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Contribution from the Chemistry Department, Faculty of Science,
Australian National University, Canberra, 2600, Australia

Mechanism of the Reaction of *cis*-Bis(*N,N*-diethyldithiocarbamato)dinitrosylmolybdenum with Azide or Cyanate and Related Reactions

JOHN A. BROOMHEAD* and JOHN R. BUDGE

The reaction of *cis*-bis(*N,N*-diethyldithiocarbamato)dinitrosylmolybdenum with either azide, cyanate, cyanide, or diethyldithiocarbamate in hot dimethyl sulfoxide yields dinitrogen oxide. The reactions are initiated by coordination of the anion leading to activation of a nitrosyl group. ^{15}N labeling and kinetic studies show that an intermolecular mechanism is involved. This is suggested to involve coupling of two molecules of reactive complex through a nitrosyl ligand on each to give a bridged hyponitrito type species. In the presence of excess azide the rate law is of the form $-d/dt[\text{Mo(Et}_2\text{dtc)}_2(\text{NO})_2]$ = $(k_1[\text{N}_3] + k_2)[\text{Mo(Et}_2\text{dtc)}_2(\text{NO})_2]$. At 63.7 °C k_1 is 1.86×10^{-3} L mol^{-1} s^{-1} and k_2 is 0.78×10^{-5} s^{-1} and for the second-order path $\Delta H^\ddagger$ is 91 ± 4 kJ mol^{-1} and $\Delta S^\ddagger$ is -29 ± 12 J deg^{-1} mol^{-1}.

Introduction

In a previous paper[1] we reported the unusual reaction between *cis*-bis(*N,N*-diethyldithiocarbamato)dinitrosylmolybdenum (Mo(Et$_2$dtc)$_2$(NO)$_2$) and either azide or cyanate which gives dinitrogen oxide and complexes of the type [MoL(Et$_2$dtc)$_2$(CH$_3$)$_2$SONO] (L = N$_3$, NCO). The gas originates entirely from the nitrosyl ligands. Several reactions which appear to be related to the above have recently been described in which various metal nitrosyl complexes yield dinitrogen oxide upon treatment with ligands such as CO and NO. These include compounds of Fe, Co, Rh, and Ir.[2-6] In this paper the mechanism of the reaction for molybdenum nitrosyls has been elucidated by means of ^{15}N labeled complexes and kinetic measurements.

Experimental Section

Materials. The various Mo(R$_2$dtc)$_2$(NO)$_2$ and W(R$_2$dtc)$_2$(NO)$_2$ complexes were prepared by the literature method.[8] All preparations had the correct C, H, N, and S analyses. The reagents Mo(CO)$_6$, W(CO)$_6$, Br$_2$, NaS$_2$ CN(C$_2$H$_5$)$_2$·H$_2$O, NaS$_2$CN(CH$_3$)$_2$, NaN$_3$, KN$_3$, various amines (see later), and NO were laboratory grade chemicals used without further purification. Sodium and potassium cyanates were recrystallised from water to which glacial acetic acid was added until neutral to phenolphthalein. Their purities, estimated gravimetrically using semicarbazide, were found to be 99.3 and 98.7%, respectively. Solvents were AR grade and unless otherwise stated were used as supplied. For ^{15}N labeling and kinetic experiments the dimethyl sulfoxide was freshly distilled from calcium hydride under vacuum. The ligands pyrrolidyl-, di(*n*-butyl)-, and dibenzyldithiocarbamate were generated in situ by slow addition of the appropriate diamine (1.9×10^{-2} mol) to carbon disulfide (1.45 g; 1.9×10^{-2} mol) in methanol (40 cm^3). Sodium hydroxide (0.76 g; 1.9×10^{-2} mol)

**Table I.** Isotopic Composition (Atom % ^{15}N)

NO	Mo(Et$_2$dtc)$_2$-(^{15}NO)$_2$	Mo(Et$_2$dtc)$_2$-(^{15}NO)NO	Mo(Et$_2$dtc)$_2$-(NO)$_2$
95	90.25	9.50	0.25
48	23.04	49.92	27.04

was added and the solution stirred until it had dissolved. Sodium diisopropyldithiocarbamate was prepared similarly using 1:1 ethanol–water as solvent.

