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Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Kinetics of Oxygen Atom Transfer Reactions Involving Oxomolybdenum Complexes. General Treatment for Reactions with Intermediate Oxo-Bridged Molybdenum(V) Dimer Formation

MARTHA S. REYNOLDS,[1a] JEREMY M. BERG,[1b] and R. H. HOLM*

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A general treatment of the kinetics of the irreversible forward and reverse oxygen-atom transfer reactions

$$\mathrm{Mo^{VI}O_2L_2 + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo^{IV}OL_2 + XO}$$

in the presence of the reversible dimerization equilibrium $\mathrm{Mo^{V}_2O_3L_4 \rightleftharpoons MoO_2L_2 + MoOL_2}$ has been developed. The treatment has as its only assumption equilibrium of the dimerization reaction at all points along the reaction coordinate and allows determination of rate constants by spectrophotometry regardless of the relative initial concentrations of the reactants. Previous kinetics analyses were inadequate in scope or accuracy. The method has been applied to reactions in 1,2-dichloroethane at 25 °C. For the systems $\mathrm{MoO_2(S_2CNEt_2)_2/PR_3}$ the rate constants k_1 ($\mathrm{M^{-1}\ s^{-1}}$) = 0.071 ($\mathrm{PPh_3}$), 0.23 ($\mathrm{PPh_2Et}$), 0.43 ($\mathrm{PPhEt_2}$), and 0.53 ($\mathrm{PEt_3}$) for oxygen atom transfer to substrate. These values monotonically increase with increasing phosphine nucleophilicity. For the system $\mathrm{MoO(S_2CNEt_2)_2/Me_2SO}$, $k_{-1} = 1.6 \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$. The corresponding reaction rate with *N*-methylmorpholine *N*-oxide is orders of magnitude larger, suggesting that breaking of the bond to oxygen is the dominant factor in determining reaction rate. The excellent agreement between calculated and observed absorbance vs. time behavior and the previously determined dimerization rate constant of 1470 $\mathrm{M^{-1}\ s^{-1}}$ for L = $\mathrm{S_2CNEt_2}$ complexes justify the assumption in the kinetics analysis. This study provides the most detailed treatment of oxygen atom transfer reactions involving oxomolybdenum(IV,VI) complexes. Prior observations pertinent to these reactions are summarized.

Introduction

The significance of oxygen atom transfer reactions effected by transition-element compounds derives in large measure from catalysis of the forward and reverse reactions (1) by molybdenum hydroxylases.[2-5] Prominent examples of enzymes that

$$\mathrm{X + [O] \rightleftharpoons XO} \qquad (1)$$

catalyze the oxidation (X) or reduction (XO) of substrates in the two-electron formal processes $\mathrm{X + H_2O \rightleftharpoons XO + 2H^+ + 2e^-}$ include xanthine oxidase/dehydrogenase, sulfite oxidase, and nitrate reductase. The generalized reaction (2) and its

$$\mathrm{MoO_2L_2 + X \overset{k_2}{\rightleftharpoons} MoOL_2 + XO} \qquad (2)$$

$$\mathrm{Mo_2O_3L_4 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} MoOL_2 + MoO_2L} \qquad K_3 = k_3/k_{-3} \qquad (3)$$

component $\mathrm{Mo^{VI}O_2}$ and $\mathrm{Mo^{IV}O}$ species have frequently been considered as models of enzymic reactions and catalytic sites,[6,7] respectively. EXAFS analysis of the oxidized form of sulfite oxidase and the reduced forms of this enzyme and xanthine dehydrogenase indicate the presence of the $\mathrm{MoO_2}$ and MoO groups, respectively.[8,9] The forward reaction (2) was first observed by Barral et al.[11] in 1972 in their development of a system (L = $\mathrm{R_2NCS_2^-}$) for the catalytic aerial oxidation of triphenylphosphine. In subsequent work, this catalytic aspect has been pursued,[12] the reaction has been used for synthesis of MoO complexes,[13-16] and kinetics[11,17-19] and thermochemical[20] properties have been examined. The reverse reaction (2) has not been extensively investigated, and there are few documented examples of reduction of substrates XO.[13,19,21] A complicating feature of nearly all $\mathrm{MoO_2L_2/X}$ systems is the occurrence of reaction 3, in which $\mathrm{Mo^V{-}O{-}Mo^V}$ complexes are formed. Unlike reaction 2, this process is reversible for some systems and has been detected by electrochemical,[23] spectrophotometric,[11-13,15,17,24-29] and infrared[30] methods. Rate

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and equilibrium constants[11,17,22,26-29] and thermochemical data[20] have been reported for a number of reactions 3. The majority of these systems involve dithiocarbamate complexes.

A proper understanding of reactions 2 and 3 is pertinent to the interpretation of enzymic oxygen atom transfer reactions and to the development of active-site analogues with requisite reactivity. Despite the extensive and contributory investigations of these reactions, existing kinetics treatments are not entirely satisfactory in scope or accuracy. Here we report a more complete kinetics analysis of the coupled reactions (2) and (3), rate constants for the forward reaction (2) with a series of tertiary phosphine substrates, and two demonstrations of the occurrence of the reverse reaction (2). In all cases complexes are derived from the prototypic ligand *N*,*N*-diethyldithiocarbamate.

