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KINETICS AND MECHANISM OF THE REACTION OF BIS(S-ISOPROPYL TRITHIOCARBONATO-S',S")-OXOMOLYBDENUM(IV) WITH DIMETHYL ACETYLENEDICARBOXYLATE

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$MoO(S_2CSPr^i)_2$ (1) reacts with $CH_3OOCC{\equiv}CCOOCH_3$ (DMAC) to give the 1:1 adduct with a pentagonal bipyramidal configuration, in which DMAC is placed in the equatorial plane and the terminal oxo ligand in an apex position. Kinetic studies indicate that the reaction proceeds *via* a mono-capped trigonal prismatic intermediate which is formed by the coordination of DMAC to molybdenum from the bottom of the square pyramid of 1, affording the final product by the intramolecular rearrangement.

Coordinatively unsaturated bis(dialkyldithiocarbamato)oxomolybdenum(IV), $MoO(S_2CNR_2)_2$, can reversibly add acetylene which is reduced to ethylene in the presence of $NaBH_4$ and water.[1] Several 1:1 adducts of $MoO(S_2CNR_2)_2$ with alkynes isolated so far have been suggested to adopt a pentagonal bipyramidal configuration, in which the alkyne is placed in the equatorial plane and the oxo ligand occupies an apex position.[2-4] Recently, we have found that the addition reaction of alkynes toward Mo(IV) complexes with a square pyramidal geometry consists of two successive steps. This letter reports the kinetics and mechanism for the reaction of bis(S-isopropyl trithiocarbonato-S,S")oxomolybdenum(IV), $MoO(S_2CSPr^i)_2$ (1), with dimethyl acetylenedicarboxylate, $CH_3OOCC{\equiv}CCOOCH_3$ (DMAC), in solutions. The present work is the first example of kinetic and mechanistic studies on the intramolecular rearrangement of hepta-coordinate metal complexes.

A solution of DMAC (0.25 mmol) in carbon disulfide (10 cm^3) was added to $MoOL_2$ ($L = S_2CSPr^i$) (0.25 mmol) in the same solvent (15 cm^3). After stirred for two days at room temperature, the solution was evaporated to dryness under reduced pressure. The resulting product was recrystallized from carbon disulfide-pentane (1:1) to give orange microcrystals of $MoOL_2$(DMAC) in an 80% yield, mp 73-76°C. Anal. Found: C, 29.73; H, 3.78%. Calcd for $C_{14}H_{20}O_5S_6Mo$: C, 30.21; H, 3.62%. Molecular weight determinations have indicated that the adduct is monomeric in $CHCl_3$ (Found: 550, Calcd: 557). This is in contrast with the adducts of $MoO(S_2CNR_2)_2$ with alkynes, which have been reported to dissociate partly into the parent species in CD_2Cl_2.[2] The IR spectrum of $MoOL_2$(DMAC) showed the $\nu(C{\equiv}C)$ band at 1660 cm^{-1} and $\nu(Mo{=}O)$ band at 941 cm^{-1}. These wave numbers are lower by 480 and 34 cm^{-1} than those of $\nu(C{\equiv}C)$ of free DMAC and $\nu(Mo{=}O)$ of 1, respectively, suggesting the occurrence of the oxidative addition of DMAC toward 1. The ^1H-NMR spectrum of $MoOL_2$(DMAC) in C_6H_6 displayed two singlets due to the DMAC-methyl protons and four doublets due to the isopropyl-methyl protons with the intensity ratios of 1:1 and 1:1:1:1, respectively, indicating that all methyl groups are non-equivalent. These spectroscopic results are consistent with a pentagonal bipyramidal configuration for $MoOL_2$(DMAC), in which the oxo group occupies an apex position and DMAC lies on the equatorial plane, as reported for the 1:1 adduct of $MoO(S_2CNEt_2)_2$ with ditoluoylacetylene, $MeC_6H_4C(O)C{\equiv}CC(O)C_6H_4Me$, by an X-ray crystallographic analysis.[4)]

