Kinetic Studies of Oxygen Atom Transfer Reactions between Various *cis*-Dioxobis(dithiocarbamato)molybdenum(VI) Complexes and Triphenylphosphine

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The kinetics of the oxygen atom transfer reactions between *cis*-$[MoO_2(R_2dtc)_2]$ [R=CH_3, C_2H_5, *i*-C_3H_7, *i*-C_4H_9, $C_6H_5CH_2$ (Bz), C_6H_5 (Ph)] and PPh_3 (coupled reactions 1 and 2) have been investigated.

$$[MoO_2(R_2dtc)_2] + PPh_3 \xrightarrow{k_1} [MoO(R_2dtc)_2] + OPPh_3 \quad (1)$$

$$[MoO_2(R_2dtc)_2] + [MoO(R_2dtc)_2] \rightleftharpoons[K_d] [Mo_2O_3(R_2dtc)_4] \quad (2)$$

The rate constants (k_1) of oxygen atom transfer reaction 1 correlate with the formal potentials of $[MoO_2(R_2dtc)_2]^{0/-1}$ except for R=Bz and Ph. The equilibrium constant values (K_d) of dimerization reaction 2 decrease with increase of the electron-donating ability of the substituents on the dithiocarbamate ligands.

Barral et al. reported that the *cis*-dioxobis(dithiocarbamato)molybdenum(VI) complexes $[MoO_2(R^1{}_2dtc)_2]$ (R^1=Et, *n*-Pr, and *i*-Bu)[1] undergo an oxygen atom transfer reaction to tertiary phosphine ($PR^2{}_3$; R^2=*n*-Bu and Ph) giving Mo(IV) complexes $[MoO(R^1{}_2dtc)_2]$ and $OPR^2{}_3$.[2] However, the reaction is complicated by the intervention of an Mo(V) dinuclear complex according to the following equations:

$$[MoO_2(R^1{}_2dtc)_2] + PR^2{}_3 \xrightarrow{k_1} [MoO(R^1{}_2dtc)_2] + OPR^2{}_3 \quad (1)$$

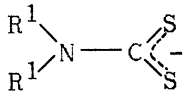
$$[MoO_2(R^1{}_2dtc)_2] + [MoO(R^1{}_2dtc)_2] \rightleftharpoons[K_d] [Mo_2O_3(R^1{}_2dtc)_4] \quad (2)$$

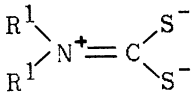
Among these molybdenum complexes, only the Mo(V) dinuclear complexes have large extinction coefficients in the vicinity of 510 nm.[3,4] Thus, if the reaction is followed at this wavelength, biphasic kinetic behavior may be observed.

This oxygen atom transfer reaction has attracted much attention, especially as models of enzymic reactions.[5] Kinetic invesitgations have been made by several reseachers.[2,6-8] Barral et al.[2] reported kinetic studies of the $[MoO_2(n\text{-}Pr_2dtc)_2]/PPh_3$ system in *o*-dichlorobenzene at 41 °C; McDonald et al.[6] studied the kinetics of the $[MoO_2(Et_2dtc)_2]/PPh_3$ system in benzene at 24 °C, and Durant et al.[7] investigated the kinetics of $[MoO_2(Et_2dtc)_2]/PPh_3$ system in acetonitrile solution by the stopped-flow technique at temperatures between 15 and 45 °C. However, the kinetic results of these investigations were contradictory.

Holm et al.[8] extensively investigated the kinetics of reactions between $[MoO_2(Et_2dtc)_2]$ and $PPh_n(Et)_{3-n}$ (n=0—3) in 1,2-dichloroethane and developed a general treatment of the kinetics which provided a satisfactory explanation for the biphasic kinetic behavior. The rate constant k_1 was found to increase with increasing nucleophilicity of $PPh_n(Et)_{3-n}$.

Chemical properties of dithiocarbamate complexes are sensitive to the nature of the substituent on the dithiocarbamate ligand because of the existence of two resonance forms.[9]


(I)


(II)

An increase of the electron-donating ability of the R^1 group favors resonance form II and hence leads to the increase of the electron density on the sulfur atoms bound to the metal atom.

