higher affinity of Me_2SO than that of Hacac for uranyl ion. Furthermore, the larger size of Hacac could make it more difficult for Hacac to approach into the inner sphere of the uranyl ion as compared with Me_2SO.

In conclusion, it is more likely that the acac exchange in $UO_2(acac)_2Me_2SO$ proceeds through mechanism 1 (I → II → IV → IV′ → I′), but mechanism 2 cannot be discarded, because the Me_2SO exchange in $UO_2(acac)_2Me_2SO$ in CD_2Cl_2 proceeds through the I mechanism.[17]

Vasilescu[11] studied the exchange of acac in $UO_2(acac)_2$ in acetonitrile and proposed that the acac exchange proceeds through both unimolecular and bimolecular processes. However, the rate constant for the unimolecular process decreases with increasing temperature. It is well-known that uranyl β-diketonato complexes form a binuclear complex, $[UO_2(\beta\text{-diketonato})_2]_2$, in the absence of adduct ligands.[22,23] The basic difficulty in Vasilescu's study might arise from the fact that the dimerization of $UO_2(acac)_2$ was not considered.

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Registry No. acac, 123-54-6; $UO_2(acac)_2Me_2SO$, 71357-22-7.

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Ligand Control of *cis*-Dioxomolybdenum(VI) Redox Chemistry: Kinetic and Activation Parameter Data for Oxygen Atom Transfer

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The oxygen atom transfer reactions for MoO_2(5-X-SSP) and MoO_2(5-X-SSE) (5-X-SSP^{2-} = 2-((5-X-salicylidene)amino)benzenethiolate; 5-X-SSE^{2-} = 2-((5-X-salicylidene)amino)ethanethiolate; X = Br, Cl, H, CH_3O) with $PEtPh_2$ were studied in detail between 30 and 60 °C. The applicable rate law is $-d[Mo^{VI}O_2L]/dt = k_1[Mo^{VI}O_2L][PEtPh_2]$. The specific rate constants span the range from 8.4×10^{-4} M^{-1} s^{-1} (X = CH_3O) to 19.6×10^{-4} M^{-1} s^{-1} (X = Br) for MoO_2(5-X-SSP) at 30 °C and from 21.4×10^{-4} M^{-1} s^{-1} (X = CH_3O) to 34.8×10^{-4} M^{-1} s^{-1} (X = Br) for MoO_2(5-X-SSE) at 60 °C. Only oxo–Mo(IV) complexes are observed as products of these reactions. A linear dependence is observed between log (k_{1X}/k_{1H}) and the Hammett σ_p parameter for the ligand X substituents for the two series MoO_2(5-X-SSP) ($\rho = +0.75$) and MoO_2(5-X-SSE) ($\rho = +0.42$). Activation parameter data were obtained for MoO_2(5-H-SSP) ($E_a = 67.9$ kJ/mol, $\Delta H^\ddagger = 65.2$ kJ/mol, $\Delta S^\ddagger = -86.5$ J/(mol K)) and MoO_2(5-H-SSE) ($E_a = 72.0$ kJ/mol, $\Delta H^\ddagger = 70.3$ kJ/mol, $\Delta S^\ddagger = -82.6$ J/(mol K)). There exists a correlation between E_{p_c} and the specific rate constants for MoO_2(5-X-SSP) and MoO_2(5-X-SSE).

Introduction

A number of redox enzymes are known to depend upon a molybdenum-containing cofactor for enzyme activity.[1,2] Recent EXAFS studies[3-6] have implicated sulfur and nitrogen or oxygen as ligand donor atoms in the coordination sphere of the molybdenum. In addition, EXAFS data also suggest that the oxidized forms of xanthine oxidase[3,5] and sulfite oxidase[4,5] contain the MoO_2^{2+} unit while the reduced forms of xanthine dehydrogenase and reduced sulfite oxidase contain a single terminal oxo ligand.[6] The current understanding of these enzymes indicates that the molybdenum cycles between the +6 and +4 oxidation states in their reactions with substrate and subsequent reactivation.[7] In examining the reactions carried out by xanthine, sulfite, and aldehyde oxidase and also nitrate reductase, one finds that the only difference between the substrate before and after the reaction is the addition or removal of an oxygen atom. The two-electron oxygen atom transfer reaction[8] may be relevant to the understanding of the reactions of molybdoenzymes, although other mechanisms are certainly possible.[9]

