Kinetic and Mechanistic Studies on the Disproportionation Equilibrium of μ-Oxo-bis[bis(isopropyl thioxanthato)oxomolybdenum(V)] † and on the Decomposition Reaction of Bis(isopropyl thioxanthato)dioxomolybdenum(VI) ‡

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μ-Oxo-bis[bis(isopropyl thioxanthato)oxomolybdenum(V)], $[\mathrm{Mo^{V}{}_2O_3(S_2CSPr^i)_4}]$, undergoes a disproportionation reaction in solution to exist as an equilibrium mixture with $[\mathrm{Mo^{IV}O(S_2CSPr^i)_2}]$ and $[\mathrm{Mo^{VI}O_2(S_2CSPr^i)_2}]$. This reaction is followed by slow decomposition of the latter to give $[\mathrm{Mo^{V}{}_2O_4(S_2CSPr^i)_2}]$ and $[\mathrm{-SC(S)SPr^i}]_2$. Rates of the disproportionation of $[\mathrm{Mo^{V}{}_2O_3(S_2CSPr^i)_4}]$ and of the decomposition of $[\mathrm{Mo^{VI}O_2(S_2CSPr^i)_2}]$ have been determined by concentration-jump relaxation and conventional spectrophotometric techniques respectively, in 1,2-dichloroethane. The decomposition reaction is interpreted to proceed *via* a molybdenum(VI) complex with a unidentate thioxanthato-ligand as an intermediate, which decomposes in a rate-determining step, yielding unstable $[\mathrm{Mo^{V}O_2(S_2CSPr^i)}]$ and the $\cdot\mathrm{S_2CSPr^i}$ radical, both of which rapidly dimerize to give $[\mathrm{Mo^{V}{}_2O_4(S_2CSPr^i)_2}]$ and $[\mathrm{-SC(S)SPr^i}]_2$, respectively.

MUCH attention has been paid to μ-oxo-molybdenum(V) complexes of the $[\mathrm{Mo_2O_3L_4}]$ type (L = dialkyldithiocarbamate, 1-piperidinecarbodithioate, diphenylphosphinodithioate, and related ligands),[1-5] since the complexes undergo disproportionation in solution to generate molybdenum(IV) and molybdenum(VI) species [equation (1)], which may be model compounds for enzymatic

$$[\mathrm{Mo^{V}{}_2O_3L_4}] \rightleftharpoons [\mathrm{Mo^{IV}OL_2}] + [\mathrm{Mo^{VI}O_2L_2}] \qquad (1)$$

molybdenum-containing reductases and oxidases, respectively. We have recently reported a kinetic study on the disproportionation equilibrium of μ-oxo-bis[bis(*NN*-diethyldichalcogenocarbamato)oxomolybdenum(V)], $[\mathrm{Mo_2O_3(XYCNEt_2)_4}]$ (XY = SeSe, SeS, or SS).[4] The corresponding alkyl thioxanthato-complexes, $[\mathrm{Mo_2O_3(S_2CSR)_4}]$ (R = $\mathrm{C_2H_5}$, i-$\mathrm{C_3H_7}$, or t-$\mathrm{C_4H_9}$), are known to undergo a similar disproportionation [equation (1)] followed by the decomposition of $[\mathrm{Mo^{VI}O_2(S_2CSR)_2}]$ in solution [equation (2)].[5]

$$2[\mathrm{Mo^{VI}O_2(S_2CSR)_2}] \longrightarrow [\mathrm{Mo^{V}{}_2O_4(S_2CSR)_2}] + [\mathrm{-SC(S)SR}]_2 \qquad (2)$$

This paper describes kinetic and mechanistic studies on the disproportionation of $[\mathrm{Mo^{V}{}_2O_3(S_2CSPr^i)_4}]$ [equation (1)] and on the decomposition of $[\mathrm{Mo^{VI}O_2(S_2CSPr^i)_2}]$ [equation (2)] in 1,2-dichloroethane.