Experimental Section

Compounds and Solvents. Dioxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(VI), $MoO_2(S_2CNEt_2)_2$, was prepared by the method of Moore and Larsen[31] and was recrystallized from benzene–hexane (ϵ_{512} = 18 M^{-1} cm^{-1}). Oxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(IV), $MoO(S_2CNEt_2)_2$, was prepared as described by Chen et al.[13] and was similarly recrystallized (ϵ_{512} = 430 M^{-1} cm^{-1}). Triphenylphosphine (Aldrich) was twice recrystallized from ethanol–water. Triethylphosphine, diethylphenylphosphine, and diphenylethylphosphine (Strem) and *N*-methylmorpholine *N*-oxide hydrate (Eastman Kodak) were used as received. Dimethyl sulfoxide (Fisher) was distilled from CaH_2, degassed, and stored under dinitrogen. 1,2-Dichloroethane (Baker) was distilled from P_4O_{10}, degassed, and stored under dinitrogen or argon over 4-Å molecular sieves.

Kinetics Measurements. Preparation of 1,2-dichloroethane solutions was performed anaerobically, and all measurements were made on solutions under an argon atmosphere. Reaction systems were monitored spectrophotometrically at 512 nm. At this wavelength, a λ_{max} value of $Mo_2O_3(S_2CNEt_2)_4$, substantial absorbance changes occur over the course of reaction, in contrast to other wavelengths where there is appreciable absorbance.[24] In a typical experiment a cell containing a known concentration of $MoO_2(S_2CNEt_2)_2$ (~2 mM) was fitted with a serum cap and placed in a thermostated cell compartment at 25 °C. After thermal equilibration, a known amount of substrate in solution (5–100 mM, also at 25 °C) was injected through the serum cap and the cell contents were quickly mixed by shaking. The time dependence of absorbance was measured with a Cary Model 17D spectrophotometer. For each phosphine substrate two experiments were performed using different initial phosphine concentrations. The initial phase of the reaction was examined with a Durrum-Gibson Model 13701 stopped-flow apparatus, combined with a Zeiss Model PMQ II spectrophotometer and a Hewlett-Packard 6281A power supply. The photomultiplier detector was powered by a Hewlett-Packard Harrison Model 6515A dc power supply. Output from the photomultiplier was displayed as transmittance vs. time on a Tektronix type 564 storage oscilloscope, and traces were recorded photographically. The drive syringes and cell block were thermostated at 25 °C. Equal volumes of $MoO_2(S_2CNEt_2)_2$ and phosphine solutions of known concentrations were mixed in the cell, which had first been flushed with the phosphine solution. Kinetics of reverse reaction 2 in systems containing $MoO(S_2CNEt_2)_2$ and Me_2SO were determined by spectrophotometric monitoring of the time dependence of the absorbance at 512 nm. Procedures were similar to those used in the $MoO_2(S_2CNEt_2)_2$/phosphine systems. The reaction with *N*-methylmorpholine *N*-oxide proved too rapid for the measurement of kinetics by conventional spectrophotometry. All computations for data analysis were performed with locally written programs on a VAX 11-780 computer.

Results

Table I. Kinetics and Equilibrium Parameters for Reactions 2 ($X = PPh_3$) and 3 of Dithiocarbamate Complexes

L	solvent	*t*, °C	data[a,b]	ref
S_2CNPr_2	*o*-$C_6H_4Cl_2$	41	$k_2 = 2.3, K_3 = 4 \times 10^{-3}$	11
S_2CNEt_2	C_6H_6	24	$k_2 = 0.12, E_{a_2} = 14$	17
	MeCN	25	$k_2 = 1.1 \pm 0.3, \Delta H_2^{\ddagger} = 8.4 \pm 0.5, \Delta S_2^{\ddagger} = -30 \pm 1.6$	18, 19
	CH_2Cl_2	25	$K_3 = 2.1 \times 10^{-3}, k_3 = 4.9, k_{-3} = 2350$	22
	1,2-$C_2H_4Cl_2$	25	$\Delta H_2 = -29.0 \pm 2.5$	20
	1,2-$C_2H_4Cl_2$	25	$K_3 = (2.0 \pm 0.2) \times 10^{-3}, k_3 = 2.93 \pm 0.29, k_{-3} = 1470 \pm 20, E_{a_3} = 17.6 \pm 0.4, \Delta H_3^{\ddagger} = 17.0 \pm 0.4, \Delta S_3^{\ddagger} = 0.1 \pm 0.8, \Delta H_3 = 12.1 \pm 0.6, \Delta S_3 = 27.7 \pm 3.4$	27, 28

[a] Reactions denoted by subscripts. [b] Units: k_2, k_{-3}, M^{-1} s^{-1}; k_3, s^{-1}; E_a, ΔH, $\Delta H^{\ddagger}$, kcal/mol; ΔS, $\Delta S^{\ddagger}$, cal/(K mol); K_3, M.