Hitherto, the effect of the substituents on the dithiocarbamate ligands on the kinetics of the oxygen atom transfer reactions has not been investigated. This is the motive of this work in which the kinetics of the reactions between *cis*-$[MoO_2(R^1{}_2dtc)_2]$ (R^1=Me, Et, *i*-Pr, *i*-Bu, Bz, and Ph) and PPh_3 are dealt with. Kinetic traces were analyzed by essentially the same procedure that developed by Holm et al.[8]

Experimental

Materials. 1,2-Dichloroethane ($1,2\text{-}C_2H_4Cl_2$), obtained from Wako Pure Chemicals Industries, was purified by fractional distillation over P_2O_5. Triphenylphosphine (Nacalai Tesque Inc.) was purified twice by recrystallization from ethanol–water. Sodium salts of dithiocarbamates $R^1{}_2dtc^-$

(R^1=*i*-Pr, *i*-Bu, Bz, Ph) were prepared by literature methods.[10,11] Sodium salts of dimethyldithiocarbamate and diethyldithiocarbamate were purchased from Nacalai Tesque Inc. The complexes $[MoO_2(R^1{}_2dtc)_2]$ were prepared according to literature methods.[12,13]

Apparatus and Procedures. Procedures for kinetic measurements were almost identical with those reported previously.[8] The change of absorbance vs. time was measured with a UV-160 spectrophotometer (Shimadzu Co.).

Calculations in the kinetic analysis were performed by an ACOS 630/10 computer. For the nonlinear least-squares fitting between experimental data and theoretical values, the SALS (Statistical Analysis with Least Squares fitting) program developed by Nakagawa and Oyanagi[14] was used.

Results and Discussion

Biphasic kinetic behavior was observed for all $[MoO_2(R^1{}_2dtc)_2]/PPh_3$ systems, and is due to the formation and decay of $[Mo_2O_3(R^1{}_2dtc)_4]$ (Fig. 1). The kinetic traces are also found to be sensitive to the nature of substituents on the dithiocarbamate ligands.

The kinetic analysis of coupled reactions 1 and 2 was developed by Holm et al.[8] The absorbance of the reaction solution is expressed by equation 3 ($L=R^1{}_2dtc_2^-$).

$$A = l(\varepsilon_4 \frac{(C-[MoO_2L_2])}{1+2K_d[MoO_2L_2]} + \varepsilon_5 \frac{K_d[MoO_2L_2]\,(C-[MoO_2L_2])}{1+2K_d[MoO_2L_2]} + \varepsilon_6[MoO_2L_2]) \quad (3)$$

where l and C denote the optical path length and the initial concentration of $[MoO_2L_2]$, respectively. Symbols ε_4, ε_5, and ε_6 are the molar extinction coefficients of $[MoOL_2]$, $[Mo_2O_3L_4]$, and $[MoO_2L_2]$, respectively, the lattermost of which can be determined independently by spectroscopic measurement of $[MoO_2L_2]$. The time dependence of $[MoO_2L_2]$ is given by

$$-k_1t = \frac{1+K_dC}{P-C}\ln\left(\frac{[MoO_2L_2]}{C}\right) + 2K_d\ln\left(\frac{2K_d[MoO_2L_2]+1}{2K_dC+1}\right) - \frac{1+K_d(2P-C+Q^{1/2})}{2(P-C)}\times \ln\left(\frac{1+K_d(2[MoO_2L_2]+2P-C-Q^{1/2})}{1+K_d(2P+C-Q^{1/2})}\right) - \frac{1+K_d(2P-C-Q^{1/2})}{2(P-C)}\times \ln\left(\frac{1+K_d(2[MoO_2L_2]+2P-C+Q^{1/2})}{1+K_d(2P+C+Q^{1/2})}\right), \quad (4)$$

where $P\neq C$ and $Q=K_d^{-2}+4P^2+C^2+2K_d^{-1}C-4PC$. Here, k_1 is the rate constant for the forward reaction of reaction 1 and P is the initial concentration of PPh_3. The time dependence of $[MoO_2L_2]$ was numerically obtained from equation 4 by the Newton–Raphson method, and the absorbance vs. time curve was calculated from equation 3. The kinetic parameters are obtained by the nonlinear least-sqaures fitting between the observed data and the values calculated from equation 3. The fitting parameters are k_1, K_d, ε_4, and ε_5 in this study.

The results of kinetic analysis are summarized in Table 1. Most of the kinetic runs were obtained under the conditions $[MoO_2(R^1{}_2dtc)_2]_0$=1.0 mM and $[PPh_3]_0$=50.0 mM (1 M=1 mol dm^{-3}). However, in the $[MoO_2(Bz_2dtc)_2]/PPh_3$ system, the initial concentrations of $[MoO_2(Bz_2dtc)_2]$ and PPh_3 were varied to confirm the validity of the kinetic analysis. The agreements among the parameters obtained are satisfactory. Furthermore, the parameters k_1, K_d, ε_4, and ε_5 determined for the system $[MoO_2(Et_2dtc)_2]/PPh_3$ in this study are in fair agreement with the values reported by Holm et al.[8]

The rate constant for oxygen atom transfer reaction 1 is influenced by the nature of the substituents on the dithiocarbamate ligands. As shown in Fig. 2, the log k_1 values correlate linearly with the formal potentials for the one-electron reduction of $[MoO_2(R^1{}_2dtc)_2]$,[15] except for R^1=Bz and Ph. This suggests that one-electron transfer from PPh_3 to $[MoO_2(R^1{}_2dtc)_2]$ plays an important role in the rate determining step of the oxygen atom transfer reactions. The values of log k_1 for the systems $[MoO_2(Bz_2dtc)_2]/PPh_3$ and $[MoO_2(Ph_2dtc)_2]/PPh_3$ deviate from the correlation line between log k_1 and the formal potentials. This may be due to the electron-withdrawing effect of the benzyl and phenyl groups; in these cases, the contribution of resonance form I becomes more important than that of form II.