EXPERIMENTAL

Materials and General Procedure.—Dichlorodioxomolybdenum(VI), $[\mathrm{MoO_2Cl_2}]$,[6] and sodium isopropyl thioxanthate, $\mathrm{Na[S_2CSPr^i]}$,[5] were prepared according to the literature methods. 1,2-Dichloroethane, used as a solvent in the kinetic experiments, was purified in the usual manner,[7] and deoxygenated by bubbling through dry nitrogen immediately before use. All synthetic reactions and physical measurements were carried out under dry nitrogen.

μ-Oxo-bis[bis(isopropyl thioxanthato)oxomolybdenum(V)], $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$. A methanol (20 cm^3) solution of $[\mathrm{MoO_2Cl_2}]$ (1.06 g, 5.33 mmol) was added to a solution of $\mathrm{Na[S_2CSPr^i]}$ (1.86 g, 10.7 mmol) in methanol (30 cm^3) at −8 °C. The resulting brown precipitate was filtered off, washed with methanol and then water, and dried *in vacuo*; 45% yield, m.p. 96—98 °C (Found: C, 22.4; H, 3.5. Calc. for $\mathrm{C_{16}H_{28}Mo_2O_3S_{12}}$: C, 22.7; H, 3.3%). This complex has already been synthesized by the reaction of $[\mathrm{NH_4}]_2[\mathrm{MoOCl_5}]$ with $\mathrm{Na[S_2CSPr^i]}$,[5] but the melting point is not specified.

Bis(isopropyl thioxanthato)oxomolybdenum(IV), $[\mathrm{MoO(S_2CSPr^i)_2}]$, *and di-μ-oxo-bis[(isopropyl thioxanthato)oxomolybdenum*(V)], $[\mathrm{Mo_2O_4(S_2CSPr^i)_2}]$. A carbon disulphide solution of $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ was poured onto a silica column (Wakogel-C-300) to develop four bands in the column; the leading yellow, the second blue, the third red, and the last yellow bands. The order of these bands is different from that reported previously on a silica column.[5] The first and the second bands were eluted using carbon disulphide, collected, and evaporated to dryness *in vacuo*, affording $[\mathrm{-SC(S)SPr^i}]_2$ and $[\mathrm{Mo(S_2CSPr^i)_4}]$, respectively. These were identified by elemental analyses and i.r. spectra and compared with those of authentic samples.[8,9] The third eluate was treated by the same procedure. The resulting solid was recrystallized from carbon disulphide–pentane (1 : 1) to yield red needles of $[\mathrm{MoO(S_2CSPr^i)_2}]$ in a 30% yield, m.p. 108—110 °C (Found: C, 23.2; H, 3.3. Calc. for $\mathrm{C_8H_{14}MoOS_6}$: C, 23.2; H, 3.4%). A solid material similarly obtained from the last eluate was recrystallized from carbon disulphide to give yellowish orange needles of $[\mathrm{Mo_2O_4(S_2CSPr^i)_2}]$ in a 10% yield, m.p. 115—118 °C (Found: C, 17.4; H, 2.6. Calc. for $\mathrm{C_8H_{14}Mo_2O_4S_6}$: C, 17.2; H, 2.5%).

Kinetic and Spectral Measurements.—Rates of the disproportionation reaction in 1,2-dichloroethane were determined as described previously.[4] Pseudo-first-order rate constants, $k_{\mathrm{obs.}}$, were calculated from the slope of the $\ln(A_t - A_\infty)$ against time plots, where A_t and A_∞ are absorbances at time t and the end of the reaction, respectively. Infrared spectra were measured with a Hitachi 215 spectrophotometer.

RESULTS AND DISCUSSION

Disproportionation Equilibrium.—When a 1,2-dichloroethane solution of $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ was mixed

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† μ-Oxo-bis[bis(*S*-isopropyl trithiocarbonato-*S′*,*S″*)oxomolybdenum(V)].