Preparation of ^{15}N Labeled Complexes. The literature synthesis[8] of *cis*-Mo(R$_2$dtc)$_2$(NO)$_2$ using labeled NO and adapted to vacuum line techniques was employed. ^{15}NO (95 atom %) was obtained from the reaction of K^{15}NO$_3$ (Bio-Rad, Richmond, Calif.; 0.09 g; 8.8×10^{-4} mol) and mercury (2 g; 1×10^{-2} mol) in concentrated sulfuric acid (2.5 cm^3; 4.5×10^{-2} mol).[9] ^{15}NO (48 atom %) was obtained similarly using a 1:1.07 mixture of KNO$_3$ to 95 atom % K^{15}NO$_3$. A mass spectrum using a freshly prepared sample of NO showed that the only impurity was a trace of N$_2$O. The isotopic compositions of the cis complexes so prepared are shown in Table I. For experiments using ^{15}N labeled complexes all solutions were prepared in a glovebox under dry N$_2$ and degassed on the vacuum line. Reactions between *cis*-Mo(R$_2$dtc)$_2$(NO)$_2$ and azide or cyanate were completed by heating the dimethyl sulfoxide solutions at 60 °C for 12–14 h. The gaseous products were transferred using vacuum line techniques into a vessel cooled to –196 °C. Mass spectra were recorded with an AEI MS10-C2 mass spectrometer. Prior to measurement the gas vessel was cooled at –76 °C to remove traces of dimethyl sulfoxide.

Gas Volume Measurements. The volume of gas evolved has been measured using a thermostated gas buret system. In a typical experiment *cis*-Mo(Et$_2$dtc)$_2$(NO)$_2$ (0.2 g; 4.42×10^{-4} mol) and KNCO (0.073 g; 8.95×10^{-4} mol) were dissolved in dimethyl sulfoxide (5 cm^3). The solution was degassed on the vacuum line and then heated at 60 °C for 13 h. The gas evolved was transferred into a measuring
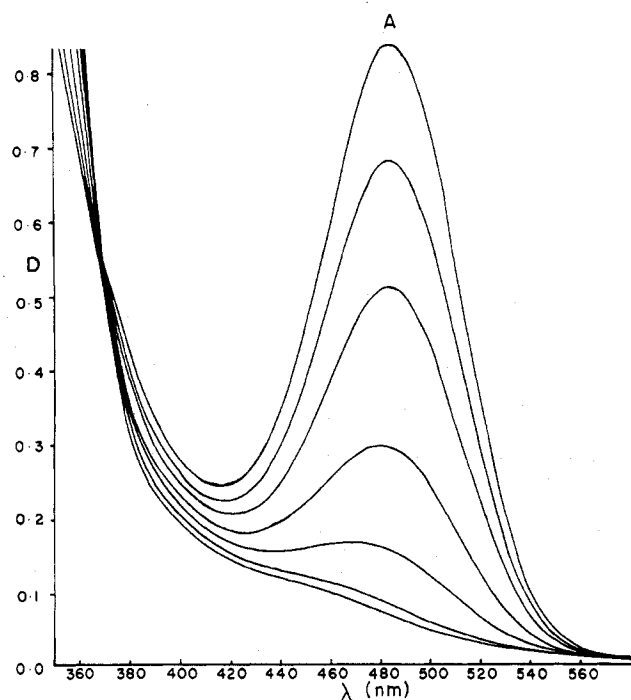
Figure 1. Absorption spectral time scans for the reaction of *cis*-Mo(Et$_2$dtc)$_2$(NO)$_2$ (4.4 × 10^{-4} M) with NaN$_3$ (4.94 × 10^{-2} M) at 63.7 °C in dimethyl sulfoxide. Curve A is the initial trace followed successively by traces at 55, 115, 245, 475, 1405, and 2855 min, respectively.