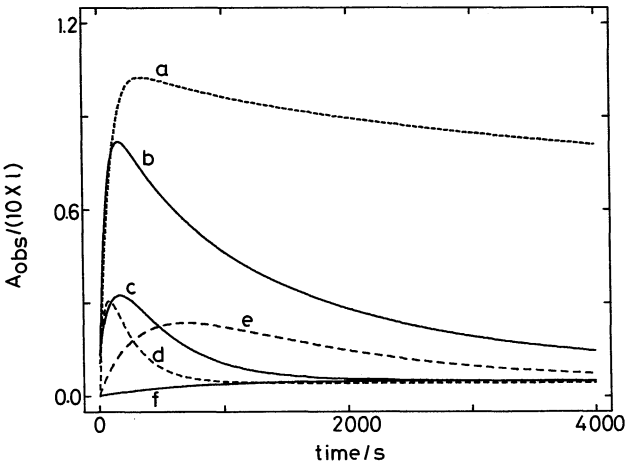


Fig. 1. Change of absorbance as a function of time for the reaction between 1.0 mM $[MoO_2(R^1{}_2dtc)_2]$ and 50.0 mM PPh_3 in 1,2-dichloroethane at 25°C. (a) R^1=Ph, (b) R^1=Bz, (c) R^1=Et, (d) R^1=Me, (e) R^1=*i*-Bu, (f) R^1=*i*-Pr. Absorbance (A_{obs}) was measured in a quartz cell with optical path length (l)=0.1 cm for (a)—(e) and 1 cm for (f).

Table 1. Kinetic Data for the Oxygen Atom Transfer Reaction between $[MoO_2(R^1{}_2dtc)_2]$ and PPh_3 in $1,2\text{-}C_2H_4Cl_2$ at 25 °C[a)]

R^1	$k_1/M^{-1}\,s^{-1}$	K_d/M^{-1}	$\varepsilon_4/M^{-1}\,cm^{-1}$	$\varepsilon_5/M^{-1}\,cm^{-1}$	$\varepsilon_6/M^{-1}\,cm^{-1}$[b)]
i-Pr[c)]	0.0120(1)	$5(3)\times10^1$	$4.60(2)\times10^2$	$1.7(8)\times10^4$	30
i-Bu	0.0241(5)	$5.0(8)\times10^2$	$5.2(5)\times10^2$	$2.4(3)\times10^4$	17
Et	0.085(3)	$7.9(4)\times10^2$	$4.8(2)\times10^2$	$2.44(6)\times10^4$	17
Et[d)]	0.071(3)	$5.9(10)\times10^2$	$4.3\times10^{2b)}$	$2.80(25)\times10^4$	18
Me	0.203(7)	$1.18(6)\times10^3$	$4.7(2)\times10^2$	$2.12(9)\times10^4$	12
Bz	0.15(1)	$1.47(6)\times10^4$	$7.1(3)\times10^2$	$2.5(2)\times10^4$	13
Bz[e)]	0.155(9)	$1.27(3)\times10^4$	$7.7(5)\times10^2$	$2.43(7)\times10^4$	13
Bz[f)]	0.138(1)	$1.43(4)\times10^4$	$6.9(3)\times10^2$	$2.39(2)\times10^4$	13
Ph	0.113(9)	$4(2)\times10^5$	$4.7(2)\times10^2$	$2.2(2)\times10^4$	57

a) Each value is the average of four determinations, unless otherwise stated. Standard deviations are given in parentheses. Initial concentrations of $[MoO_2(R^1{}_2dtc)_2]$ and PPh_3 are 1.0 and 50.0 mM, respectively, unless otherwise stated. The symbols ε_4, ε_5, and ε_6 denote molar extinction coefficients at 512 nm of $[MoO(R^1{}_2dtc)_2]$, $[Mo_2O_3(R^1{}_2dtc)_4]$, and $[MoO_2(R^1{}_2dtc)_2]$, respectively. b) The extinction coefficient values were determined by independent spectroscopic measurements. c) Average of two determinations. d) From Ref. 8. e) $[MoO_2(Bz_2dtc)_2]$= 0.5 mM; $[PPh_3]$=50 mM. f) $[MoO_2(Bz_2dtc)_2]$=1.0 mM; $[PPh_3]$=100 mM.

