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KINETIC STUDY ON TWO TYPES OF NOVEL INTRAMOLECULAR REARRANGEMENTS OF HEPTA-COORDINATE OXOMOLYBDENUM(IV) COMPLEXES: MoO(S_2CNEt_2)$_2$(EtOOCN=NCOOEt) AND MoO(S_2CSPr^i)$_2$(MeOOCC≡CCOOMe)

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A kinetic study reveals that the reaction of MoO(S_2CNR_2)$_2$ with ROOCN=NCOOR (R = Me, Et) proceeds *via* two successive steps which consist of the formation of a mono-capped trigonal prismatic intermediate followed by intramolecular rearrangement, affording the final product with a pentagonal bipyramidal configuration. The entropy and the volume of activation in the rearrangement (R = Et) are both positive ($\Delta S^{\neq} = +38.0$ J mol^{-1}K^{-1}, $\Delta V^{\neq} = +13.6$ cm^{3}mol^{-1}), which are in marked contrast to the negative values for a similar rearrangement of MoO(S_2CSPr^i)$_2$(MeOOCC≡CCOOMe) ($\Delta S^{\neq} = -83.5$ J mol^{-1}K^{-1}, $\Delta V^{\neq} = -9.9$ cm^3 mol^{-1}). Based on these results, two different mechanisms are suggested for the intramolecular rearrangement of hepta-coordinate molybdenum complexes.

The reactions of coordinatively unsaturated oxomolybdenum(IV) complexes such as MoO(S_2CNR_2)$_2$ with diazenes and activated acetylenes have been studied as a possible model system for N_2-fixing molybdoenzymes.1-5) Recently, we have demonstrated that the reaction of MoO(S_2CSPr^i)$_2$ with MeOOCC≡CCOOMe (DMAC) affords a 1:1 adduct with mono-capped trigonal prismatic configuration as intermediate, which undergoes an intramolecular rearrangement *via* a non-bond breaking mechanism to give a pentagonal bipyramidal complex.6) This letter reports (i) the kinetic study on the reaction of MoO(S_2CNEt_2)$_2$ with EtOOCN=NCOOEt (DEAZ) under atmospheric pressure, and (ii) the pressure dependence of the reaction rates not only for the MoO(S_2CNEt_2)$_2$-DEAZ but the MoO(S_2CSPr^i)$_2$-DMAC systems. The results reveal that there may be two different mechanisms in the intramolecular rearrangements from a mono-capped trigonal prism to a pentagonal bipyramid.

When a CH_2Cl_2 (5 cm^3) solution of DEAZ (0.17 mmole) was added to MoO(S_2CNEt_2)$_2$ (0.17 mmole) in the same solvent (20 cm^3), the solution was colored to violet without delay, and turned into yellow in a few minutes; from the solution was isolated yellow microcrystalline MoO(S_2CNEt_2)$_2$(DEAZ), a known compound,1) quantitatively. The violet solution transiently appeared, which is stable below -40°C, may result from a reaction intermediate. The intermediate was isolated as violet microcrystals from the CH_2Cl_2 solution at -40°C, but it gradually changed to yellow in color even at -10°C. The reaction of MoO(S_2CNMe_2)$_2$ with MeOOCN=NCOOMe (DMAZ) in CH_2Cl_2 proceeded quite similarly and the adduct was also isolated quantitatively, mp 90°C (decomp).

The ^{1}H-nmr spectrum of MoO(S_2CNMe_2)$_2$(DMAZ) in CH_2Cl_2 at room temperature shows two O-CH_3 (δ 3.65, 3.83) and four N-CH_3 (δ 3.11, 3.41, 3.46, 3.50) signals with intensity ratios 1:1 and 1:1:1:1, respectively (Fig. 1a), suggesting a pentagonal bipyramidal configuration of the adduct, in which the two nitrogen atoms of DMAZ are placed in an equatorial plane and the oxo ligand in an apex position (see C in eq. 1). This configuration is similar to those of $MoO(S_2CNPr^n_2)(TCNE)$[7] and $MoO(S_2CNMe_2)_2(MeC_6H_4C(O)C{\equiv}CC(O)C_6H_4Me)$[5] determined by X-ray crystallographic analyses. On the other hand, a violet solution prepared by mixing equimolar $MoO(S_2CNMe_2)_2$ and DMAZ in CH_2Cl_2 at -78°C exhibits two N-CH_3 signals (δ 3.34, 3.45) of the S_2CNMe_2 moiety and two O-CH_3 signals (δ 3.62, 3.77) of DMAZ with different intensities in each methyl proton (Fig. 1b). These signals shift upfield compared with those of free $MoO(S_2CNMe_2)_2$ (δ 3.47) or DMAZ (δ 4.03) in CH_2Cl_2, indicating that there is no dissociative species in solution. Thus, the spectrum of the violet solution may be interpreted as an equilibrium mixture of two isomeric mono-capped trigonal prismatic $MoO(S_2CNMe_2)_2$-(DMAZ), in which the relative orientation of coordinated DMAZ are different from each other with respect to the chelate ligands, as shown in A and B. Such configurations are readily achieved by the coordination of DMAZ to a vacant site of the square pyramidal configuration of $MoO(S_2CNMe_2)_2$.