Oxygen Atom Transfer to Phosphine Substrates. With reference to generalized irreversible[20] reaction 2 and reversible reaction 3, the rates of concentration change with time of each species are given by eq 4–7. With the assumption that the

$$\frac{d[MoO_2L_2]}{dt} = [MoO_2L_2](-k_2[X] - k_{-3}[MoOL_2]) + k_3[Mo_2O_3L_4] \quad (4)$$

$$\frac{d[Mo_2O_3L_4]}{dt} = -k_3[Mo_2O_3L_4] + k_{-3}[MoOL_2][MoO_2L_2] \quad (5)$$

$$\frac{d[MoOL_2]}{dt} = [MoO_2L_2](k_2[X] - k_{-3}[MoOL_2]) + k_3[Mo_2O_3L_4] \quad (6)$$

$$\frac{d[X]}{dt} = -k_2[MoO_2L_2][X] \quad (7)$$

rate of dimerization is very fast compared to oxygen atom transfer ($k_{-3} >> k_2$), the system is always at equilibrium with respect to the dimerization process. The rate of this process depends on both the rate constant k_{-3} and the concentrations of MoO_2L_2 and $MoOL_2$. At very early times in the reaction system, the concentration of $MoOL_2$ is quite small, affording a relatively slow rate of dimerization. At longer times, the amount of $Mo_2O_3L_4$ increases until depletion of MoO_2L_2 by reaction with X drives reaction 3 toward dissociation. If $Mo_2O_3L_4$ is the most strongly absorbing species at a given wavelength, it is expected that the absorbance will increase as this species accumulates and decrease as it dissociates.

The systems $MoO_2(S_2CNEt_2)_2/PPh_{3-n}Et_n$ (*n* = 0–3) in 1,2-dichloroethane solutions at 25 °C were subjected to a kinetics investigation. Coupled reactions 8 and 9, specific cases

$$MoO_2(S_2CNEt_2)_2 + PPh_{3-n}Et_n \xrightarrow{k_1} MoO(S_2CNEt_2)_2 + OPPh_{3-n}Et_n \quad (8)$$

$$Mo_2O_3(S_2CNEt_2)_4 \overset{K}{\rightleftharpoons} MoO(S_2CNEt_2)_2 + MoO_2(S_2CNEt_2)_2 \quad (9)$$

of reactions 2 and 3, occur in these systems. Kinetics and equilibrium data from prior studies are collected in Table I. Reaction 8 has previously been examined with PPh_3 as the only phosphine substrate. The products of this reaction and the existence of equilibrium 9 have been abundantly demonstrated in earlier work. In addition, the distorted cis-octahedral structure of $MoO_2(S_2CNR_2)_2$ (R = *n*-Pr,[32] Et[33]), the μ-oxo arrangement of $Mo_2O_3(S_2CNR_2)_4$ (R = *n*-Pr,[32] Et[34]), and the

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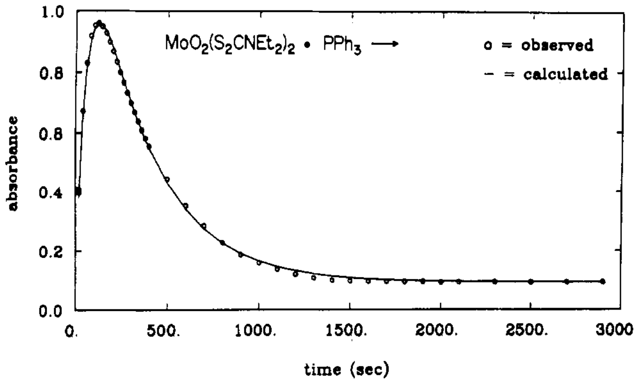

Figure 1. Plot of observed and calculated time dependence of absorbance at 512 nm for a system initially containing 2.16 mM $MoO_2(S_2CNEt_2)_2$ + 101 mM PPh_3. The parameters of best fit, used in this and the following figures, are given in the text.

square-pyramidal configuration of $MoO(S_2CN\text{-}n\text{-}Pr_2)_2$[32] have been established by X-ray diffraction. Consequently, the Mo(IV,V,VI) species involved in reactions 8 and 9 are well-defined.

The reaction of $MoO_2(S_2CNEt_2)_2$ with a 25- or 50-fold excess of PPh_3 gave an absorbance vs. time curve, shown in Figure 1, consistent with the foregoing prediction. The initial yellow color of the reaction system, due to $MoO_2(S_2CNEt_2)_2$, changed to violet ($Mo_2O_3(S_2CNEt_2)_4$) and then to red ($MoO(S_2CNEt_2)_2$) as the reaction proceeded. The kinetics of the system have been analyzed in detail, with the only assumption being that the dimerization equilibrium is rapidly established at all points along the reaction coordinate. This treatment, developed in the Appendix, permits calculation of absorbance vs. time (eq A-15), dependent only on the unknown parameters K, k_1, and ϵ_5, the molar extinction coefficient of $Mo_2O_3(S_2CNEt_2)_4$. The values of ϵ_5 and K are independent of substrate, and k_1 for a particular substrate can be determined from K, ϵ_5, and t_{max}, the time at maximum absorbance (eq A-17).

Absorbance data for the system $MoO_2(S_2CNEt_2)_2/PPh_3$ were analyzed by finding the values of ϵ_5 and K, and the corresponding value of k_1, which minimize the function $f = \sum_{i,j} w_{ij}(A_{ij}^{calcd} - A_{ij}^{obsd})^2$, where ij refers to the jth point in the ith experiment and $w_{ij} = 1/(n_i(A_{ij}^{obsd})^2)$. The best fit gave values of $\epsilon_5 = 28\,000 \pm 2500$ M^{-1} cm^{-1}, $K = (1.7 \pm 0.3) \times 10^{-3}$ M, and $k_1 = 0.071 \pm 0.003$ M^{-1} s^{-1}. Values of the first two parameters are in good agreement with ϵ_5(512 nm) = 24 000 M^{-1} cm^{-1} and $K = (2.0 \pm 0.2) \times 10^{-3}$ M determined by Matsuda et al.[27] in their study of equilibrium 9 in 1,2-dichloroethane solution by the concentration-jump method. The satisfactory conformance between the observed and calculated time dependence of absorbance is illustrated in Figure 1. The time dependence of the concentrations of the Mo(IV,V,VI) complexes is provided in Figure 2. At the reaction coordinate 0.5, the time at which 0.5 equiv of PPh_3 is consumed in reaction 8, the mole fraction of $Mo_2O_3(S_2CNEt_2)_4$ is 0.18, its maximum value. At this point the mole fractions of $MoO_2(S_2CNEt_2)_2$ and $MoO(S_2CNEt_2)_2$ are both 0.41.