Figure 1 demonstrates the variation of IR spectra with time after mixing a 1,2-dichloroethane solution of 1 with an equimolar amount of DMAC in the same solvent. Immediately after mixing, a new band assignable to the $\nu(C{\equiv}C)$ vibration appears at 1845 cm^{-1}, which is lower by about 300 cm^{-1} than the $\nu(C{\equiv}C)$ frequency of free DMAC, indicating the coordination of DMAC to 1. The 1845 cm^{-1} band is intensified with time, and reaches a maximum intensity in about 5 h after mixing, followed by gradual decay. After 24 h, this band completely disappears and the final spectrum is the same as that of a 1,2-dichloroethane solution of isolated $MoOL_2(DMAC)$. Hence, the $\nu(C{\equiv}C)$ band at 1845 cm^{-1} is associated with an intermediate in the reaction of 1 with DMAC.

The presence of a reaction intermediate is confirmed also from time dependent ^1H-NMR spectra (Fig. 2, a~d); in several minutes after mixing in CS_2, the solution displays a new DMAC-methyl signal at δ 3.85 and a broad isopropyl-methyl signal around δ 1.50. They are gradually intensified with time at the expense of the methyl signals of free DMAC (δ 3.77) and the isopropyl-methyl signals of 1 (δ 1.46 and 1.39), and gain maximum intensities after 5 h. Thereafter, those signals are gradually weakened with time and completely disappear after 24 h. On the other hand, the DMAC-methyl signals of the final product (δ 3.64 and 3.49) begin to appear in 0.3 h after mixing. These are intensified with time and remained in the final spectrum.[5)]

The intermediate can be frozen at low temperatures; on cooling the solution which was allowed to stand for 5 h at room temperature, the DMAC-methyl signal of the intermediate (δ 3.85) began to broaden around +5°C, followed by the split into two sharp signals (δ 3.92 and 3.84) as well as the appearance of complicated multiplets due to the isopropyl-methyl protons at -20°C (Fig. 2e). Although the assignment for the multiplets in the isopropyl-methyl region is not obvious, non-equivalency of the DMAC-methyl

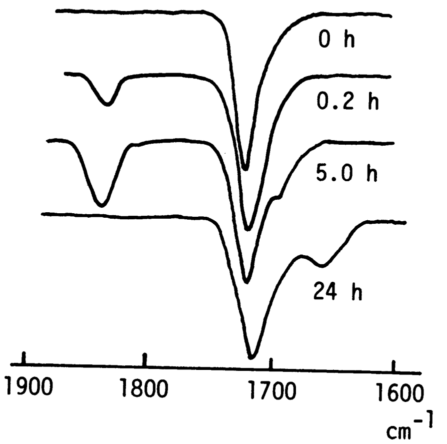


Fig. 1. IR spectra of the 1 (2.9×10^{-2} mol dm^{-3})-DMAC (2.9×10^{-2} mol dm^{-3}) system in CH_2ClCH_2Cl at 20°C.