Table II. Wavelengths Used for Rate Studies

complex[a,c]	λ, nm	isosbestic points, nm
Mo(Bz$_2$dtc)$_2$(NO)$_2$	483	390, 553, 612
Mo(Me$_2$dtc)$_2$(NO)$_2$	484.5	370, 562, 603
Mo(Et$_2$dtc)$_2$(NO)$_2$	484, 484.5[b]	370, 578, 355[b]
Mo(pyr(dtc))$_2$(NO)$_2$	485	373, 563, 604
Mo(n-Bu$_2$dtc)$_2$(NO)$_2$	486	370, 584
Mo(i-Pr$_2$dtc)$_2$(NO)$_2$	489.5	375

[a] With NaN$_3$ excepting footnote b. [b] With NaNCO. [c] Temperature 63.7 °C.

vessel cooled at −196 °C by eight applications of a pentane slush (−130 °C) freeze–distill–thaw cycle. Mass spectral and VPC measurements confirmed that the gas was dinitrogen oxide. Duplicate values of the percent N$_2$O evolved per mole of *cis*-Mo(Et$_2$dtc)$_2$(NO)$_2$ gave 48.3, 47.9 for cyanate and 50.3, 50.4 for azide.

Kinetic Studies. The reactions of *cis*-Mo(R$_2$dtc)$_2$(NO)$_2$ complexes with either azide or cyanate ion were followed using a Cary 14 spectrophotometer equipped with a thermostated (±0.1 °C) cell holder. For reactions with half-lives greater than 2 h, measurements were taken every hour; otherwise the reactions were monitored continuously. The light employed had no measurable effects on the rates.

Two types of reaction cell were used. Both were fitted with a Teflon tap and O-ring seals. For azide reactions the cell was filled and sealed under dry N$_2$ before being placed in the spectrophotometer compartment. The first reading was taken after temperature equilibration (i.e., 10 min). For cyanate reactions a fresh solution of sodium or potassium cyanate was first stored in a side chamber of a divided cell and allowed to reach the desired temperature before mixing with the solid molybdenum complex and commencing to record.

Repetitive scanning of the visible spectral region during reaction of *cis*-Mo(Et$_2$dtc)$_2$(NO)$_2$ with sodium azide gave well-defined isosbestic points. Typical spectral changes are shown in Figure 1. Wavelengths at which the other complex reactions have been measured along with the isosbestics are given in Table II. Beer's law was found to be obeyed for all complexes over the concentration ranges used. Also the spectra of *cis*-Mo(R$_2$dtc)$_2$(NO)$_2$ complexes in dimethyl sulfoxide at 63.7 °C remained unchanged over a 20-h interval.

Reactions were carried out using at least a tenfold excess of azide. At smaller (stoichiometric) concentrations of anion the rates were too slow. A pseudo-first-order rate law was obeyed for the azide

Table III. Reactions of Various Labeled Mo(Et$_2$dtc)$_2$(NO)$_2$ Complexes with KNCO, NaN$_3$, NaS$_2$CNEt$_2$·3H$_2$O, or KCN