‡ Bis(*S*-isopropyl trithiocarbonato-*S′*,*S″*)dioxomolybdenum(VI).

with the same volume of 1,2-dichloroethane on a stopped-flow apparatus, the absorbance at 545 nm due to $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ decreased exponentially with time. By analogy with the dilution-jump experiments for $[\mathrm{Mo_2O_3(XYCNEt_2)_4}]$ solutions (XY = SeSe, SeS, or SS),[4] this behaviour can be explained in terms of the shift of the equilibrium shown in equation (3) to the right, where

$$[\mathrm{Mo_2O_3(S_2CSPr^i)_4}] \xrightleftharpoons[k_{-1}]{k_1} [\mathrm{MoO(S_2CSPr^i)_2}] + cis\text{-}[\mathrm{MoO_2(S_2CSPr^i)_2}] \quad (3)$$

cis-$[\mathrm{MoO_2(S_2CSPr^i)_2}]$ is produced by fission of a Mo–O bond of the Mo–O–Mo linkage, since the terminal oxo- and μ-oxo-ligands in $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ are located in a mutually *cis* position.[5] The molybdenum(IV) complex, $[\mathrm{MoO(S_2CSPr^i)_2}]$, was isolated as red needles, but the isolation of the corresponding molybdenum(VI) complex, $[\mathrm{MoO_2(S_2CSPr^i)_2}]$, has been unsuccessful, probably because of its instability, as suggested for a related molybdenum(VI) complex, $[\mathrm{MoO_2\{S_2P(OEt)_2\}_2}]$.[10]

Decomposition of $[\mathrm{MoO_2(S_2CSPr^i)_2}]$.—Complexes of the cis-$[\mathrm{MoO_2L_2}]$ type are known to exhibit two strong ν(Mo=O) bands around 900 $\mathrm{cm^{-1}}$.[1] A solution of $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ displays a weak but sharp absorption band at 896 $\mathrm{cm^{-1}}$ and a weak broad one at 795 $\mathrm{cm^{-1}}$ immediately after dissolution in carbon disulphide, while the solid-state spectrum shows no bands with any appreciable intensity in the 800—900 $\mathrm{cm^{-1}}$ region, as depicted in Figure 1. The band at 896 $\mathrm{cm^{-1}}$ in the solution spectrum may be assigned to one of the two ν(Mo=O) frequencies of cis-$[\mathrm{MoO_2(S_2CSPr^i)_2}]$, while another ν(Mo=O) band is probably obscured by the strong ν(C⸗S) band around 920 $\mathrm{cm^{-1}}$. On the other hand, the band at 795 $\mathrm{cm^{-1}}$ may be associated with the ν(Mo=O) vibration of $trans$-$[\mathrm{MoO_2(S_2CSPr^i)_2}]$, since *trans*-dioxo-molybdenum(IV), -rhenium(V), and -osmium(VI) complexes reported so far display only one strong ν(metal–O) band around 800 $\mathrm{cm^{-1}}$.[11-14] Thus, cis-$[\mathrm{MoO_2(S_2CSPr^i)_2}]$ in equation (3) is suggested to isomerize readily to the *trans* isomer both of which coexist in solution. The bands at 896 and 795 $\mathrm{cm^{-1}}$, however, gradually decreased in intensity with time; the former completely disappeared after 24 h, while the latter was obscured by the absorption at 807 $\mathrm{cm^{-1}}$, probably due to di-isopropylthioxanthogen, $[\mathrm{{-}SC(S)SPr^i}]_2$, one of the decomposition products of $[\mathrm{MoO_2(S_2CSPr^i)_2}]$, which gradually appeared and intensified with time. The instability of $[\mathrm{MoO_2(S_2CSPr^i)_2}]$ in solution is also evidenced by the electronic spectra, as shown in Figure 2. The absorption band at 545 nm due to $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ in 1,2-dichloroethane gradually weakens with time, to disappear almost completely after 48 h. In its place there appears a weak absorption at 515 nm (ε = 700 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) which is assigned to $[\mathrm{MoO(S_2CSPr^i)_2}]$. The resulting solution was evaporated to dryness *in vacuo* to give a product whose carbon disulphide solution was chromatographed on silica affording $[\mathrm{MoO(S_2CSPr^i)_2}]$, $[\mathrm{Mo(S_2CSPr^i)_4}]$,* $[\mathrm{Mo_2O_4(S_2CSPr^i)_2}]$, and $[\mathrm{{-}SC(S)SPr^i}]_2$, as described in the Experimental section. Zubieta and co-workers [5] have mentioned that equimolar solutions of the appropriate concentrations of $[\mathrm{MoO(S_2CSR)_2}]$, $[\mathrm{Mo_2O_4(S_2CSR)_2}]$, and $[\mathrm{{-}SC(S)SR}]_2$ showed spectra identical with those of $[\mathrm{Mo_2O_3(S_2CSR)_4}]$. In the present study, however, a 1,2-dichloroethane