In this treatment, the parameters ϵ_5 and K are strongly correlated; i.e., increasing or decreasing both by appropriate amounts gives fits that are essentially as satisfactory as that obtained with the above values. Meaningful standard deviations for these parameters, therefore, cannot be calculated. For this reason, the uncertainties given for ϵ_5 and K are estimates obtained by finding values of the parameters that gave fits of comparable quality. The uncertainty in k_1 was calculated by using limiting values of ϵ_5 and K in eq A-17 to give boundaries on the rate constant.

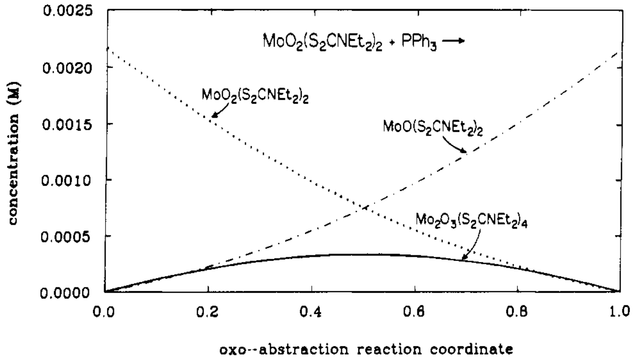

Figure 2. Plot of the concentrations of Mo(IV,V,VI) complexes with time for a system initially containing 2.16 mM $MoO_2(S_2CNEt_2)_2$ and 101 mM PPh_3, calculated from eq A-1, A-3, and A-4. The reaction coordinate refers to the fraction of 1 equiv of PPh_3 consumed in reaction 4.

Table II. Rate Constants for Oxygen Atom Transfer Reactions

substrate	[Mo], mM	[substrate], mM	t_{max}, s	k_1,[a] M^{-1} s^{-1}
PPh_3	2.16	101	119	0.071 (3)[a]
		50.6	256	
PPh_2Et	2.27	10.1	379	0.23 (2)
		5.05	918	
$PPhEt_2$	1.72	10.2	213	0.43 (2)
		5.08	427	
PEt_3	2.08	9.20	191	0.53 (1)
	2.37	10.5	173	
Me_2SO	2.01	1000	5019	0.00016 (1)[b]
	2.12	1000	5020	

[a] Values calculated from eq A-17 with use of $\epsilon_4 = 430$ M^{-1} cm^{-1} and $\epsilon_6 = 18$ M^{-1} cm^{-1}. For each run, two values of k_1 were calculated with use of $K = 0.0014$ M, $\epsilon_5 = 25\,000$ M^{-1} cm^{-1} and $K = 0.0020$ M, $\epsilon_5 = 30\,500$ M^{-1} cm^{-1}, which represent acceptable extremes of these parameters. The value quoted is the mean of four values so obtained. The esd values in parentheses were calculated from the equation $\sigma = [\Sigma_{i=1}^{n} (x_i - \bar{x})^2/(n-1)]^{1/2}$. [b] k_{-1}, reaction 10.

For the other substrates $PPh_{3-n}Et_n$ (n = 1–3), the rate constants k_1 were calculated from the time at maximum absorbance using the values of ϵ_5 and K obtained from the PPh_3 system. Values of the rate constants for the complete set of phosphine substrates, listed in Table II, are the average values from two experiments. Uncertainties in these values were calculated as described above.

In order to demonstrate the slow rate of dimerization (reaction 9) at short reaction times, the system $MoO_2(S_2CNEt_2)_2/PPh_3$ was examined for the first 100 ms by stopped-flow spectrophotometry. The results are plotted in Figure 3. The solid line represents a numerical solution of eq 4–7 using the above values of k_1 ($=k_2$) and ϵ_5, the k_3 and k_{-3} values of Matsuda et al.[27] (Table I), and initial concentrations of $MoO_2(S_2CNEt_2)_2$ and phosphine. The dotted line, calculated from eq A-15 (converted to transmittance), describes the case where equilibrium is instantaneously established at all points. It is identical with the curve obtained from the numerical solution of eq 4–7 at the limit of infinite k_3 and k_{-3}. The experimental points do not fall off as rapidly with time as does the dotted line, indicating that equilibrium has not been established during this initial period.