Coordination complexes of molybdenum in the higher oxidation states also contain the molybdenum oxo group. In particular, Mo(VI) complexes possess exclusively the *cis*-dioxomolybdenum moiety.[10] Attempts have been made to prepare molybdenum coordination complexes that can carry out oxygen atom transfer reactions. Mo(VI) complexes have been found to oxidize thiols,[11] hydrazine,[12] polyketones,[13] and tertiary phosphines.[8] The *cis*-dioxomolybdenum(VI) dialkyldithiocarbamates ($MoO_2(S_2CNR_2)_2$) have been extensively studied with regard to these reactions. Barral et al.[8] have reported on the oxidation of triphenylphosphine (PPh_3) by $MoO_2(S_2CNPr_2)_2$. For the reaction in *o*-dichlorobenzene they report a specific rate constant at 41 °C of 2.3 M^{-1} s^{-1}. McDonald and Schulman[14] have described an analytical procedure for the spectrophotometric determination of PPh_3

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using $MoO_2(S_2CNEt_2)_2$. This procedure is based on the oxidation of PPh_3 by the Mo(VI) complex. They report a specific rate constant of 0.12 M^{-1} s^{-1} in benzene at 24 °C. Durant et al.[15] found for the oxidation of PPh_3 by $MoO_2(S_2CNEt_2)_2$ in CH_3CN a specific rate constant of 1.1 M^{-1} s^{-1} at 25 °C, $\Delta H^{\ddagger} = 35.2$ kJ/mol, and $\Delta S^{\ddagger} = -126$ J/(mol K). Deli and Speier[16] have studied the oxidation of PPh_3 by MoO_2(ethyl-L-cysteinate)$_2$ in benzene. At 35 °C they report a specific rate constant of 2.95×10^{-4} M^{-1} s^{-1}, $\Delta H^{\ddagger} = 46$ kJ/mol, and $\Delta S^{\ddagger} = -153$ J/(mol K).

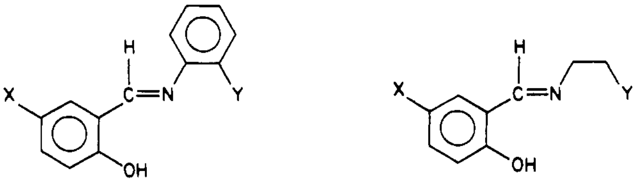
The following equilibrium is established for a number of $Mo^{V}{}_2O_3L_4$ complexes:[8,17]

$$Mo^{VI}O_2L_2 + Mo^{IV}OL_2 \overset{K}{\rightleftharpoons} Mo^{V}{}_2O_3L_4 \qquad (1)$$

The magnitude of the equilibrium constant, *K*, is a function of the type of ligand, L. For most complexes studied L is a bidentate chelate containing oxygen, nitrogen, and/or sulfur donor atoms. The complexes, $Mo_2O_3L_4$ (L = methyl-L-cysteinate, ethyl-L-cysteinate, acetylacetonate, and 8-hydroxyquinolinate),[18] obey Beer's law, which indicates that *K* is very large for these ligands. For $Mo_2O_3L_4$ (L = S_2CNR_2 and S_2PR_3)[18] Beer's law is not obeyed due to the formation of MoO_2L_2 and $MoOL_2$ from $Mo_2O_3L_4$. For L = S_2CNEt_2 Matsuda, Tanaka, and Tanaka[19] have determined *K* to be 5×10^2 L/mol at 25 °C.

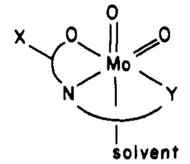
Boyd and Spence[20] have examined the products of the reaction of MoO_2(mpe) and MoO_2(mee) with ethyldiphenylphosphine ($PEtPh_2$) (mpe = *N,N'*-bis(2-mercapto-2-methylpropyl)ethylenediamine and mee = *N,N'*-bis(2-mercaptoethyl)ethylenediamine). Although these complexes are similar and closely related to each other, the reduction products are different. While the reduction proved successful for the synthesis of MoO(mpe), only the μ-oxo Mo(V) dimer was obtained from MoO_2(mee). They speculated that this difference may be a result of the steric effect of the methyl groups on the carbon atoms adjacent to sulfur in mpe. These methyl groups interact sterically in the μ-oxo dimer, $Mo_2O_3(mpe)_2$, thus destabilizing it and shifting the equilibrium in 1 to the left. There is the possibility that no $Mo_2O_3(mpe)_2$ is formed at all in this reaction.