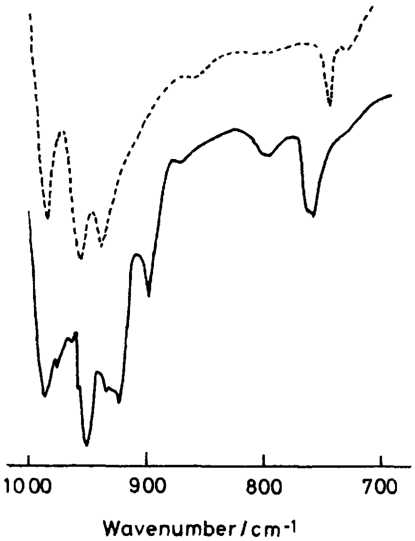

FIGURE 1 Infrared spectra of $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ in Nujol (– – – –) and immediately after dissolution in $\mathrm{CS_2}$ (2.0 × 10^{-2} mol $\mathrm{dm^{-3}}$) (——); the mole ratio of $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ and $[\mathrm{MoO_2(S_2CSPr^i)_2}]$ in $\mathrm{CS_2}$ is calculated to be *ca.* 85 : 15 on the assumption that the K_1 value in $\mathrm{CS_2}$ is the same as that in $\mathrm{CH_2ClCH_2Cl}$ at 25 °C (Table 2)

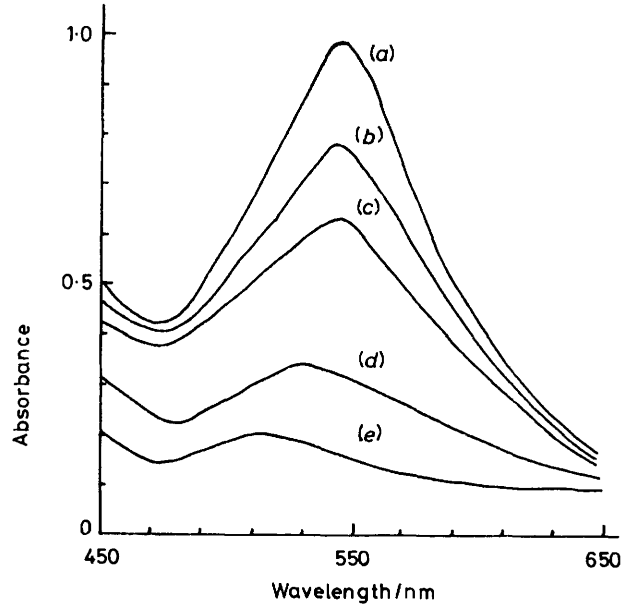

FIGURE 2 Decay of the absorbance with time after dissolving $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ (3.0 × 10^{-4} mol $\mathrm{dm^{-3}}$) in $\mathrm{CH_2ClCH_2Cl}$ at 25 °C; cell length = 1.0 cm. (*a*) 0 h, (*b*) 3 h, (*c*) 6 h, (*d*) 24 h, (*e*) 48 h

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* No absorption due to $[\mathrm{Mo(S_2CSPr^i)_4}]$ ($\lambda_{\mathrm{max.}}$ = 619 nm, ε = 7 500 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$) occurred in the final visible spectrum of $[\mathrm{Mo_2O_3(S_2CSPr^i)_4}]$ in 1,2-dichloroethane (Figure 2), suggesting that $[\mathrm{Mo(S_2CSPr^i)_4}]$ may be formed in the silica column.

solution containing the three species exhibited no absorption band due to $[Mo_2O_3(S_2CSPr^i)_4]$ in the visible spectra. Moreover, the rate of decay of the band at 545 nm in the solution spectrum of $[Mo_2O_3(S_2CSPr^i)_4]$ with time was not influenced by the addition of a large amount of $[Mo_2O_4(S_2CSPr^i)_2]$ (see below).

