

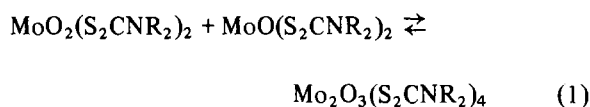
Kinetic Study of the Oxidation of Ethyldiphenylphosphine by *cis*-Dioxo-[N-(5-X-Salicylidene)-2-aminoethanethiolato] Molybdenum(VI)

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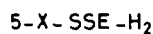
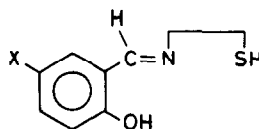
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Molybdenum has been found to be an essential component of aldehyde, sulfite and xanthine oxidase and nitrate reductase [1, 2]. In examining the reactions carried out by these enzymes, it is found that the substrate is changed by the addition or removal of an oxygen atom. The two-electron oxygen atom transfer reaction [3] may be relevant to the understanding of the reactions of molybdoenzymes. Attempts have been made to prepare molybdenum coordination complexes which can carry out oxygen atom transfer reactions. Thiols [4], hydrazine [5, 6], polyketones [7] and tertiary phosphines [3] can be oxidized by Mo(VI) complexes. The *cis*-dioxomolybdenum(VI) dialkyldithiocarbamates [MoO₂(S₂CNR₂)₂] have been extensively studied with regard to these reactions. Barral *et al.* [3] have reported on the oxidation of triphenylphosphine (Pφ₃) by MoO₂·(S₂CNEt₂)₂. McDonald and Shulman [8] have described an analytical procedure for the spectrophotometric determination of Pφ₃ using MoO₂·(S₂CNEt₂)₂. Newton and coworkers [9] have synthesized Mo(V)₂O₃L₄ (L = S₂CNR₂, S₂PR₂, cysteinato methyl ester, acetylacetonato and 8-hydroxyquinolinato) and Mo(IV)OL₂ (L = S₂CNR₂ and S₂PR₂) complexes starting with the Mo(VI) complexes and using ethyldiphenylphosphine (PEtφ₂) to carry out the oxo abstraction. Durant *et al.* [10] have described the kinetics and mechanism of the oxygen atom transfer reaction between MoO₂(S₂CNEt₂)₂ and Pφ₃. Deli and Speier [11] have described a similar study involving MoO₂(ethyl-L-cysteinato)₂ and Pφ₃. Oxygen atom abstraction from MoO₂(S₂CNR₂)₂ can also be effected by acids [12, 13]. For Mo(VI) dialkyldithiocarbamates an equilibrium is established [3, 14] from oxo abstraction with phosphines when excess Mo(VI) complex is present.



We have examined the reaction of a series of *cis*-dioxomolybdenum(VI) Schiff base coordination complexes with PEtφ₂. The synthesis and char-

acterization of the Mo(VI) complexes have been previously described [15]. Tridentate ligands with the following structure were employed.

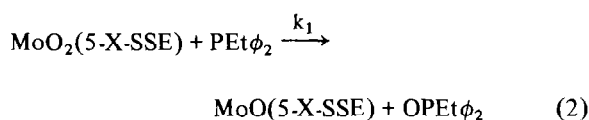


(X = Cl, Br, H, CH₃O)

The MoO₂(5-X-SSE) complexes are soluble and stable indefinitely in dimethylsulfoxide (Me₂SO) and N,N-dimethylformamide (DMF). In solution, a solvent molecule occupies the vacant coordination site *trans* to an oxo group. Since the molybdoenzymes are redox enzymes, it would be interesting to see if ligand modifications would alter the relative reactivities of the Mo(VI) complexes toward suitable redox substrates. To this end, the Mo(VI) complexes were reacted with PEtφ₂. This paper reports on the kinetic data obtained and its relationship to ligand structure.

Results and Discussion

The reactions of MoO₂(S₂CNR₂)₂ with Pφ₃ are well documented in the literature [3, 8-11, 14]. This substrate, however, did not react at any reasonable rate with the Mo(VI) Schiff base complexes described in this report. A more suitable phosphine substrate, ethyldiphenylphosphine, was chosen because it reacted with the Mo(VI) complexes at reasonable rates between 30 °C and 60 °C. The reaction followed in this study was



A qualitative examination of this reaction showed that it was a slow reaction that could be followed spectrophotometrically by observing changes in the optical spectra. The MoO₂(5-X-SSE) complexes exhibit charge transfer electronic transitions below 350 nm in the electronic spectrum. For all the MoO₂·(5-X-SSE) complexes, the intensities of the electronic transitions associated with the Mo(VI) species decreased as a function of time on reaction with PEtφ₂. A new absorbance appeared around 475 nm and increased in intensity as the reaction proceeded. Absorbance changes in this region of the spectrum