Recent work in our laboratory[21-25] has focused on the chemical properties of a series of *cis*-dioxomolybdenum(VI) coordination complexes prepared from the following tridentate Schiff base ligands:



Y = OH: 5-X-SAP-H_2 Y = OH: 5-X-SAE-H_2
X = NO_2, Br, Cl, H, CH_3O
Y = SH: 5-X-SSP-H_2 Y = SH: 5-X-SSE-H_2
X = Br, Cl, H, CH_3O

The idealized Mo(VI) complex structure[26] is shown in **1**. The kinetics, mechanism, activation parameters, and electrochemistry for these complexes will be discussed and compared with



1, Y = O, S

those of other molybdenum complexes described in the literature. The results discussed here will provide a keener insight into the redox chemistry of Mo(VI) complexes as a function of ligand structure.

Experimental Section

Materials. Ethyldiphenylphosphine was obtained from Strem Chemicals and used without further purification. *N,N*-Dimethylformamide (DMF) was reagent grade and was dried over type 3A molecular sieves. The synthesis, characterization, and cyclic voltammetry of the Mo(VI) complexes have been previously described.[22,23]

Kinetic Measurements and Activation Parameters. All manipulations associated with the kinetic measurements were performed under a nitrogen atmosphere. Mo(VI) complex solutions approximately 10^{-3} M in DMF were employed. Pseudo-first-order conditions were used throughout the study of these reactions by maintaining the concentration of $PEtPh_2$ between 25-fold and 100-fold molar excess over the molybdenum concentration. The solutions were maintained at a constant temperature with a thermostated bath. Spectra were recorded for several hours at convenient time intervals, between 650 and 300 nm, with a Beckman Acta M VII spectrophotometer. The pseudo-first-order rate constants, k_{obsd} ($k_{obsd} = k_1[PEtPh_2]$), were determined for each reaction from plots of $\ln (A_\infty - A_t)$ vs. time. A_t is the optical density at time *t*. A_∞ was determined as the optical density when the final two spectral traces overlapped. Kinetic experiments were performed at least 3 times for each molybdenum complex studied, with the plots in each case being linear over at least 3 half-lives. A plot of $\ln k_1$ vs. $1/T$[27] yielded the activation energy, E_a, and the frequency factor, *A*. While a plot of $\ln (k_1/T)$ vs. $1/T$[27] gave the activation enthalpy ($\Delta H^{\ddagger}$), $\Delta S^{\ddagger}$ was obtained from the relationship[27] $\ln A = \ln (RT/Nh) + \Delta S^{\ddagger}/R + 1$, where $R = 8.314$ J/(mol K) and $R/Nh = 2.084 \times 10^{10}$ K^{-1} s^{-1}.

Results and Discussion

Kinetics. Boyd and Spence[20] have synthesized MoO(5-H-SSP) and MoO(5-H-SAP) from the corresponding Mo(VI) complexes using $PEtPh_2$ as the reducing agent. We have examined these and other Mo(VI) redox reactions in an effort to identify those features of the ligand structure that affect the rates of these reactions. The following oxygen atom transfer reactions[24,25] have been studied in detail:

$$Mo^{VI}O_2(5\text{-X-SSP}) + PEtPh_2 \xrightarrow[30\ ^\circ C]{k_1} Mo^{IV}O(5\text{-X-SSP}) + OPEtPh_2 \qquad (2)$$

$$Mo^{VI}O_2(5\text{-X-SSE}) + PEtPh_2 \xrightarrow[60\ ^\circ C]{k_1} Mo^{IV}O(5\text{-X-SSE}) + OPEtPh_2 \qquad (3)$$

Figure 1 shows a series of spectra recorded as a function of time for the reaction of MoO_2(5-H-SSP) with $PEtPh_2$ in DMF. This result is typical of the spectral changes observed for the reactions of MoO_2(5-X-SSP) and MoO_2(5-X-SSE) with $PEtPh_2$. The reactions were found[24,25] to be first order in both Mo(VI) complex and phosphine so that the applicable rate law is $-d[Mo^{VI}O_2L]/dt = +d[Mo^{IV}OL]/dt = k_1[Mo^{VI}O_2L][PEtPh_2]$. The specific rate constants, k_1, are listed

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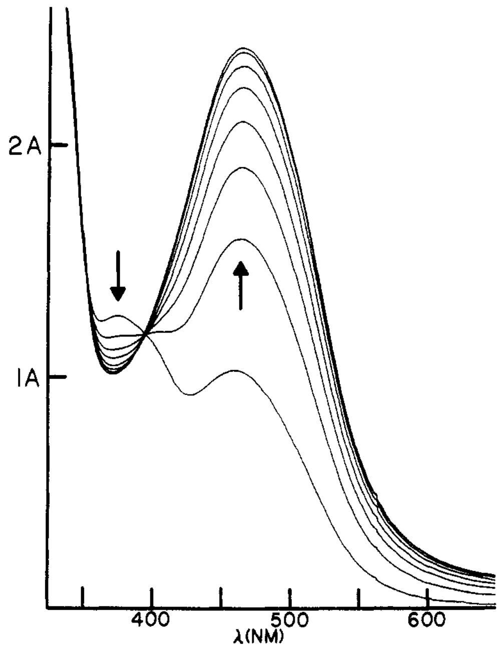