Kinetics and Mechanisms.—When a 1,2-dichloroethane solution containing $[Mo_2O_3(S_2CSPr^i)_4]$ and a large amount of $[MoO(S_2CSPr^i)_2]$ was mixed with the same volume of 1,2-dichloroethane, the intensity of the 545 nm band due to $[Mo_2O_3(S_2CSPr^i)_4]$ decreased exponentially. Table 1 lists the relaxation times obtained for the $[Mo_2O_3(S_2CSPr^i)_4]$–$[MoO(S_2CSPr^i)_2]$ system at various concentrations.

TABLE 1

Relaxation times for the disproportionation equilibrium of $[Mo_2O_3(S_2CSPr^i)_4]$ in CH_2ClCH_2Cl

Temperature (θ_c/°C)	$10^5[Mo_2O_3(S_2CSPr^i)_4]$ / mol dm^{-3}	$10^5[MoO(S_2CSPr^i)_2]$ / mol dm^{-3}	$10^2\tau$ / s
15.2	1.89	57.6	5.62
	2.84	86.4	4.27
	3.78	115	3.51
	4.73	143	2.74
	5.68	173	2.25
19.7	1.89	57.6	4.44
	2.84	86.4	3.38
	3.78	115	2.91
	4.73	143	2.25
	5.68	173	1.88
25.3	6.57	67.6	2.90
		128	1.85
		197	1.56
		227	1.23
		261	1.00
29.4	6.57	67.6	2.29
		128	1.51
		197	1.18
		227	0.943
		261	0.847

The τ value in the equilibrium reaction (3) is written as equation (4),[15] where $[MoO(S_2CSPr^i)_2]_{eq.}$ and $[MoO_2(S_2CSPr^i)_2]_{eq.}$ are the equilibrium concentrations of

$$1/\tau = k_1 + \{[MoO(S_2CSPr^i)_2]_{eq.} + [MoO_2(S_2CSPr^i)_2]_{eq.}\}k_{-1} \quad (4)$$

$[MoO(S_2CSPr^i)_2]$ and $[MoO_2(S_2CSPr^i)_2]$ respectively. Equation (4) becomes equation (5) in the presence of a

$$1/\tau = k_1 + [MoO(S_2CSPr^i)_2]k_{-1} \quad (5)$$

large amount of $[MoO(S_2CSPr^i)_2]$. This equation predicts that the τ value is not influenced by the $[Mo_2O_3(S_2CSPr^i)_4]$ concentration. Figure 3 shows the plots of $1/\tau$ against the concentration of $[MoO(S_2CSPr^i)_2]$. The k_1 and k_{-1} values obtained from the intercept and slope, respectively, of the straight line are listed in Table 2. The K_1 (= k_1/k_{-1}) value obtained for $[Mo_2O_3(S_2CSPr^i)_4]$ is smaller than that for $[Mo_2O_3(S_2CNEt_2)_4]$ [(2.0 ± 0.2) × 10^{-3} mol dm^{-3} at 25 °C].[4] This result may be explained in terms of a weak donor ability of the thioxanthate ligand compared with the dithiocarbamate ligand.[9] Bonding and non-bonding π orbitals of the three-centre Mo–O–Mo bonds may be occupied by four electrons; two from oxygen (2*p*) and one from each molybdenum.[1] The thioxanthate ligand can, therefore, donate less electron density into the antibonding Mo–O–Mo π orbitals through the molybdenum atom than the dithiocarbamate ligand. This assumption predicts that $[Mo_2O_3(S_2CSPr^i)_4]$ is less destabilized than $[Mo_2O_3(S_2CNEt_2)_4]$.

TABLE 2

Rate and equilibrium constants for the disproportionation reaction of $[Mo_2O_3(S_2CSPr^i)_4]$ in CH_2ClCH_2Cl *

Temperature (θ_c/°C)	k_1/s^{-1}	$10^{-4}k_{-1}$/dm^3 mol^{-1} s^{-1}	10^4K_1/ mol dm^{-3}
15.2	3.58 ± 3.35	2.31 ± 0.31	1.55 ± 1.45
19.7	6.24 ± 4.69	2.66 ± 0.18	2.35 ± 1.77
25.3	12.2 ± 8.6	3.20 ± 0.22	3.81 ± 2.70
29.4	16.7 ± 11.5	3.80 ± 0.29	4.39 ± 3.04

* Errors quoted are standard deviations.