Oxygen Atom Transfer from Substrates. The reverse of reaction 2 has been examined in the form of reactions 10 and 11. The kinetics treatment is equivalent to that described for forward reaction 2. The rate constant is calculated from eq A-17 with C = [Mo(IV)], P = [substrate], and $k_1 = k_{-1}$ and

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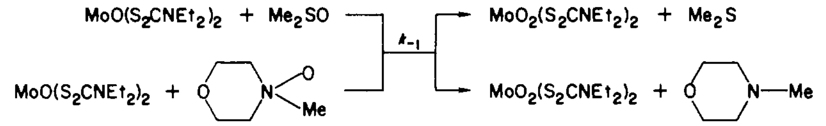

(10)

(11)

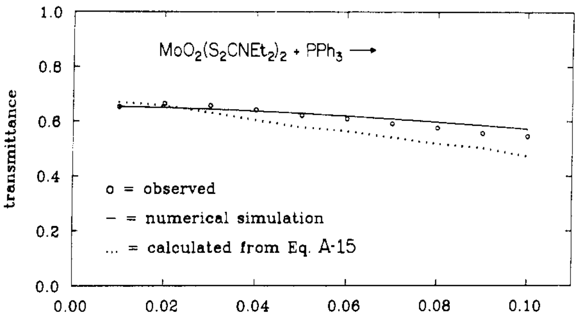

Figure 3. Plot of observed and calculated time dependence of transmittance at 512 nm for a system initially containing 5.13 mM $MoO_2(S_2CNEt_2)_2$ and 100 mM PPh_3. The numerical simulation was obtained with use of the dimerization rate constants of Matsuda et al.[27] The curve calculated from eq A-15 is that expected for instantaneous attainment of the dimerization equilibrium. A slight adjustment of the observed data was applied to account for the characteristics of the stopped-flow spectrophotometer.

with ϵ_4 and ϵ_6 reversed in eq A-16. The reaction rate with Me_2SO in 1,2-dichloroethane solution proved to be very slow and required a ~500-fold excess of substrate in a 2 mM solution of $MoO(S_2CNEt_2)_2$ to reduce t_{max} to ~5000 s. For this reaction, $k_{-1} = (1.6 \pm 0.1) \times 10^{-4}$ M^{-1} s^{-1} (Table II). Reaction 11, with a 2 mM solution of the Mo(IV) complex and 2.5 equiv of *N*-methylmorpholine *N*-oxide in 1,2-dichloroethane solution, was complete in less than 10 s and thus is too fast to be followed by conventional spectrophotometry. Upon the addition of up to 1 equiv of the *N*-oxide to a solution of $MoO(S_2CNEt_2)_2$ (red), the color changed to violet and then to yellow. The ^1H NMR spectrum of a $CDCl_3$ solution initially containing equimolar quantities of $MoO(S_2CNEt_2)_2$ and the *N*-oxide exhibited the spectrum of *N*-methylmorpholine (δ(Me) 2.27); resonances of the *N*-oxide (δ(Me) 3.11) were absent. In a second experiment, solvent was removed from an equimolar solution of the reactants in 1,2-dichloroethane. The infrared spectrum of the solid residue contained the characteristic very strong ν_{MoO} features at 907 and 878 cm^{-1} of $MoO_2(S_2CNEt_2)_2$[14] and was otherwise identical with the spectrum of an authentic sample of this compound. The ν_{MoO} band of $MoO(S_2CNEt_2)_2$ at 962 cm^{-1} (vs) and similar bands of $Mo_2O_3(S_2CNEt_2)_4$[14] at 969 (vs) and 952 (s) cm^{-1} were absent. These observations demonstrate the occurrence of reaction 11.

Discussion

Oxygen Atom Transfer to Substrate. (a) Kinetics. The treatment developed here for coupled reactions 2 and 3 and applied to the specific cases of reactions 8 and 9 accounts for all dynamic aspects of these reactions. The assumption that, except for very short reaction times (<1 s, Figure 3), the dimerization process is at equilibrium at all points along the reaction coordinate is justified by the agreement between observed and calculated absorbance/time behavior in Figure 1. In addition, the dimerization rate constant $k_{-3} = 1470$ M^{-1} s^{-1} for reaction 9 (Table I) is about 3 orders of magnitude greater than the oxygen atom transfer rate constants in Table II. The treatment is sufficiently general to allow determination of these rate constants regardless of the relative initial concentrations of the reactants. For systems with known initial concentrations and greater than 1 equiv of substrate, the rate constants can be obtained very simply by measurement of the time at maximum absorbance.

(b) Prior Results. The kinetics of reaction 2 ($L = S_2CNR_2$ and $X = PPh_3$) have been investigated in several contexts. The reported rate constants vary from 0.12 to 2.3 M^{-1} s^{-1} (Table I), a range too large to be accountable in terms of differences in solvent, temperature, or R substituent. McDonald and Shulman,[17] in their development of an assay for PPh_3 in benzene solution based on monitoring of the visible absorbance of $Mo_2O_3(S_2CNEt_2)_4$ with time, obtained a rate constant (0.12 M^{-1} s^{-1}) that is correct. However, their method is applicable only under pseudo-first-order conditions, with a large excess of $MoO_2(S_2CNEt_2)_2$ over phosphine. Durant et al.[18] examined the system $MoO_2(S_2CNEt_2)_2/PPh_3$ in acetonitrile solution with excess phosphine. They assumed no contribution to the absorbance at 514 nm from $Mo_2O_3(S_2CNEt_2)_4$; i.e., $MoO_2(S_2CNEt_2)_2$ is fully converted to $MoO(S_2CNEt_2)_2$ by excess phosphine before any dimer is formed. The assumption results in a rate constant (1.1 M^{-1} s^{-1}) that is too large. Barral et al.[11] report a rate constant (2.3 M^{-1} s^{-1}) for the oxidation of PPh_3 by $MoO_2(S_2CNPr_2)_2$ in *o*-dichlorobenzene solution at 41 °C. The details of the kinetics analysis were not given; we conclude that this value is erroneously high. Recent work by Topich and Lyon[35] on the oxidation of PPh_2Et by tridentate Schiff-base complexes of $Mo^{VI}O_2$ at 60 °C yielded rate constants on the order of 10^{-3} M^{-1} s^{-1}. For a given ligand system, a single absorbing species was produced that was claimed to be the $Mo^{IV}O$ complex; however, the evidence that the chromophore is this complex rather than a μ-oxo Mo(V) species appears to be inconclusive.