Figure 1. Spectral changes observed during the reaction of MoO_2(5-H-SSP) with $PEtPh_2$. The initial MoO_2(5-H-SSP) and $PEtPh_2$ concentrations were 3.12×10^{-3} and 3.12×10^{-1} M, respectively. Spectra were recorded at 30 °C at 30 min intervals.

Table I. Kinetic, Electrochemical, and IR Data for the Molybdenum(VI) Complexes

Mo complex	$10^4 k_1$, $M^{-1}\ s^{-1}$		E_{p_c}, V[a]	ν(Mo=O), cm^{-1}
	30 °C	60 °C		
MoO_2(5-Br-SSP)	19.6 ± 0.6		−1.05	926, 940[b]
MoO_2(5-Cl-SSP)	18.7 ± 0.2		−1.06	934, 943[b]
MoO_2(5-H-SSP)	10.2 ± 0.9	116.0 ± 6.2	−1.11	925[b]
MoO_2(5-CH_3O-SSP)	8.4 ± 0.4		−1.13	912[b]
MoO_2(5-Br-SSE)		34.8 ± 2.8	−1.22	914, 922[b]
MoO_2(5-Cl-SSE)		34.6 ± 2.7	−1.22	918[b]
MoO_2(5-H-SSE)	2.1 ± 0.2	28.1 ± 1.8	−1.25	902, 947
MoO_2(5-CH_3O-SSE)		21.4 ± 0.6	−1.27	887, 906, 920[b]
MoO_2(5-NO_2-SAP)	*c*		−1.11	896, 923, 945
MoO_2(5-Br-SAP)			−1.17	896, 920
MoO_2(5-Cl-SAP)			−1.17	888, 912
MoO_2(5-H-SAP)			−1.24	910, 931
MoO_2(5-CH_3O-SAP)			−1.25	910, 937[b]
MoO_2(5-NO_2-SAE)	*d*		−1.25	915[b]
MoO_2(5-Br-SAE)			−1.48	912[b]
MoO_2(5-Cl-SAE)			−1.48	912[b]
MoO_2(5-H-SAE)			−1.49	890, 929, 940
MoO_2(5-CH_3O-SAE)			−1.53	886, 924

[a] Volts vs. NHE with reference to the ferrocenium/ferrocene redox couple. [b] IR spectra indicate the possible presence of oligomers (Mo=O→Mo) in the solid state. [c] MoO_2(5-X-SAP) did not react with $PEtPh_2$ at any appreciable rate at these temperatures. [d] MoO_2(5-X-SAE) did not react with $PEtPh_2$ at any appreciable rate at these temperatures.

in Table I. Note that the k_1's for MoO_2(5-X-SSP) were obtained at 30 °C while those for MoO_2(5-X-SSE) were obtained at 60 °C.

Some comment is necessary concerning the nature of the molybdenum-containing reduction products in reactions 2 and 3. Consider the reaction sequence

$$Mo^{VI}O_2L_n + PR_3 \xrightarrow{k_1} Mo^{IV}OL_n + OPR_3 \qquad (4)$$

$$Mo^{VI}O_2L_n + Mo^{IV}OL_n \xrightarrow{k_2} Mo^{V}{}_2O_3L_{2n} \qquad (5)$$

If $k_2 >> k_1$, then $Mo^{VI}O_2L_n$ would be consumed twice as fast as $Mo^V{}_2O_3L_{2n}$ would appear even if reaction 4 were the rate-determining step. If $k_2 << k_1$ or reaction 5 does not proceed at all, then the rate of the disappearance of $Mo^{VI}O_2L_n$ would equal that of the appearance of the reduced molybdenum species, presumably $Mo^{IV}OL_n$. For L = ethyl-L-cysteinate, Deli and Speier[16] have shown that $k_2 >> k_1$ with the result that $-d[MoO_2(Et\text{-}L\text{-}cys)_2]/dt = +2d[Mo_2O_3(Et\text{-}L\text{-}cys)_4]/dt$, in which case the μ-oxo Mo(V) dimer is being formed rapidly via the oxo-abstraction reaction and subsequent dimer formation.