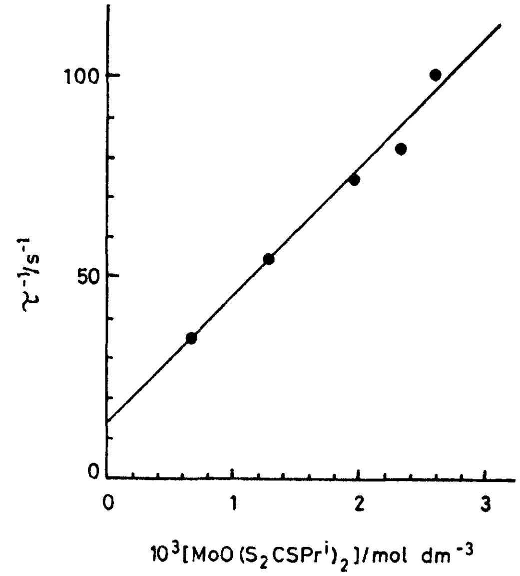


FIGURE 3 Plots of $1/\tau$ against $[MoO(S_2CSPr^i)_2]$ at 25 °C; $[Mo_2O_3(S_2CSPr^i)_4]$ = 6.6 × 10^{-5} mol dm^{-3}

Activation and thermodynamic parameters calculated from the k_1, k_{-1}, and K_1 values at four different temperatures are summarized in Table 3, which shows that the activation entropy of the disproportionation reaction is a small positive value, while that of the coupling reaction is a large negative one. This result suggests that in the transition state of the disproportionation reaction the Mo–O–Mo bond is weakened markedly, but the binuclear structure is still maintained, as in the previous

TABLE 3

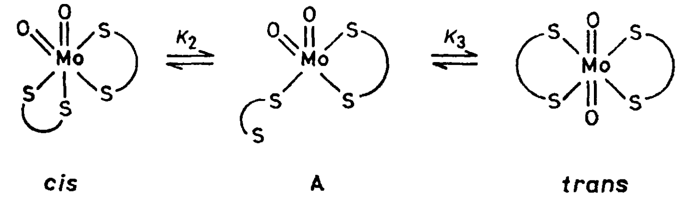
Activation and thermodynamic parameters for the disproportionation equilibrium of $[Mo_2O_3(S_2CSPr^i)_4]$ in CH_2ClCH_2Cl at 25 °C *

	$\Delta H^\ddagger$ or ΔH / kJ mol^{-1}	$\Delta S^\ddagger$ or ΔS / J K^{-1} mol^{-1}
k_1	79.2 ± 3.0	40.5 ± 20.5
k_{-1}	25.6 ± 2.5	−81.5 ± 16.7
K_1	53.7 ± 4.6	−132 ± 31

* Errors quoted are standard deviations.

works on $[Mo_2O_3(XYCNEt_2)_4]$ (XY = SeSe, SeS, or SS)[4] and $[Mo_2O_3L_4]$ [L = S_2PPh_2 or $S_2P(OEt)_2$].[16]

The decomposition reaction of $[MoO_2(S_2CSPr^i)_2]$ was followed by monitoring the slow decay of the absorbance at 545 nm with time in the presence of various large amounts of $[MoO(S_2CSPr^i)_2]$ or $[Mo_2O_4(S_2CSPr^i)_2]$. Table 4 lists pseudo-first-order rate constants, $k_{\mathrm{obs.}}$, and shows that the rate constants are essentially the same irrespective not only of the initial concentration of $[Mo_2O_3(S_2CSPr^i)_4]$ but also of the amount of $[MoO(S_2CSPr^i)_2]$ or $[Mo_2O_4(S_2CSPr^i)_2]$. This result may reasonably be explained by the following pathways [equations (6)—(9)] for the decomposition of $[MoO_2(S_2CSPr^i)_2]$. Equation (6)



