time in which PPh_3 is completely consumed and $OPPh_3$ generated in equimolar amounts (Figure 11). This is another indication of catalyst stability. The slope gives the catalytic velocity, which proved to be insensitive to variations in the initial concentration of phosphine and linearly dependent on catalyst complex concentration. Thus, slopes divided by $[Mo^{VI}(S_2C_6H_4)_3]_0$ are constant and give the value of 5.2×10^{-4} s^{-1}, close to the rate constant of reaction 14. This result demonstrates that the catalytic rate is limited by the component half-reaction 14, the Mo(V) oxidation by O_2, as would be expected from the above values of specific rate constants for reactions 3 and 14.

Oxygen Isotope Tracing Experiments. Mass spectroscopy confirms that water is the source of oxygen atoms incorporated to the phosphine. When the above catalytic oxidation of PPh_3 is carried out in labeled water ($H_2{}^{18}O$), the label is partially incorporated into the phosphine. For the aerobic ($^{16}O_2$) $Mo^{VI}(S_2C_6H_4)_3/H_2{}^{18}O$(95 atom % ^{18}O)/PPh_3 reaction mixture in proportions 1/5000/10, the EI mass spectra showed that the phosphine oxide product contained approximately 70 atom % ^{18}O. Experimental conditions for the catalytic oxidation of PPh_3 were identical to those used in the nonlabeled system. According to Scheme 2, reaction 3 allows direct incorporation of oxygen from $H_2{}^{18}O$ into PPh_3, while direct oxidation of PPh_3 by the $H_2{}^{16}O_2$ produced from complementary reaction of reduction of $^{16}O_2$ by $Mo^V(S_2C_6H_4)_3{}^-$ (reactions 14 and 15) accounts for the 30% yield in $^{16}OPPh_3$. This low yield suggests that partial decomposition of $H_2{}^{16}O_2$ and/or oxidation of THF solvent by $H_2{}^{16}O_2$ are possible side reactions.

Concluding Remarks. Herein we have presented an unusual reduction of a trisdithiolene−molybdenum (VI) complex using PPh_3 as a reducing agent in the presence of water. The reaction occurs smoothly in THF. It is fast and demonstrates for the first time that phosphine oxidation by a water ligand (H_2O or OH^-), bound directly to a molybdenum−dithiolene site, is a feasible reaction pathway that has a quite lower activation energy than the oxygen atom transfer from a Mo═O group to phosphine. The evidence points to a mechanism that involves initial coordination of a water molecule to the molybdenum center, followed by proton dissociation and concerted abstraction of $2e^-$, H^+ by the Mo(VI) center to give the dianionic Mo(IV) trischelate and phosphine oxide. Such a mechanism is important in the context of biological processes catalyzed by some molybdoenzymes. Therefore, while we do not propose tris(dithiolene)−Mo(VI) complexes as structural models for any specific molybdoenzyme, we show that their interactions with phosphines in the presence of water incorporates the key features of Scheme 1, proposed for the catalytic cycle of molybdenum hydroxylase enzymes. Clearly, delocalized orbitals in these complexes that involve metal and multiple sulfur centers must be considered as strong candidates for the binding and activation of water and/or the stabilization of key intermediates. Reported results of density functional theory calculations provide a description of the delocalized ground states, which are well separated in energy from other orbitals and dominantly ligand in character.[29] On this basis other Mo and W trisdithiolene complexes might also be expected to behave in a similar way, and indeed we have recently indicated that $W^{VI}(S_2C_6H_4)_3$ is also an excellent catalyst for the oxidation of PPh_3.[15] Detailed kinetic studies of the reactions of the tungsten complex along with a comparative discussion will appear in a forthcoming paper.

Supporting Information Available: Derivation of the rate law for the reaction in buffered and unbuffered media. This material is available free of charge via the Internet at http://pubs.acs.org.

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