Examination of Figure 1 shows the presence of an isosbestic point at 396 nm for the collection of spectra recorded during the reaction of MoO_2(5-H-SSP) with $PEtPh_2$. This observation strongly suggests[28] that the reaction is proceeding directly from reactants to products without any reaction intermediate being formed and also eliminates the possibility of consecutive reactions taking place. In addition we find that the rate of disappearance of the Mo(VI) species (λ = 374 nm) is equal to the rate of appearance of the molybdenum species at 465 nm. These results suggest that $k_1 >> k_2$.

Additional experimental results can also be considered. The μ-oxo Mo(V) dimer has a unique absorption spectrum[10] with an intense transition at approximately 525 nm. This electronic transition is insensitive to the nature of the ligand, L, and is believed to be associated with a charge-transfer transition that is localized in the Mo–O–Mo bridge. The electronic transition around 525 nm is so characteristic of the μ-oxo Mo(V) dimer that serious doubts are raised as to its presence if this band is not observed. For reactions 2 and 3 no electronic transitions are observed that are characteristic of μ-oxo Mo(V) dimers. Finally, Boyd and Spence[20] have described the electronic spectrum of the characterized Mo(IV) complex, MoO(5-H-SSP). They report a λ_{max} at 465 nm, which is identical with that observed for the product found in the reaction of MoO_2(5-H-SSP) with $PEtPh_2$.

From these results it is apparent that during the course of reactions 2 and 3 only Mo(IV) species are produced, and no Mo(V) dimers are being formed via reaction 1. The reason for this result is unclear, but it may be steric as in the case of MoO_2(mpe). Although MoO(5-H-SAP) has been synthesized[20] under refluxing conditions in DMF/CH_3CN from MoO_2(5-H-SAP) and $PEtPh_2$, neither MoO_2(5-X-SAP) nor MoO_2(5-X-SAE) reacted with $PEtPh_2$ at any appreciably rates even at elevated temperatures (up to 60 °C) so no kinetic data are available for these two series of complexes.

Linear Substituent Effects. The *cis*-dioxomolybdenum(VI) complexes (Table I) contain ligand substituents that span the range from electron withdrawing (Cl, Br) to electron donating (CH_3O). Even though the X substituents are not directly bonded to the molybdenum, their effect is transmitted through the ligand to the Mo–oxo core. Electron-withdrawing substituents remove electron density from the Mo–oxo core, making the oxo groups more electrophilic. The opposite effect is observed for electron-donating substituents in that the oxo groups are less electrophilic. This difference in the electrophilic character of the molybdenum complexes is manifested in the systematic variation of the specific rate constants, k_1, that are obtained for their reactions with $PEtPh_2$.

For the data shown in Table I there is a linear dependence of log (k_{1X}/k_{1H}) (where k_{1X} is the specific rate constant for MoO_2(5-X-SSP) or MoO_2(5-X-SSE) and k_{1H} is the specific rate constant for MoO_2(5-H-SSP) or MoO_2(5-H-SSE) as standards) vs. the Hammett σ_p parameter for the X substituent on the ligands for MoO_2(5-X-SSP) and MoO_2(5-X-SSE). From plots of log (k_{1X}/k_{1H}) vs. σ_p (Figure 2) the reaction

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Table II. Kinetic and Activation Parameter Data for MoO_2(5-H-SSP) and MoO_2(5-H-SSE)

	10^4k_1, M^{-1} s^{-1}				E_a, kJ/mol	$\Delta H^\ddagger$, kJ/mol	$\Delta S^\ddagger$, J/(mol K)
	30 °C	40 °C	50 °C	60 °C			
MoO_2(5-H-SSP)	10.2 ± 0.9	24.7 ± 1.0	56.1 ± 1.5	116.0 ± 6.2	67.9	65.2	−86.5
MoO_2(5-H-SSE)	2.1 ± 0.2	6.0 ± 0.2	13.9 ± 1.9	28.1 ± 1.8	73.0	70.3	−82.6

Table III. Comparison of Kinetic and Activation Parameter Data for Molybdenum(VI) Complexes in Oxygen Atom Transfer Reactions

Mo complex	ligand donor atoms	PR_3	*T*, °C	k_1, M^{-1} s^{-1}	$\Delta H^\ddagger$, kJ/mol	$\Delta S^\ddagger$, J/(mol K)
$MoO_2(S_2CNEt_2)_2$[a]	S_4	PPh_3	25	1.1	35.2	−126
MoO_2(Et-L-cys)$_2$[b]	N_2S_2	PPh_3	35	2.9×10^{-4}	46.0	−153
MoO_2(5-H-SSP)[c]	ONS	$PEtPh_2$	30	10.2×10^{-4}	65.2	−86.5
MoO_2(5-H-SSE)[c]	ONS	$PEtPh_2$	30	2.1×10^{-4}	70.3	−82.6
MoO_2(5-H-SAP)[c]	ONO	$PEtPh_2$	30	no reaction		
MoO_2(5-H-SAE)[c]	ONO	$PEtPh_2$	30	no reaction		

[a] Data from ref 15. [b] Data from ref 16. [c] This work.