(c) Trend in Substrate Reactivity. In terms of phosphine substrate, the rate constants for reaction 8 increase in the order $PPh_3 < PPh_2Et < PPhEt_2 < PEt_3$. This is the order of phosphine nucleophilicity in reactions with alkyl halides[36,37] and a coordinated organic ligand,[38] based on linear relationships between the reaction rate (log *k*) and nucleophilicity parameters derived from carbonyl stretching frequencies of Ni(0) complexes[39] and acidity constants of phosphonium cations[40] and phosphoroorganic acids.[41] While the rate constants for the oxygen atom transfer reactions increase monotonically with increasing nucleophilicity, no linear relationship exists with these parameters.[42] A related monotonic trend has been noted for the reaction of several phosphines with $MoO_2(Et\text{-}L\text{-}cys)_2$[12a] (Et-L-cys = ethyl L-cysteinate). In the formulation of a simple mechanism for reaction 8 it is unlikely, for steric reasons, that the phosphine attacks directly at the Mo(VI) site in the initial event. Sequence 12 is reasonable. Attack at the oxygen atom,[21] possibly involving a vacant π* orbital of a MoO fragment,[19] and concerted two-electron transfer to Mo are followed by Mo–O bond-breaking

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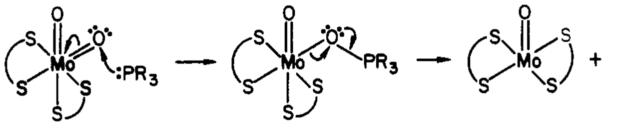
(42) The lack of linearity, or even monotonicity, of reaction rates of nucleophilies with organic substrates and metal complexes is not uncommon; cf., e.g.: Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319.



$+ \; OPR_3$ (12)

and P–O bond-making steps. Elimination of phosphine oxide from the coordination sphere and rearrangement to the square-pyramidal structure of $MoO(S_2CN\text{-}n\text{-}Pr_2)_2$[32] complete the reaction.

The anaerobic oxygen atom transfer reaction 2 is well defined, in terms of kinetics and reaction products, only for tertiary phosphine substrates. Slight to trace quantities of Ph_3AsO, Ph_3SbO, and Et_3NO have been claimed to result from reactions of $MoO_2(S_2CNEt_2)_2$ and the appropriate unoxidized compounds in benzene solutions at 40–45 °C.[43] The report[44] that $MoO_2(Et\text{-}L\text{-}cys)_2$ is capable of oxidizing (unspecified) aldehydes to the corresponding carboxylic acids was not confirmed.[45] In another report[46] no reaction was observed between this complex and benzaldehyde in several aprotic solvents; in DMF a reaction did occur but no evidence for the formation of benzoic acid was obtained. Further, Nakamura et al.[47] found that attempts to oxidize aldehydes with $MoO_2(S_2CNEt_2)_2$ were unsuccessful. It has been briefly reported that one Mo(VI) complex of the type MoO_2LH_2 ($LH_2 = N_2S_2$ tetradentate ligand) is reduced to the Mo(V) species $[MoOL]^-$ in the presence of excess sulfite.[48] The oxidation product of sulfite was not described.

Oxygen Atom Transfer from Substrates. Earlier qualitative indications of a reaction between $MoO(S_2CNEt_2)_2$ and Me_2SO[21,23] have been confirmed here by a kinetics study of reaction 10 in 1,2-dichloroethane solution. With *N*-methylmorpholine *N*-oxide the reaction rate is orders of magnitude larger, suggesting that breaking of the bond to oxygen is the most important factor (in the absence of steric effects) in governing the rate of oxygen atom transfer from substrate to a common Mo(IV) complex. Given that $MoO(S_2CNEt_2)_2$ forms weak adducts with pyridine and PPh_2Et[22] and with an oxygen atom of $MoO_2(S_2CNEt_2)_2$ as the first event in dimerization reaction 9, similar association with the substrates employed here is assured. The reverse of sequence 12 provides a simple description of the reaction.

Reactions 10 and 11 are currently the best defined examples of oxygen atom transfer to a Mo(IV) center. In addition, there are numerous reported observations of the oxidation of $MoOL_2$ complexes to MoO_2L_2 and $Mo_2O_3L_4$ by dioxygen. These reactions are an integral part of the sequences for the aerial oxidation of tertiary phosphines catalyzed by MoO_2L_2 complexes.[11,12] Mitchell and Scarle[21] have recorded visual color changes of reactions of $MoO(S_2CNEt_2)_2$ with various compounds XO in chloroform solution. The rapid reactions with Me_3CONO_2 and pyridine *N*-oxide, affording a yellow color at $\lesssim 1$ min reaction time, are presumably correctly described as producing Me_3CONO and pyridine, respectively. The claim that Ph_3PO and N_2O also react was shown to be incorrect under anaerobic conditions.[13] The purple color of $Mo_2O_3(S_2CNEt_2)_4$ observed in the original experiments[21] could not be reproduced in either case, and dinitrogen was not detected as a reaction product. Thus these compounds are not capable of oxygen atom transfer to $MoO(S_2CNEt_2)_2$; the formation of the μ-oxo complex doubtless was a consequence of incomplete anaerobicity. In addition, it has been reported that equimolar quantities of $MoO(S_2CNEt_2)_2$ and $(Et_4N)NO_3$ in chloroform do not yield $(Et_4N)NO_2$ as described,[21] and $MoO_2(S_2CNEt_2)_2$ was not identified as a reaction product.[19] Among biological processes reaction 10 is related to that catalyzed by biotin sulfoxide reductase, a molybdoenzyme from *Escherichia coli*.[49]