(6)

$$A \xrightarrow{k_4} [Mo^VO_2(S_2CSPr^i)] + {\cdot}S_2CSPr^i \quad (7)$$

$$[Mo^VO_2(S_2CSPr^i)] \xrightarrow{\text{fast}} \tfrac{1}{2}[Mo^V{}_2O_4(S_2CSPr^i)_2] \quad (8)$$

$$\cdot S_2CSPr^i \xrightarrow{\text{fast}} \tfrac{1}{2}[-SC(S)SPr^i]_2 \quad (9)$$

represents the *cis–trans* isomerization equilibrium of $[MoO_2(S_2CSPr^i)_2]$, where A is the dioxomolybdenum(VI) complex containing both bidentate and unidentate ligands as an intermediate of the isomerization. The existence of such an intermediate may be suggested from the fact that the intramolecular isomerization of octahedral complexes usually proceeds *via* a five-co-ordinate complex formed by the opening of a chelate ring.[17] The intermediate A may be decomposed in a rate-determining step [equation (7)], which involves the cleavage of a Mo–S bond to give unstable $[Mo^VO_2(S_2CSPr^i)]$ and the $\cdot S_2CSPr^i$ radical. These species rapidly dimerize to afford a di-μ-oxo-molybdenum(V) complex and di-isopropylthioxanthogen [equations (8) and (9)].

TABLE 4

Pseudo-first-order rate constants for the decomposition reaction of $[MoO_2(S_2CSPr^i)_2]$ in CH_2ClCH_2Cl

Temperature (θ_c/°C)	$10^4[Mo_2O_3L_4]$ * / mol dm^{-3}	$10^4[MoOL_2]$ * / mol dm^{-3}	10^5k_{obs} / s^{-1}
25.5	0.631	9.52	4.08
	1.42	21.4	4.08
	2.84	42.8	4.23
30.2	0.500	12.1	7.28
	0.500	12.1 †	7.09
	0.503	7.15	6.90
	1.51	21.5	6.69
	3.02	42.9	6.81
	3.31	35.1	6.34
	3.31	68.0	16.54
34.6	0.533	9.47	0.4
	1.60	28.4	10.9
39.0	0.513	7.12	12.8
	1.50	21.4	14.1
	3.08	42.7	13.9

* L = S_2CSPr^i. † $10^4[Mo_2O_4L_2] = 9.85 \times 10^{-4}$ mol dm^{-3}.

According to the pathways of equation (3) and (6)—(9), the observed rate constant, $k_{\mathrm{obs.}}$, in the presence of an excess of $[MoO(S_2CSPr^i)_2]$ is expressed by equation (10).

$$k_{\mathrm{obs.}} = \frac{k_4K_2}{\{[MoO(S_2CSPr^i)_2]/K_1\} + 1 + K_2 + K_2K_3} \quad (10)$$

In the present work, the value of $[MoO(S_2CSPr^i)_2]/K_1$ is in the range 1.6—16 (Tables 2 and 4). If one assumes that $K_2 + K_2K_3 \gg \{[MoO(S_2CSPr^i)_2]/K_1\} + 1$, equation (10) can be reduced to equation (11), which predicts $k_{\mathrm{obs.}}$

$$k_{\mathrm{obs.}} = k_4/(1 + K_3) \quad (11)$$

being constant. This is consistent with the observed rate profile. Table 5 lists the value of $k_4/(1 + K_3)$ and activation parameters determined from the Arrhenius plots of ln $[k_4/(1 + K_3)]$ against $1/T$. As the k_4 and K_3 values have unfortunately not been determined separately, no more detail on the mechanism can be discussed in the present work.

TABLE 5

Rate constants and activation parameters for the decomposition reaction of $[MoO_2(S_2CSPr^i)_2]$ in CH_2ClCH_2Cl *

Temperature (θ_c/°C)	$10^5k_4/(1 + K_3)$ / s^{-1}	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K^{-1} mol^{-1}
25.5	4.13 ± 0.07	67.1 ± 6.9	−111 ± 45
30.2	6.81 ± 0.30		
34.6	10.7 ± 0.3		
39.0	13.6 ± 0.6		

* Errors quoted are standard deviations.

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