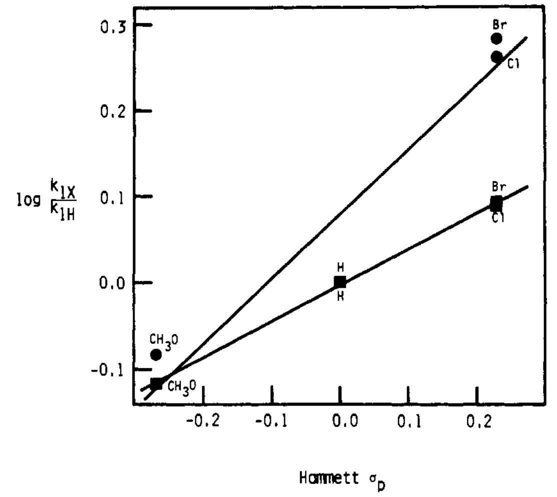

Figure 2. Plot of log (k_{1X}/k_{1H}) vs. Hammett σ_p for MoO_2(5-X-SSP) (●) and MoO_2(5-X-SSE) (■) (X = Br, Cl, H, CH_3O).

constants, ρ, were found to be +0.75 (MoO_2(5-X-SSP)) and +0.42 (MoO_2(5-X-SSE)). The positive ρ values are consistent with the reaction mechanism described in a later section. The larger ρ value for MoO_2(5-X-SSP) indicates that the 5-X-SSP^{2-} ligand with an extended π-electron system is more effective than the 5-X-SSE^{2-} ligand in transmitting the electron-withdrawing or electron-donating substituent effect to the Mo–oxo core.

Activation Parameters. Kinetic data for reactions 2 and 3 for MoO_2(5-H-SSP) and MoO_2(5-H-SSE) were obtained at several different temperatures between 30 and 60 °C (Table II). The activation parameters for the reaction of these and other Mo(VI) complexes with organophosphines are collected in Table III. Even though the data shown in Table III were not obtained under identical experimental conditions, there are definite trends that are apparent. $MoO_2(S_2CNEt_2)_2$[15] and MoO_2(Et-L-cys)$_2$[16] were reacted with PPh_3 while the remaining complexes were reacted with the more basic $PEtPh_2$. Speier[29] has shown similar rates for the oxygenation of PPh_3 and $PEtPh_2$ using MoO_2(Et-L-cys)$_2$ as the catalyst. Thus, from these data, reasonable correlations can be drawn with regard to the reactivity of Mo(VI) complexes as a function of ligand structure. It is apparent that when the coordination sphere contains four sulfur atoms, the rate of reaction with organophosphines is substantially enhanced. The rate of reaction for $MoO_2(S_2CNEt_2)_2$[15] is at least 2–3 orders of magnitude greater than that for any of the other complexes described here. We also see that this complex has the lowest activation enthalpy of the group. The quantitative reactivity data presented here parallel the qualitative results of Nakamura et al.[30] for the oxidation of hydrazines, organophosphines, and alcohols by Mo(VI) complexes. On the basis of activation enthalpies, we find the reactivity of Mo(VI) complexes with organophosphines to decrease in the following order as a function of ligand donor atoms:

$$S_4 > N_2S_2 > ONS > ONO$$

Reaction Mechanism. Newton et al.[31] have described the reaction of $MoO_2(S_2CNR_2)_2$ with PR_3 as an electrophilic attack of the oxo ligand on the electron-rich base. This mechanism is consistent with the kinetic data presented here for MoO_2(5-X-SSP) and MoO_2(5-X-SSE). The mechanism is most likely a simple bimolecular reaction involving the interaction between one MoO_2L complex and one $PEtPh_2$ molecule in the activated complex. The formation of the activated complex could lead to the transfer of an oxygen atom by way of the donation of the lone pair of electrons of the phosphorus atom into the antibonding Mo–O π^* orbital. This will lead to the formation of the P–O bond and an oxomolybdenum(IV) complex with a $4d_{xy}{}^2$ electron configuration. A mechanism of this type is consistent with the values of ΔH^* obtained here since the formation of the activated complex does not require any significant bond breaking or intramolecular reorganization.