Rates of the reaction of $MoO(S_2CNEt_2)_2$ with DEAZ were measured in CH_2ClCH_2Cl with a Union Giken RA-413 stopped flow spectrophotometer. Immediately after mixing these reactants at atmospheric pressure, the resulting violet solution exhibits an absorption maximum at 550 nm, which is weakened with time and concomitantly a band around 400 nm is strengthened with an isosbestic point at 447 nm, as shown in Fig. 2. Thus, the reaction proceeds *via* two succes-

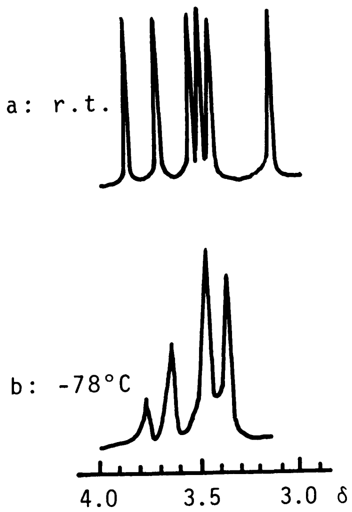
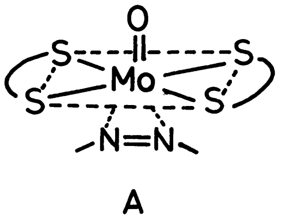
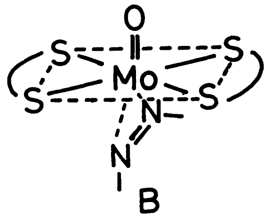


Fig. 1. ^1H-nmr spectra of $MoO(S_2CNMe_2)_2$-DMAZ in CH_2Cl_2.



A



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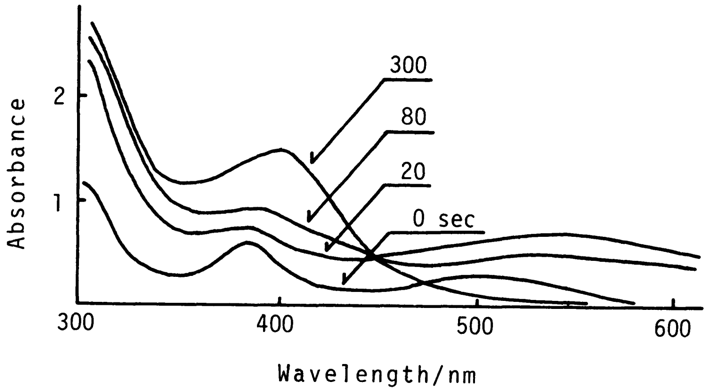
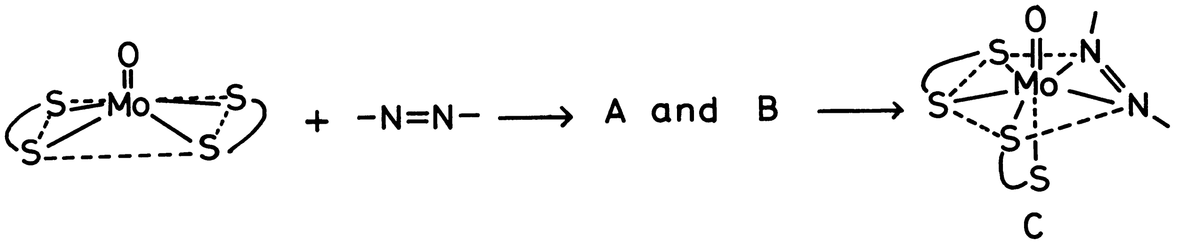


Fig. 2. Spectral change after mixing $MoO(S_2CNEt_2)_2$ (1.24×10^{-4} mol dm^{-3}) with DEAZ (1.66×10^{-4} mol dm^{-3}) in CH_2ClCH_2Cl at 25°C.



(1)

sive steps (eq. 1). Observed rate constants for the first and the second steps were determined by monitoring the absorbance at 511 nm under pseudo-first-order conditions with at least a 20-fold excess amount of DEAZ at four different temperatures. All the plots of pseudo-first-order rate constants of the first-step *vs.* the concentration of DEAZ at each temperature yielded straight lines with a zero intercept, suggesting that there exists no backward reaction. On the other hand, the rate constants of the second step were essentially independent of the DEAZ concentration. In addition, the reaction rate of the second step was not influenced at all by the addition of large amounts of $[Et_4N][S_2CNEt_2]$ (2-30 times the amount of $MoO(S_2CNEt_2)_2$) to the reaction mixture. This fact rules out the dissociation of the S_2CNEt_2 ligand in the intramolecular rearrangement.