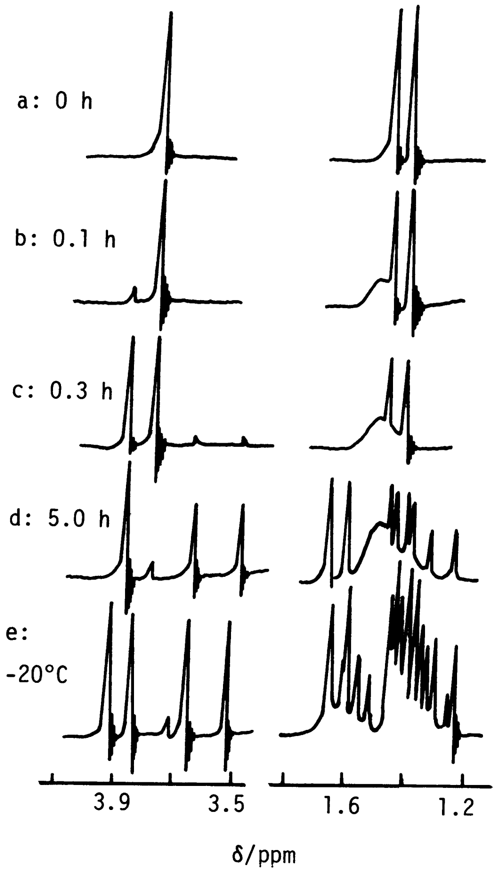


Fig. 2. ^1H-NMR spectra of the 1 (2.5×10^{-2} mol dm^{-3})-DMAC (2.5×10^{-2} mol dm^{-3}) system in CS_2; a-d at +20°C and e at -20°C.

protons at -20°C confirms the existence of two isomeric intermediates. Most likely configurations for the intermediate are mono-capped trigonal prisms, in which the relative orientation of coordinated DMAC are different with respect to the chelate ligands (Fig. 3). Non-rigidity of the intermediate at room temperature is in contrast with the final product $MoOL_2(DMAC)$ with a pentagonal bipyramidal configuration, whose ^1H-NMR spectrum in benzene showed no broadening of the methyl siganls at all up to 80°C. The stronger coordination of DMAC to the molybdenum atom in the pentagonal bipyramid than in the mono-capped trigonal prism is supported by the fact that the $\nu(C\equiv C)$ frequency in the former configuration (1660 cm^{-1}) is lower than that in the latter (1845 cm^{-1}). Thus, the present reaction would proceed through two successive steps (Eq. 1).

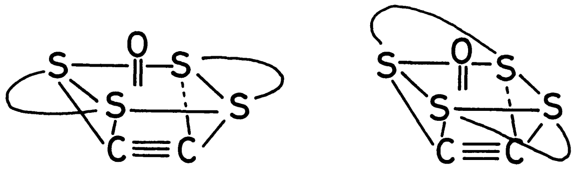
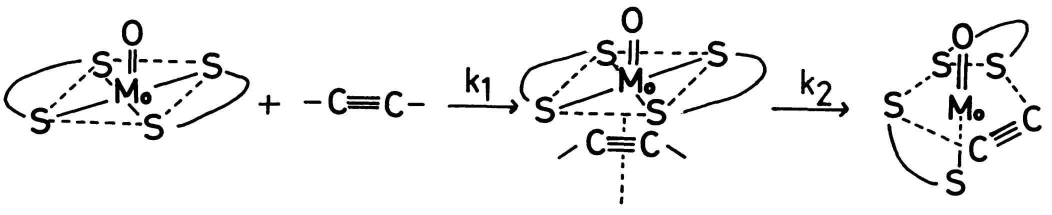


Fig. 3. Two isomeric intermediates.



(1)

That the reaction consists of two successive steps is evidenced also from visible spectra of the **1**-DMAC system (Fig. 4), which show the appearance of two alternative isosbestic points; one is at 470 nm for about 10 min in the initial step and the other at 430 nm after the lapse of 1 h. Pseudo-first-order rate constants for the first and second steps of the reaction were obtained from the change of absorbances at 515 and 480 nm with time, respectively. The plots of the pseudo-first-order rate constant for the first step *vs.* the concentration of DMAC yielded a straight line with a zero intercept, while the rate constants for the second step are essentially the same irrespective of the DMAC concentration. These results suggest that no backward reaction occurs in either step. Table 1 lists the rate constants and activation parameters calculated from the Arrhenius plots of ln k *vs.* 1/T. It is noted that the $\Delta S^{\ddagger}$ values are large negative not only in the first step but also in the second step. This