Electrochemistry. The reaction of *cis*-dioxomolybdenum(VI) complexes with organophosphines is a two-electron redox/oxygen atom transfer process. For all the Mo(VI) complexes described here we observe irreversible redox behavior.[22,23] No detectable oxidation wave was seen in the cyclic voltammogram during reverse anodic scans. Electrochemical studies[32-36] on similar *cis*-dioxomolybdenum(VI) complexes have generally shown irreversible or quasi-reversible behavior. For a series of oxomolybdenum complexes it has been shown[33] that it is impossible to obtain oxomolybdenum(V) monomers by electrochemical reduction of the corresponding dioxomolybdenum(VI) complexes in nonaqueous solvents. Likewise, oxomolybdenum(V) monomers cannot be oxidized to the corresponding dioxomolybdenum(VI) complexes. The failure of this redox process is most likely due to the difficulty in adding or removing an oxygen atom from the oxomolybdenum core during the oxidation or reduction in nonaqueous solvents.

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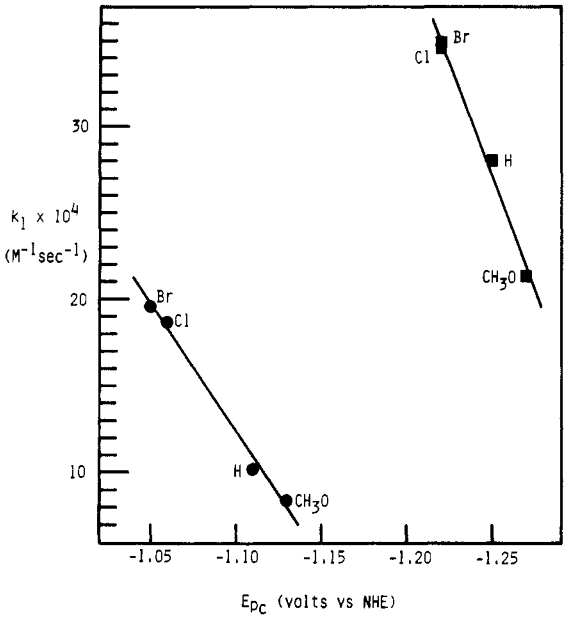

Figure 3. Plot of k_1 vs. E_{p_c} for MoO_2(5-X-SSP) (●; at 30 °C) and MoO_2(5-X-SSE) (■; at 60 °C) (X = Br, Cl, H, CH_3O).

The Mo(IV) complexes, MoO(5-H-SAP) and MoO(5-H-SSP), can be oxidized[20] to the corresponding monomeric oxomolybdenum(V) complexes. However, the reduction products for both the oxomolybdenum(IV) and oxomolybdenum(V) complexes have identical electronic spectra,[20] and the reductions occur at essentially the same potentials (i.e. ~−1.0 V vs. SCE). Thus, oxomolybdenum(V) monomers cannot be reduced to the corresponding oxomolybdenum(IV) complexes. There does not exist a simple and reversible electrochemical pathway that connects the +6, +5, and +4 oxidation states of molybdenum. Although the course of the chemical and electrochemical reductions for Mo(VI) complexes are different, there are still correlations between cathodic reduction potentials (E_{p_c}) and specific rate constants that are observed.

Since all the reductions being discussed are irreversible, the electrochemical data included in Table I are for the E_{p_c}, which is the potential measured at the maximum cathodic peak current. It must be emphasized that these cyclic voltammetry data are for E_{p_c}'s and not thermodynamic reduction potentials, which are obtained from reversible cyclic voltammograms. As the ligand X substituent becomes more electron withdrawing (X = NO_2 > Br, Cl > H > CH_3O) the Mo(VI) E_{p_c}'s are shifted in the anodic direction, which means the Mo(VI) complexes become easier to reduce. For each series there is a linear relationship between E_{p_c} and the Hammett σ_p parameter for the X substituent.[23] In addition, ligands with extended π-electron systems (5-X-SAP^{2-} and 5-X-SSP^{2-} vs. 5-X-SAE^{2-} and 5-X-SSE^{2-}) also facilitate molybdenum complex reducibility. A third ligand effect is also operative. When a sulfur donor atom is substituted in the ligand for an oxygen donor atom (5-X-SSP^{2-} and 5-X-SSE^{2-} vs. 5-X-SAP^{2-} and 5-X-SAE^{2-}), significant anodic shifts in E_{p_c} are observed for these Mo(VI) complexes.