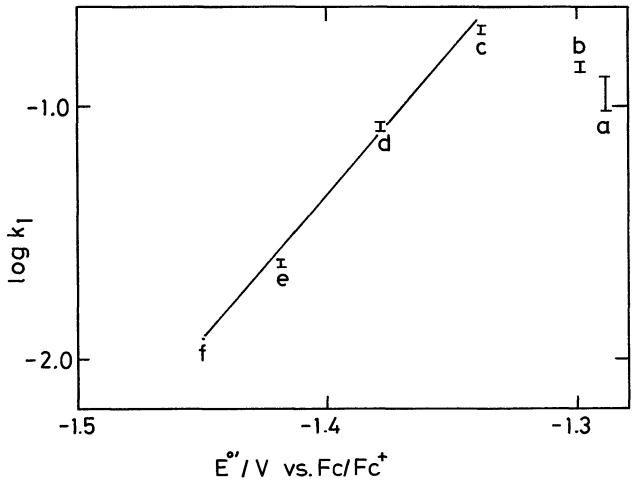


Fig. 2. Correlation between $\log k_1$ and the formal potentials for the one-electron reduction of $[MoO_2(R^1{}_2dtc)_2]$.[15] (a) R^1=Ph, (b) R^1=Bz, (c) R^1=Me, (d) R^1=Et, (e) R^1=*i*-Bu, (f) R^1=*i*-Pr.

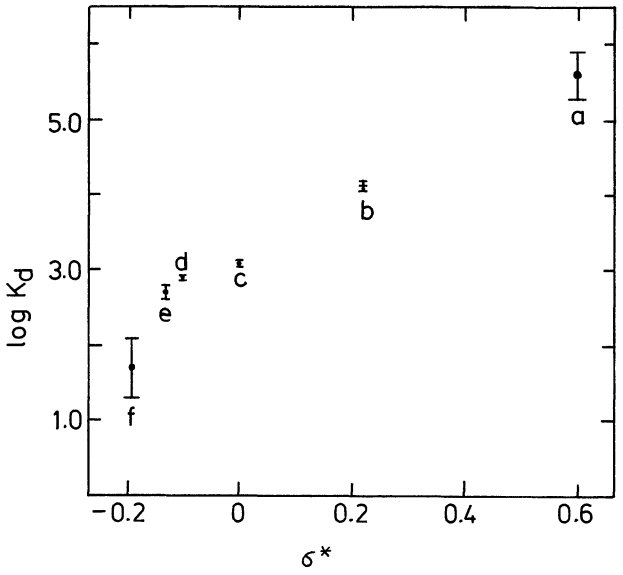


Fig. 3. Plots of $\log K_d$ vs. Taft's polar substituent constant of the substituents on dithiocarbamate ligands. (a) R^1=Ph, (b) R^1=Bz, (c) R^1=Me, (d) R^1=Et, (e) R^1=*i*-Bu, (f) R^1=*i*-Pr.

The equilibrium constant of reaction 2, K_d, also varies with the nature of the substituents on the dithiocarbamate ligands. The $\log K_d$ value correlates well with Taft's polar substituent constant (σ^*)[16] as shown in Fig. 3: The $\log K_d$ value decreases with increase of the electron-donating ability of substituents.

The $[Mo_2O_3]^{4+}$ moiety in $[Mo_2O_3(n\text{-}Pr_2dtc)_4]$ has a nearly linear Mo–O–Mo linkage and the two terminal-oxygen atoms are in the cis-positions.[17] The electronic structure of the $[Mo_2O_3]^{4+}$ moiety was described by Cotton et at.[18] Two electrons from oxygen and one electron from each molybdenum atom fill bonding and nonbonding orbitals derived by the interaction between the d_{xz} orbitals of each Mo atom and the p_x orbital of bridging oxygen to form a three-center π-bond over the Mo–O–Mo linkage. The energy level of the bonding orbital of the three-center π-bond rises with the increase of electron-donating ability of the substituents on the dithiocarbamate ligands. Censequently, $[Mo_2O_3(R^1{}_2dtc)_4]$ becomes less stable with increasing electron-donating ability of the substituents.

References

1) Abbreviations, R_2dtc^-=dithiocarbamate, Et=C_2H_5, Me=CH_3, Bz=$C_6H_5CH_2$, Ph=C_6H_5, *i*-Bu=*i*-C_4H_9, *n*-Bu=*n*-C_4H_9, *i*-Pr=*i*-C_3H_7, *n*-Pr=*n*-C_3H_7.

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