	reagent quantities, mol			
reac-tion[a]	Mo(Et$_2$-dtc)$_2$-(^{15}NO)$_2$	Mo(Et$_2$-dtc)$_2$-(NO)$_2$	salt	N$_2$O ratios[b] ^{15}N$_2$O:^{15}NNO:N$_2$O
1	1.1 × 10^{-5}		2.5 × 10^{-5}	1:0.1:0.02[c] (1:0.1:0.003)
2	1.1 × 10^{-5}	1.1 × 10^{-5}	2.5 × 10^{-5}	1:2.0:1.1 (1:2.2:1.2)
3[d]	1.05 × 10^{-5}		5.3 × 10^{-5}	1:0.4:0.2
4[d]			6.16 × 10^{-5}	N$_2$O (trace)
5[d]	1.23 × 10^{-5}			N$_2$O (trace)
6[e]		1.1 × 10^{-4}	2.5 × 10^{-4}	N$_2$O only
7	2.2 × 10^{-5}	2.16 × 10^{-5}		no N$_2$O
8[f]		4.49 × 10^{-5}	9.5 × 10^{-5}	1:0.1:1 (1:0.1:1.1)
9	7.84 × 10^{-6}	7.82 × 10^{-6}	4.61 × 10^{-5}	1:2.1:1.1 (1:2.2:1.2)
10[d]	1.52 × 10^{-5}		4.92 × 10^{-5}	1:0.84:0.2
11[d]			4.6 × 10^{-5}	N$_2$O (trace)
12		2.21 × 10^{-4}	2.23 × 10^{-3}	N$_2$O evolved
13	1.53 × 10^{-5}	1.54 × 10^{-5}	3.06 × 10^{-4}	1:2.1:1.2 (1:2.2:1.2)
14[d]	1.1 × 10^{-5}		2.43 × 10^{-4}	1:1.35:0.57
15		2.21 × 10^{-5}	9.21 × 10^{-5}	N$_2$O evolved
16	1.12 × 10^{-5}	1.34 × 10^{-5}	1.07 × 10^{-4}	1:2.6:1.6 (1:2.6:1.7)
17[d]	1.14 × 10^{-5}		1.01 × 10^{-4}	1:1.7:2.3
18[d]			1.29 × 10^{-4}	N$_2$O evolved[g]

[a] All reactions 12 h in Me$_2$SO (3 cm^3) at 60 °C under vacuum unless otherwise indicated. For reactions 1–8, salt is KNCO; 9–11, NaN$_3$; 12–14, NaS$_2$CNEt$_2$·3H$_2$O at 70 °C; 15–18, KCN (at room temperature). [b] Theoretical ratios given in parentheses. [c] This result confirms 95% ^{15}NO in the complex. [d] Under NO pressure of 20 mmHg. [e] Under O$_2$ pressure of 300 mmHg. [f] Under (^{15}N$_2$O + ^{15}NNO) obtained by reaction of Mo(Et$_2$dtc)$_2$(^{15}NO)$_2$ (4.68 × 10^{-5} mol) + KNCO (9.49 × 10^{-3} mol) in Me$_2$SO (3 cm^3). [g] Presumably from the reaction 2NO + CN$^-$ → N$_2$O + NCO$^-$.

reaction but no satisfactory interpretation could be made for reactions with cyanate. Reactions were much faster for cyanate than for azide and in addition a period of induction was observed before the absorbance began to diminish. The length of this induction period was dependent on the concentration of *cis*-Mo(Et$_2$dtc)$_2$(NO)$_2$ and on the nature of the cyanate counterion. For example, at a complex concentration of 4.9 × 10^{-4} M and a sodium cyanate concentration of 3.8 × 10^{-2} M an induction period of 110 min at 63.7 °C was found. Under almost identical conditions using potassium cyanate there was no induction period.

For the reactions of azide with various *cis*-Mo(R$_2$dtc)$_2$(NO)$_2$ complexes the absorbance values at infinite time were not constant and the Guggenheim method was therefore used to evaluate rate constants (k_{obsd}). Other rate parameters have been calculated by standard methods while the method of least squares has been used in fitting graphical data. Each rate constant has been determined in triplicate. As the added salt concentrations were low (1–5 × 10^{-2} M) and the substrate molybdenum complexes are neutral, ionic strength effects should be minimal, and consequently no background electrolyte was added.