E_{p_c} and k_1. The relationship between k_1 and E_{p_c} for MoO_2(5-X-SSP) and MoO_2(5-X-SSE) is worth considering since both parameters relate to a redox process. Figure 3 shows plots of k_1 vs. E_{p_c} for the two series MoO_2(5-X-SSP) (at 30 °C) and MoO_2(5-X-SSE) (at 60 °C). It is interesting to note the linear relationship that exists between k_1 and E_{p_c} within each series. The same electronic effects that cause systematic changes in the E_{p_c}'s for these complexes also alter the electrophilic character of the Mo(VI) oxo ligand for its reaction with organophosphines.

It must be pointed out that the magnitude of the cathodic reduction potential in itself is not sufficient to establish the rate of the reaction of a Mo(VI) complex toward organophosphines. The E_{p_c}'s for MoO_2(5-X-SAP) and MoO_2(5-X-SSE) fall into the same range between −1.27 and −1.11 V. Since the MoO_2(5-X-SSE) complexes reacted with $PEtPh_2$ at reasonable rates at 60 °C,[25] it was expected that the MoO_2(5-X-SAP) complexes would react with $PEtPh_2$ as well because their E_{p_c}'s are very similar and even slightly more anodic than those for their MoO_2(5-X-SSE) counterparts. This was found not to be the case, and there was no appreciable reaction of MoO_2(5-X-SAP) with $PEtPh_2$ even at 60 °C. The subtle role that sulfur plays in altering the rates of these chemical reductions goes beyond the electronic effect that alters the electrochemistry. Another example is seen in the electrochemistry and reactivity of $MoO_2(S_2CNEt_2)_2$. In this complex the molybdenum is coordinated by four sulfur donor atoms. The E_{p_c} for this complex is −0.93 V when the cyclic voltammogram is measured under experimental conditions identical with those used for all the Mo(VI) complexes listed in Table I. The specific rate constant for the reaction of $MoO_2(S_2CNEt_2)_2$ with PPh_3 at 25 °C is 1.1 M^{-1} s^{-1}.[15] This rate constant is approximately 3 orders of magnitude larger than that obtained for MoO_2(5-Br-SSP) reacting with $PEtPh_2$ (k_1 = 19.6 × 10^{-4} M^{-1} s^{-1}; E_{p_c} = −1.05 V). One would not have predicted so large a rate constant for $MoO_2(S_2CNEt_2)_2$ from just a consideration of its E_{p_c}. These results suggest that sulfur plays a key role in accelerating the rate of reaction of Mo(VI) complexes with organophosphines, possibly by stabilizing the Mo(IV) complex that is produced.

Summary. There are three ligand features for the *cis*-dioxomolybdenum(VI) Schiff base complexes described here whose effects are to alter systematically the Mo(VI) specific rate constants and E_{p_c}'s. A Mo(VI) complex with a ligand having an extended π-electron system, a sulfur donor atom, and an effective electron-withdrawing substituent will be easier to reduce and more effective in oxidizing organophosphines. MoO_2(5-X-SSP) and MoO_2(5-X-SSE) react with $PEtPh_2$ in DMF between 30 and 60 °C. The reactions are first order in both Mo(VI) complex and $PEtPh_2$. The specific rate constants, k_1, show a correlation with cathodic reduction potentials within each series. The kinetic and activation parameter data are consistent with a bimolecular reaction involving electrophilic attack of the oxo ligand on the basic $PEtPh_2$ leading to an oxomolybdenum(IV) complex and $OPEtPh_2$. This work has shown that within a series of structurally similar *cis*-dioxomolybdenum(VI) coordination complexes the rate of reactivity toward a particular substrate can be systematically altered through specific ligand design. The change in reactivity within each series is also paralleled by a change in cathodic reduction potentials. For each series, MoO_2(5-X-SSP) and MoO_2(5-X-SSE), the rate of $PEtPh_2$ oxidation is increased as the Mo(VI) complex is more easily electrochemically reduced.

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Registry No. MoO_2(5-Br-SSP), 89485-13-2; MoO_2(5-Cl-SSP), 89485-12-1; MoO_2(5-H-SSP), 75780-89-1; MoO_2(5-CH_3O-SSP), 89485-14-3; MoO_2(5-Br-SSE), 87962-16-1; MoO_2(5-Cl-SSE), 87962-17-2; MoO_2(5-H-SSE), 87962-18-3; MoO_2(5-CH_3O-SSE), 87962-19-4; $PEtPh_2$, 607-01-2.