The kinetics treatment described here is capable of abstracting rate constants for the forward and reverse oxygen atom transfer reactions (2) in the presence of dimerization equilibrium 3. The latter does not, of course, interfere with the occurrence of these reactions. If, as in $MoO_2(S_2CNEt_2)_2/PR_3$ systems, the equilibrium is reversible and rapidly established compared to the rate of oxygen atom transfer, the concentration of the μ-oxo dimer rises and falls, ultimately to zero, as the reaction proceeds (Figure 2). In the event of an irreversible equilibrium, reactions 13 and 14 may

$$2MoO_2L_2 + X \rightarrow Mo_2O_3L_4 + XO \qquad (13)$$

$$2MoOL_2 + XO \rightarrow Mo_2O_3L_4 + X \qquad (14)$$

be favored by the stability of the Mo(V) product. An obvious disadvantage is that, in a stoichiometric reaction, half of the Mo(IV,VI) reactant is consumed in μ-oxo dimer formation. In attempts to simulate enzymic oxygen atom transfer reactions, the equilibrium 3 is an undesirable complication. All evidence supports the existence of mononuclear catalytic sites, particularly for the well-studied cases of xanthine oxidase/dehydrogenase and sulfite oxidase. Molybdenum(V) intermediates have been detected by EPR spectroscopy;[2–5] dimerization to Mo^V–O–Mo^V units is eliminated by the constraints of protein structure. One approach to the suppression of reaction 3, taken by Topich,[50] is the attachment of a molybdenum reactant to a polymer support. An anchored Mo(VI)–tripeptide complex is described as reduced to Mo(IV) by PPh_3 and reoxidized to Mo(VI) by NO_3^-, with formation of Ph_3PO, and NO_2^- and other products, respectively.[50] In this laboratory, MoO_2 and MoO complexes of tridentate NX_2-type ligands (X = O, S), designed to provide a steric impediment to oxo-bridge formation, have been prepared.[51] Their structures and properties, including reactions with sulfoxides, will be detailed in subsequent reports. The inability of synthetic MoO_2 and MoO complexes thus far tested by others to effect clean oxygen atom tranfer reactions of the biological substrates SO_3^{2-} (HSO_3^-), NO_3^-, and RCHO (with several possible exceptions[48,50]) underscores the need for continued efforts in modeling the reactions of this class of molybdoenzymes.

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Appendix

Kinetics Treatment of Coupled Oxygen Atom Transfer and Mo(IV)–Mo(VI) Dimerization Reactions. Consider the generalized reactions 2 and 3 with $X = PR_3$, $k_2 = k_1$, and $K_3 = K$. The treatment is based on the premise that the dimerization equilibrium is rapidly obtained, such that the system is always at equilibrium with respect to that process. For an initial concentration C of MoO_2L_2

$$C = [MoO_2L_2] + [MoOL_2] + 2[Mo_2O_3L_4] \qquad \text{(A-1)}$$

The equilibrium quotient of reaction 3 is defined by

$$K = [MoO_2L_2][MoOL_2]/[Mo_2O_3L_4] \qquad \text{(A-2)}$$

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These equations are readily solved in terms of $[MoO_2L_2]$:

$$[MoOL_2] = \frac{K(C - [MoO_2L_2])}{K + 2[MoO_2L_2]} \tag{A-3}$$

$$[Mo_2O_3L_4] = \frac{[MoO_2L_2](C - [MoO_2L_2])}{K + 2[MoO_2L_2]} \tag{A-4}$$

The equilibrium concentration of MoO_2L_2 is affected by the oxygen atom transfer reaction and the concomitant shift in the dimerization equilibrium. Take dx to be an infinitesimal concentration change along the oxo atom abstraction reaction coordinate and dy to be the corresponding change along the dimerization reaction coordinate to maintain equilibrium. Thus

$$K = \frac{([MoO_2L_2] - dx - dy)([MoOL_2] + dx - dy)}{[Mo_2O_3L_4] + dy} \tag{A-5}$$

With use of $[MoO_2L_2][MoOL_2] - K[Mo_2O_3L_4] = 0$, one obtains

$$\frac{dy}{dx} = \frac{[MoO_2L_2] - [MoOL_2]}{K + [MoO_2L_2] + [MoOL_2]} \tag{A-6}$$

If P is the initial phosphine concentration, the concentration of free phosphine at any time is given by

$$[PR_3] = P - [MoOL_2] - [Mo_2O_3L_4] \tag{A-7}$$

Therefore, the disappearance of MoO_2L_2 is governed by

$$\frac{d[MoO_2L_2]}{dt} = -k_1[MoO_2L_2][PR_3]\left(1 + \frac{dy}{dx}\right) \tag{A-8}$$

$$= -k_1[MoO_2L_2](P - [MoOL_2] - [Mo_2O_3L_4]) \times \left(1 + \frac{[MoO_2L_2] - [MoOL_2]}{K + [MoO_2L_2] + [MoOL_2]}\right) \tag{A-9}$$

$$= -k_1\{[MoO_2L_2] \times (K + 2[MoO_2L_2])([MoO_2L_2]^2 + (K + 2P - C)[MoO_2L_2] + K(P - C))\}/\{2[MoO_2L_2]^2 + 2K[MoO_2L_2] + K^2 + CK\} \tag{A-10}$$