Labeling Experiments. Reactions using ^{15}NO labeled complexes and various control experiments are listed in Table III. For reaction 6 of Table III the dioxygen was pumped off at −196 °C. For two of the reactions described in Table III the *cis*-Mo(Et$_2$dtc)$_2$(NO)$_2$ complexes were recovered for infrared spectral measurements as follows. The solution from Table III was opened to air and dichloromethane (20 cm^3) added. The dimethyl sulfoxide was removed by extraction into water (3 × 100 cm^3) and the dichloromethane solution dried over anhydrous sodium sulfate. The solution was filtered and evaporated to dryness, the residue being dissolved in chloroform (1–2 cm^3). This solution was placed on an 18 × 0.5 cm column packed with silica gel (70–230 mesh) and eluted with a 1:1 mixture of hexane/chloroform. The eluate was evaporated to dryness and the product recrystallized from aqueous methanol, being dried in vacuo over P$_4$O$_{10}$. In reaction 7 the complexes were recovered by addition of dichloromethane (10 cm^3) and extraction with water (3 × 50 cm^3)

(a) M—N≡O
(−)A—N
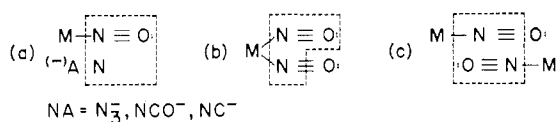
(b) M⟨N≡O
N≢O

(c) M—N≡O
O≡N—M

NA = N₃⁻, NCO⁻, NC⁻

Figure 2. Possible origins of the N₂O.
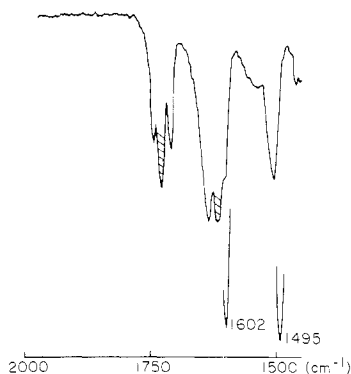
Figure 3. The infrared spectrum (KBr disk) in the nitrosyl (and C≡N) regions for a 1:2:1 mixture of *cis*-Mo(Et₂dtc)₂(^{15}NO)₂, *cis*-Mo-(Et₂dtc)₂(^{15}NO)NO (hatched), and *cis*-Mo(Et₂dtc)₂(NO)₂.

to remove the dimethyl sulfoxide. The column purification step was omitted but otherwise the same procedure was followed.

Results and Discussion

Three possible ways in which the N₂O released in these reactions might originate are illustrated in Figure 2. The first involves the incorporation of a nitrogen atom from the anion (a), while the others involve either an intramolecular (b) or an intermolecular (c) process. We have shown previously that pathway (a) does not apply for azide.[1] Reactions 1 and 16 (Table III) also eliminate this type of mechanism for both cyanate and cyanide.

To distinguish between an intramolecular and an intermolecular process a number of experiments with ^{15}N labeled nitrosyl ligands have been employed. For the intramolecular path shown in (b) (Figure 2) reactions 2, 9, 13, and 16 should give a 1:1 mixture of ^{15}N₂O and N₂O, which is not the case. Instead, a very good agreement is found between the calculated and observed isotope distributions expected for an intermolecular process (Table III).

It was necessary to establish that the observed N₂O isotope ratios did not arise from reactions other than those illustrated by (c) of Figure 2. To ensure that no preliminary intermolecular exchange of nitrosyl groups occurs an infrared spectrum of a 1:2:1 mixture of *cis*-Mo(Et₂dtc)₂(^{15}NO)₂, *cis*-Mo-(Et₂dtc)₂(^{15}NO)(NO), and *cis*-Mo(Et₂dtc)₂(NO)₂ (see Figure 3) was compared with that of the product from reaction 7 (Table III). In the last mentioned the intermediate nitrosyl bands due to *cis*-Mo(Et₂dtc)₂(^{15}NO)NO were absent confirming that no exchange had occurred.