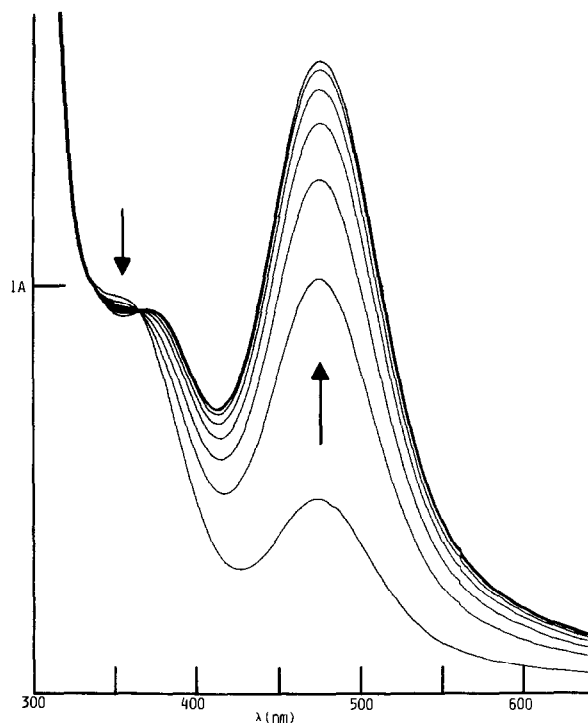


Fig. 1. Spectral changes observed during the reaction of $\text{MoO}_2(5\text{-H-SSE})$ with $\text{PEt}\phi_2$. (The initial $\text{MoO}_2(5\text{-H-SSE})$ and $\text{PEt}\phi_2$ concentrations were $2.83 \times 10^{-3} \text{ M}$ and $2.83 \times 10^{-1} \text{ M}$ respectively. Spectra were recorded at 15 min intervals).

were monitored as a function of time to obtain the kinetic parameters presented here.

All manipulations associated with the kinetic measurements were performed under a nitrogen atmosphere. Mo(VI) complex solutions of approximately 10^{-3} M in dry DMF were employed. Pseudo first order conditions were used throughout the study of these reactions by maintaining the concentration of $\text{PEt}\phi_2$ between 25-fold and 100-fold molar excess over the molybdenum concentration. The solutions were maintained at $60.0 \pm 0.5 \text{ }^\circ\text{C}$ with a thermostatted bath. Spectra were recorded for several hours at 15 to 30 min intervals, between 650 and 300 nm, using a Beckman Acta M VII spectrophotometer. The pseudo first order rate constants, k_{obs} ($k_{\text{obs}} = k_1[\text{PEt}\phi_2]$), were determined from plots of $\ln(A_\infty - A_t)$ versus 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 three times for each molybdenum complex studied, with the plots in each case being linear over at least three half lives.

Figure 1 shows a series of spectra recorded as a function of time for the reaction of $\text{MoO}_2(5\text{-X-SSE})$ with $\text{PEt}\phi_2$. This result is typical of the type of

TABLE I. Kinetic Data for the Molybdenum(VI) Complexes.

Mo Complex	k_1 ($\text{M}^{-1} \text{ sec}^{-1}$) at $60 \text{ }^\circ\text{C}$
$\text{MoO}_2(5\text{-Br-SSE})$	$34.8(\pm 2.8) \times 10^{-4}$
$\text{MoO}_2(5\text{-Cl-SSE})$	$34.6(\pm 2.7) \times 10^{-4}$
$\text{MoO}_2(5\text{-H-SSE})$	$28.1(\pm 1.8) \times 10^{-4}$
$\text{MoO}_2(5\text{-CH}_3\text{O-SSE})$	$21.4(\pm 0.6) \times 10^{-4}$

spectral changes observed for these complexes. The appearance of an isosbestic point strongly suggests [16] that the molybdenum complex reactant is being converted to product without going through some type of reaction intermediate.

It was mentioned before that $\text{MoO}_2(\text{S}_2\text{CNR}_2)_2$ complexes are reduced by phosphine to produce the corresponding Mo(IV) complexes. If excess Mo(VI) complex is present in solution, an equilibrium is established (see reaction 1) producing a $\mu\text{-oxo-Mo(V)}$ dimer. This type of Mo(V) dimer ($\text{Mo}_2\text{O}_3\text{L}_n$) has a unique absorption at $\sim 525 \text{ nm}$ [17] which is essentially unchanged as the ligands L are varied. The absorption is believed to be associated with a charge transfer transition that is localized in the Mo-O-Mo bridge. The spectral data associated with our reactions are not characteristic of Mo(V) $\mu\text{-oxo-dimers}$. The absorption band that increases in intensity around 475 nm has been observed in similar Mo(IV) complexes [18]. Thus, the spectral changes that are observed are most likely due to the conversion of the Mo(VI) complex into its Mo(IV) analog by way of the oxygen atom abstraction reaction producing $\text{OPet}\phi_2$. There does not appear to be an equilibrium between the Mo(VI) and Mo(IV) complexes to produce the $\mu\text{-oxo-Mo(V)}$ dimer.