The Table lists the rate constants and activation parameters calculated from the Arrhenius plot of ln k *vs.* 1/T. The activation entropy $\Delta S_1^{\ddagger}$ of the first step is a large negative value as expected from the bimolecular addition reaction. In the second step, however, the $\Delta S_2^{\ddagger}$ value is positive. This is in marked contrast to a large negative $\Delta S^{\ddagger}$ value (-83.5 $J\,mol^{-1}K^{-1}$) of the second step in an analogous reaction of $MoO(S_2CSPr^i)_2$ with DMAC reported previously.[6)]

Kinetic measurements were performed also at high pressures up to 2.94 kbar by the use of a Union Giken RA-413-01 static high pressure cell for the second step of

Table. Rate Constants and Activation Parameters[a] for the Reaction of $MoO(S_2CNEt_2)_2$ with DEAZ in CH_2ClCH_2Cl[b]

	Temp / °C	$10^{-2}k_1$ / $s^{-1}mol^{-1}dm^3$	$10^{2}k_2$ / s^{-1}
	19.9	1.43 ± 0.01	
	25.2	1.76 ± 0.01	1.40 ± 0.03
	29.8	2.15 ± 0.01	2.52 ± 0.01
	35.3	2.50 ± 0.04	5.09 ± 0.01
$\Delta H^{\ddagger}$ / $kJ\,mol^{-1}$		25.4 ± 1.1	95.0 ± 1.1
$\Delta S^{\ddagger}$ / $J\,mol\,K^{-1}$		-117 ± 4	38.0 ± 3.6

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

the reactions not only of $MoO(S_2CNEt_2)_2$ with DEAZ but of $MoO(S_2CSPr^i)_2$ with DMAC, by monitoring the absorbances at 511 and 480 nm, respectively. The rate constants obtained under various pressures are depicted in Fig. 3, from which the activation volumes, $\Delta V^\ddagger$, were determined as $+13.6 \pm 0.1$ and -9.9 ± 0.2 $cm^3 mol^{-1}$ for the rearrangement of $MoO(S_2CNEt_2)_2(DEAZ)$ and $MoO(S_2CSPr^i)_2(DMAC)$, respectively. The negative value of $\Delta V^\ddagger$ for the latter adduct is compatible with "non-bond breaking mechanism" for the intramolecular rearrangement, as reported previously.6) On the other hand, the dissociation of a dithiocarbamate ligand in the rearrangement of $MoO(S_2CNEt_2)_2(DEAZ)$ has been ruled out, as described above. Thus, the positive value $\Delta V^\ddagger$ may be an indication for the cleavage of a Mo-S bond of the chelate rings in the transition state of the intramolecular rearrangement. Such "bond-breaking mechanism" is consistent also with the positive value of $\Delta S^\ddagger$ for the rearrangement of $MoO(S_2CNEt_2)_2(DEAZ)$. The two mechanisms proposed for the present systems may correspond to the suggestion that in the ligand exchange reaction of octahedral transition metal complexes, negative values of $\Delta V^\ddagger$ are anticipated for an associative mechanism, and positive values for a dissociative mechanisms.8)

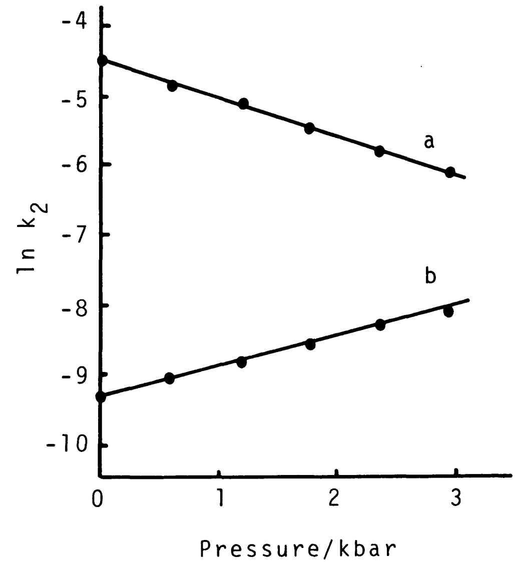


Fig. 3. Plots of ln k_2 *vs.* pressure for the reactions of $MoO(S_2CNEt_2)_2$ with DEAZ (a) and of $MoO(S_2CSPr^i)_2$ with DMAC (b).

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References

1) P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, 94, 8640 (1972).
2) J. W. McDonald, J. L. Corbin, and W. E. Newton, *Inorg. Chem.*, 15, 2056 (1976).
3) E. A. Maatta, R. A. D. Wentworth, W. E. Newton, J. W. McDonald, and G. D. Watt, *J. Am. Chem. Soc.*, 100, 1320 (1978).
4) E. A. Maata and R. A. D. Wentworth, *Inorg. Chem.*, 18, 524 (1979).
5) W. E. Newton, J. W. McDonald, J. L. Corbin, L. Richard, and R. Weiss, *Inorg. Chem.*, 19, 1997 (1980).
6) K. Tanaka, S. Miyake, and T. Tanaka, *Chem. Lett.*, 1981, 189.
7) L. Richard and R. Weiss, *Inorg. Nucl. Chem. Lett.*, 10, 217 (1974).
8) M. V. Twigg, *Inorg. Chim. Acta*, 24, L84 (1977).

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