To obtain additional information as to the dissociation of nitrosyl ligands under the reaction conditions various experiments in the presence of excess NO or O₂ have been tried. The absence of NO₂ when dioxygen is present (no. 6, Table III) confirms that there is no release of a nitrosyl ligand during reaction. However, the results obtained in the presence of NO are more complicated. In Table III (reactions 3, 10) the increased amounts of ^{15}NNO and N₂O clearly demonstrate that there is a slow exchange of NO occurring. (A small amount of CO₂ (same m/e as N₂O) could also arise from the hydrolysis of cyanate and this is believed to be the source of the small increase in N₂O found for example in reaction 1.) In interpreting the results of experiments 2, 7, 9, 13, and 16 it was necessary to consider the possibility of an isotopic equilibrium of the form ^{15}N₂O + N₂O ⇌ 2^{15}NNO. However,
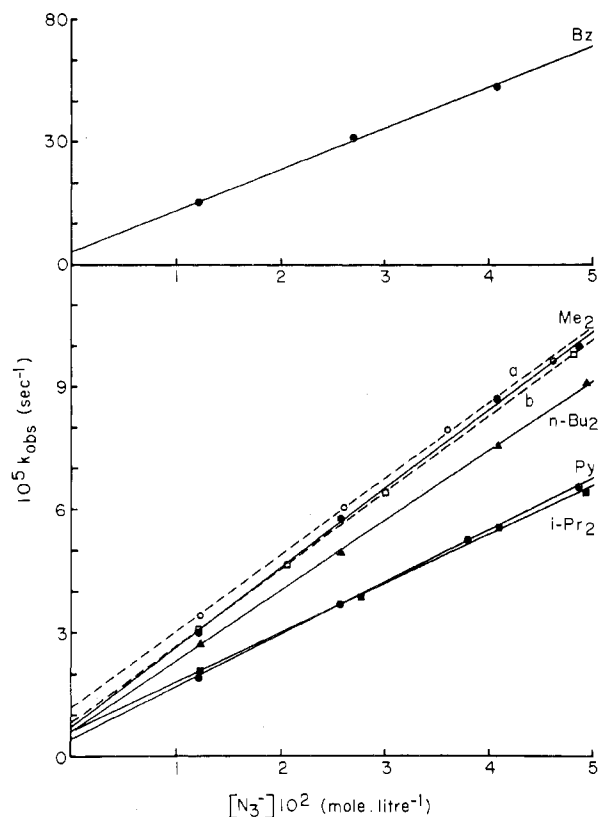
Figure 4. Dependence of k_{obsd} on azide ion concentration for *cis*-Mo(R₂dtc)₂(NO)₂ at 63.7 °C in dimethyl sulfoxide. For sodium azide, R = Me, 0.5 pyrrolidyl (pyr), *n*-Bu, *i*-Pr, Bz, Et (broken line b). For potassium azide, R = Et (broken line a).

when a 1:1 mixture of ^{15}N₂O and N₂O was stored in the presence of *cis*-Mo(Et₂dtc)₂(NO)₂ in dimethyl sulfoxide at 60 °C no ^{15}NNO was detected.

The above results together with the good agreement found for the theoretical and observed N₂O ratios in Table III are only consistent with the intermolecular path (c) of Figure 2. The theoretical ratios for the distribution of ^{15}N given in Table III have been calculated on the assumption that all nitrosyl ligands are equally available during reaction. The number of combinations giving rise to ^{15}N₂O, ^{15}NNO, and N₂O were calculated from the respective mole fractions of Mo-(Et₂dtc)₂(^{15}NO)₂, Mo(Et₂dtc)₂(^{15}NO)NO, and Mo-(Et₂dtc)₂(NO)₂, and these are proportional to their respective probabilities of formation.

The N₂O ratios obtained in reactions 14 and 17 (Table III) are clear evidence for the exchange of nitrosyl ligands with the free NO present. The apparent high value for N₂O in reaction 17 is most probably due to the reaction CN⁻ + 2NO → N₂O + NCO⁻ (see no. 18). Certainly there is no prior dissociation of NO for any of these reactions since they can be carried out in air with no NO₂ being formed. Although the reactions with cyanide and diethyldithiocarbamate have not been studied in as much detail as have those with azide and cyanate, they appear to involve a similar intermolecular process as is shown by the data of Table III.