Pseudo first order rate constant, $k_{\text{obs}} = \text{rate}/[\text{MoO}_2\text{L}]$, were determined for these reactions at $60 \text{ }^\circ\text{C}$. In order to determine the order of the reaction with respect to $[\text{PEt}\phi_2]$, experiments were run to determine the dependence of k_{obs} on $\text{PEt}\phi_2$ concentration. Since these reactions are slow, only one complex ($\text{MoO}_2(5\text{-Cl-SSE})$) was examined under conditions of varying $\text{PEt}\phi_2$ concentration. A linear dependence of k_{obs} on $[\text{PEt}\phi_2]$ was obtained. This indicates that these reactions are also first order in $\text{PEt}\phi_2$.

The kinetic data obtained in this study is interpreted as resulting from a simple second order reaction involving a Mo(VI) Schiff base complex interacting with $\text{PEt}\phi_2$. The applicable rate law is $-\text{d}[\text{MoO}_2\text{L}]/\text{dt} = k_1[\text{MoO}_2\text{L}][\text{PEt}\phi_2]$. The second order specific rate constants, k_1 , are listed in Table I. Reactions at $30 \text{ }^\circ\text{C}$ have shown the k_1 's to be at least an order of magnitude smaller. Newton

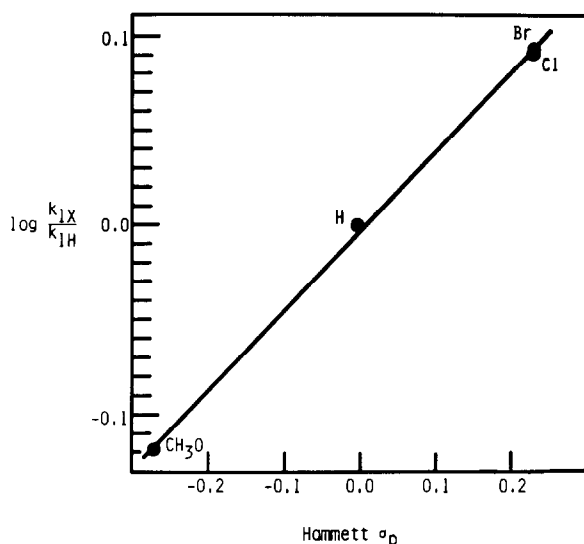


Fig. 2. Plot of $\log(k_{1X}/k_{1H})$ versus Hammett σ_p for $\text{MoO}_2\text{-(5-X-SSE)}$ ($X = \text{Cl, Br, H, CH}_3\text{O}$).

et al. [19] have discussed the reaction of $\text{MoO}_2(\text{S}_2\text{-CNR}_2)_2$ with PR_3 as an electrophilic attack of the oxo-oxygen on the electron rich PR_3 base. This mechanism is consistent with the kinetic data obtained here. The Mo(VI) complexes described here contain ligand substituents that span the range from electron-withdrawing (Cl, Br) to electron-donating (CH_3O). Figure 2 shows a plot of $\log(k_{1X}/k_{1H})$ ($X = \text{Cl, Br, H, CH}_3\text{O}$) versus the Hammett σ_p parameter. Even though the substituents are not directly bonded to the molybdenum, their effect is transmitted through the ligand to the Mo-oxo core. This transmitted electronic effect shows up in the changes that are observed for the k_1 's. For $\text{MoO}_2\text{-(5-Br-SSE)}$ the substituent makes the ligand more electronegative because of the electron-withdrawing capacity of the substituent. Some electron density is also removed from the Mo-oxo core making the oxo-oxygen the most electrophilic of the series. In contrast, the complex $\text{MoO}_2\text{-(5-CH}_3\text{O-SSE)}$ contains the methoxy group which makes this particular ligand the least electronegative of the series. The electron-donating ability of the methoxy group is also transmitted to the Mo-oxo core making the oxo-groups in this complex the least electrophilic of the series. This difference in electrophilic character of the

molybdenum complexes is manifested in the variation of the specific rate constants that are obtained for the reaction with $\text{PEt}\phi_2$. This report has shown that for a series of structurally similar *cis*-dioxomolybdenum(VI) coordination complexes the rate of reactivity toward a particular substrate can be altered systematically through careful ligand design.

Acknowledgement

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