Separation of variables affords

$$\{2[MoO_2L_2]^2 + 2K[MoO_2L_2] + K^2 + CK\}/\{[MoO_2L_2] \times (K + 2[MoO_2L_2])([MoO_2L_2]^2 + (K + 2P - C)[MoO_2L_2] + K(P - C))\}\, d[MoO_2L_2] = -k_1\, dt \tag{A-11a}$$

This can be integrated by the method of partial fractions, subject to the condition that $[MoO_2L_2] = C$ at $t = 0$. The partial fraction decomposition of this equation is

$$\left[\frac{e}{[MoO_2L_2]} + \frac{f}{2[MoO_2L_2] + K} + \frac{g}{[MoO_2L_2] - r_1} + \frac{h}{[MoO_2L_2] - r_2}\right] d[MoO_2L_2] = -k_1\, dt \tag{A-11b}$$

where

$$e = \frac{K + C}{K(P - C)} \qquad f = \frac{4}{K} \qquad g = \frac{-(K + 2P - C) - Q^{1/2}}{2K(P - C)}$$

$$h = \frac{-(K + 2P - C) + Q^{1/2}}{2K(P - C)}$$

$$r_1 = \frac{-(K + 2P - C) + Q^{1/2}}{2}$$

$$r_2 = \frac{-(K + 2P - C) - Q^{1/2}}{2}$$

$$Q = K^2 + 4P^2 + C^2 + 2KC - 4PC$$

Integration of this equation term by term yields

$$-k_1t = \frac{K + C}{K(P - C)} \ln\left(\frac{[MoO_2L_2]}{C}\right) + \frac{2}{K} \ln\left(\frac{2[MoO_2L_2] + K}{2C + K}\right) - \frac{K + 2P - C + Q^{1/2}}{2K(P - C)} \times \ln\left(\frac{2[MoO_2L_2] + K + 2P - C - Q^{1/2}}{K + 2P + C - Q^{1/2}}\right) - \frac{K + 2P - C - Q^{1/2}}{2K(P - C)} \times \ln\left(\frac{2[MoO_2L_2] + K + 2P - C + Q^{1/2}}{K + 2P + C + Q^{1/2}}\right) \tag{A-12}$$

$$= f([MoO_2L_2], K, C, P)$$

where $P \neq C$.

For the special case $P = C$, integration of the reduced form of eq A-11a affords the integrated rate equation

$$-k_1t = -\frac{(K + 2C)}{K(K + C)} \ln\left(\frac{[MoO_2L_2]}{C}\right) + \frac{4}{K} \ln\left(\frac{2[MoO_2L_2] + K}{2C + K}\right) - \frac{1}{K + C} \ln\left(\frac{[MoO_2L_2] + K + C}{2C + K}\right) - \frac{1}{[MoO_2L_2]} + \frac{1}{C} \tag{A-13}$$

These equations can be inverted numerically to yield $[MoO_2L_2]$ at time t. The absorbance is given by

$$A = l(\epsilon_4[MoOL_2] + \epsilon_5[Mo_2O_3L_4] + \epsilon_6[MoO_2L_2]) \tag{A-14}$$

where l is the path length. With use of eq A-3 and A-4, eq A-14 becomes

$$A = l\left(\epsilon_4\frac{K(C - [MoO_2L_2])}{K + 2[MoO_2L_2]} + \epsilon_5\frac{[MoO_2L_2](C - [MoO_2L_2])}{K + 2[MoO_2L_2]} + \epsilon_6[MoO_2L_2]\right) \tag{A-15}$$

Thus, after the time dependence of $[MoO_2L_2]$ is calculated from eq A-12, the absorbance as a function of time is obtained from eq A-15. The molar extinction coefficients ϵ_4 and ϵ_6 can be directly measured. Values of the correlated parameters ϵ_5 and K were obtained from the fitting procedure described in the text.

If $[MoO_2L_2]$ at the time of maximum absorbance (t_{max}) is known, eq A-12 can be used to calculate rate constant k_1. The value of $[MoO_2L_2]$ at t_{max} is obtained by differentiating eq A-15 with respect to $[MoO_2L_2]$. At $dA/d[MoO_2L_2] = 0$

$$[MoO_2L_2]' = \frac{1}{2}\left(-K + \left[\frac{K(K + 2C)(\epsilon_5 - 2\epsilon_4)}{\epsilon_5 - 2\epsilon_6}\right]^{1/2}\right) \tag{A-16}$$

Substitution of this value in eq A-12 gives a relation of the form

$$k_1 = \frac{-f([MoO_2L_2]', K, C, P)}{t_{max}} \tag{A-17}$$

so that the value of k_1 can be found simply from the time of maximum absorbance.

Registry No. $MoO_2(S_2CNEt_2)_2$, 19680-83-2; PPh_3, 603-35-0; PPh_2Et, 607-01-2; $PPhEt_2$, 1605-53-4; PEt_3, 554-70-1; $MoO(S_2CNEt_2)_2$, 25395-92-0; Me_2SO, 67-68-5; *N*-methylmorpholine *N*-oxide, 7529-22-8; oxygen, 17778-80-2.