The Mechanism of the Intermolecular Process. In the hope of elucidating the reaction mechanism with azide and cyanate in more detail, a kinetic study has been attempted. For reasons given above this has been confined to the azide reaction. The dependence of k_{obsd} on the azide ion concentration is given in Figure 4 for various substituted dithiocarbamato complexes. For the reaction of *cis*-Mo(Et₂dtc)₂(NO)₂ with sodium azide a study of the temperature dependence of k_{obsd} has also been made (Figure 5).
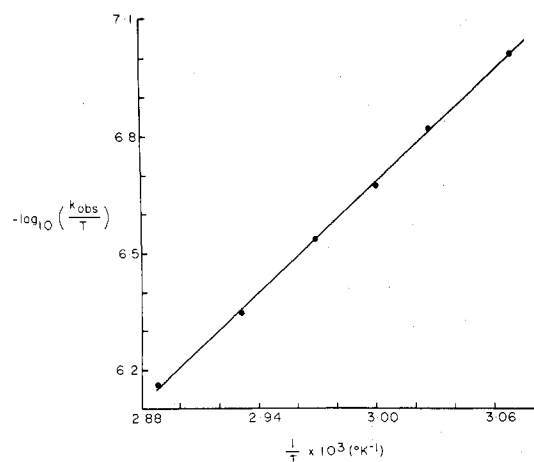
Figure 5. Temperature dependence of the pseudo-first-order rate constants for the reaction of cis-Mo(Et$_2$dtc)$_2$(NO)$_2$ with NaN$_3$ in dimethyl sulfoxide.

Table IV. Values of k_1 and k_2 for the Mo(R$_2$dtc)$_2$(NO)$_2$ Azide Reactions[a]

R	$10^3 k_1$, L mol^{-1} s^{-1}	$10^5 k_2$, s^{-1}
Me	1.93 ± 0.23	0.73 ± 0.61
Et	1.86 ± 0.22	0.78 ± 0.59
Et[b]	1.84 ± 0.24	1.15 ± 0.62
Et[c]	4.55 ± 0.54	2.00 ± 1.14
pyr	1.27 ± 0.15	0.42 ± 0.39
i-Pr	1.18 ± 0.14	0.63 ± 0.39
n-Bu	1.71 ± 0.20	0.60 ± 0.55
Bz	10.4 ± 1.3	3.13 ± 3.12

[a] All reactions with NaN$_3$ at 63.7 °C unless otherwise stated. [b] With KN$_3$ at 63.7 °C. [c] At 73.1 °C.

It is evident from Figure 4 that k_{obsd} is linearly related to the azide ion concentration leading to the rate expression

$$-\frac{d}{dt}[\text{Mo(R}_2\text{dtc)}_2\text{(NO)}_2] =$$

$$(k_1[\text{N}_3^-] + k_2)[\text{Mo(R}_2\text{dtc)}_2\text{(NO)}_2]$$

Here $k_{obsd} = k_1[\text{N}_3^-] + [k_2]$, k_1 and k_2 being second- and first-order rate constants, respectively. A mechanism which is consistent with both the kinetics and labeling experiments is shown in Figure 6.

Values of k_1 and k_2 are given in Table IV and have been obtained from a least-squares analysis of the data. For all reactions investigated the major contribution to the rates comes from the azide-dependent path. This is an associative step involving the formation of a seven-coordinate complex anion. The azide-independent step could consist of a slow dithiocarbamate ring opening followed by a rapid coordination of azide. Alternatively a molecule of solvent could be involved either before or after ring opening giving a six-coordinate stage which is then attacked by azide. No reaction takes place in the absence of added anion and it is the seven-coordinate complex which is believed to be of critical importance to the nitrosyl ligand reactivity. This reactivity may be understood to arise in the following way.