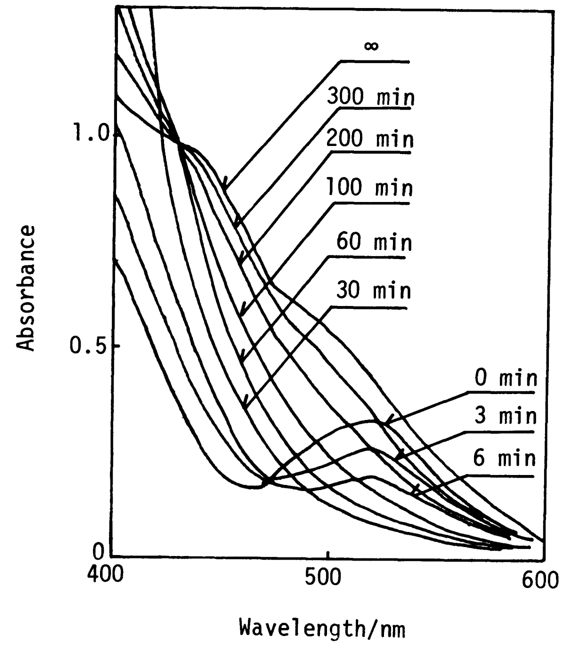
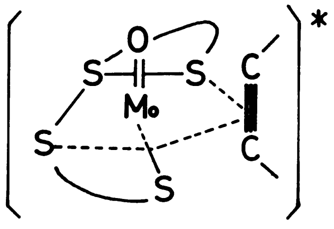


Fig. 4. Spectral changes of the **1** (5.0 x 10^{-4} mol dm^{-3})-DMAC (2.5 x 10^{-2} mol dm^{-3}) system in CH_2ClCH_2Cl at 25°C.

Table 1. Rate constants and activation parameters[a] for the reaction of 1 with DMAC in 1,2-dichloroethane[b]

	Temp / °C	10^2k_1 / $s^{-1}mol^{-1}dm^3$	Temp / °C	10^5k_2 / s^{-1}
	15.8	2.53±0.01	13.8	2.77±0.04
	22.4	4.32±0.06	18.7	4.66±0.05
	24.8	7.58±0.12	24.9	8.33±0.18
	30.9	7.58±0.12	32.2	18.2 ±0.2
$\Delta H^{\ddagger}$ / $KJ\,mol^{-1}$		50.5± 3.1		71.4± 1.7
$\Delta S^{\ddagger}$ / $J\,mol^{-1}\,K^{-1}$		-102 ±21		-83.5±11.3

[a] At 25°C. [b] Errors quoted are standard deviations.



(I)

may rule out the mechanism of dissociation of either DMAC or the S-isopropyl trithiocarbonato-S',S" ligand in the second step. In addition, the $\Delta S^{\ddagger}$ values for the intramolecular rearrangement of hexa- or hepta-coordinate metal complexes accompanied by chelate ring openings have been reported to be nearly zero.[6)] Thus, the present intramolecular rearrangement may proceed *via* "non-bond-breaking" mechanism, which may involve the migration of DMAC between the two chelating rings perpendicular to the S_4 plane and the concomitant loosening of one Mo-S bond to move the S atom out of the S_4 plane, giving a transition state (I). A similar configuration has been suggested as a stable form for $W(CO)(RC{\equiv}CR)(S_2CNMe_2)_2$ (R = H, C_6H_5) in CD_2Cl_2 at low temperature.[7)]

References and notes

1) E. A. Maata, R. A. D. Wentworth, W. E. Newton, J. W. McDonald, and G. D. Watt, *J. Am. Chem. Soc.*, 100, 1320 (1978).

2) E. A. Maata and R. A. D. Wentworth, *Inorg. Chem.*, 18, 524 (1979).

3) P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, 94, 8640 (1972).

4) W. E. Newton, J. W. McDonald, J. L. Cobbin, L. Ricard, and R. Weiss, *Inorg. Chem.*, 19, 1997 (1980).

5) The ^1H-NMR spectrum of the adduct in CS_2 showed three doublets due to the isopropyl-methyl protons with the intensity ratios of 2:1:1.

6) R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc. (A)*, 1971, 994.

7) B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, 102, 1532 (1980).

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