Enemark and Feltham[6] have considered at length the correlation diagrams which relate molecular orbital schemes for M(NO)$_2$ complexes of different geometries. They have not included seven-coordination, but it is possible to extend their approach for this purpose. The cis-Mo(R$_2$dtc)$_2$(NO)$_2$ (C$_2$ symmetry) complexes studied in this work correspond to the {M(NO)$_2$}^{6} configuration for which the molecular orbital diagram is Figure 22 of ref 6. Similar diagrams are expected for C$_2$, C$_s$, and C$_1$ symmetry. Depending upon the site of coordination of the reagent ligand L the symmetry either
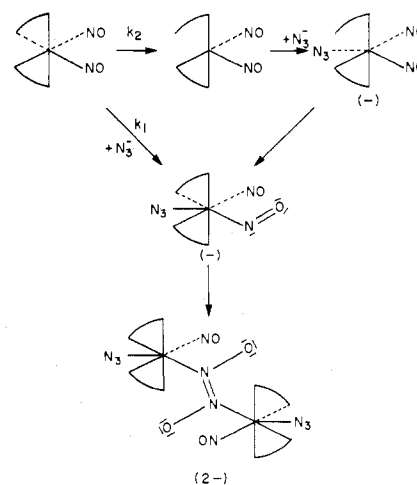
Figure 6. Mechanism proposed for the reactions of cis-Mo-(R$_2$dtc)$_2$(NO)$_2$ complexes with N$_3^-$ (and other anions).
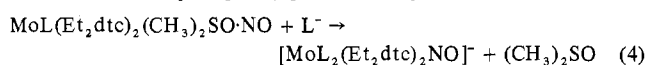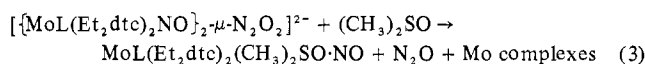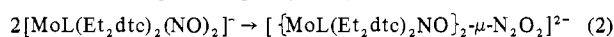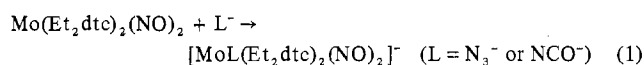
remains C$_2$ or is lowered to C$_1$.

For coordination in the equatorial plane to give a pentagonal-bipyramidal complex of C$_1$ symmetry the d$_{x^2}$ orbital becomes strongly antibonding and the π_a*(NO) orbital is now occupied by a pair of electrons. (This is π_{b_1}*(NO) in C$_{2v}$ symmetry adopting the coordinate convention of ref 6.) As the intermediate has nonequivalent nitrosyl groups the electron pair could then be localized in an sp^2-type orbital on one of the nitrosyl nitrogen atoms (cf. [RuCl(PPh$_3$)$_2$(NO)$_2$]$^{+6}$). That is, one of the nitrosyl groups bends to give a more reactive NO$^-$ group while the other remains linear and unreactive. In this way the reaction of only one nitrosyl group per molecule may be understood. Conversely if the anion coordinates so as to give a species with C$_2$ symmetry the equivalent nitrosyl groups should adopt a "repulso" configuration and show no tendency to couple.[10] Similar arguments may be applied to the nitrosyl reactions mentioned previously[2-6] and it seems likely that they are also explicable in terms of reactive NO$^-$ groups.

In the suggested mechanism (Figure 6) coupling occurs between activated nitrosyl groups on *different* complexes to give an unstable hyponitrito species. This decomposes to yield dinitrogen oxide and other products (see later). There is evidence for the partial dissociation of the dithiocarbamato ligand required in the azide-independent path. This arises from variable-temperature ^{1}H NMR studies on cis-Mo-(Me$_2$dtc)$_2$(NO)$_2$ which were interpreted[11] in terms of a chelate ring-opening mechanism. The formation of hyponitrito-bridged complexes has been observed for both cis,cis-MoCl$_2$das(NO)$_2$ and cis,cis-MoCl$_2$en(NO)$_2$[12] (das = o-phenylenebis(dimethylarsine); en = ethylenediamine). These reactions occur after methanol solutions of the complexes have aged several days and coordination of a molecule of methanol may be required to obtain coupling of the nitrosyls. A recent crystallographic study[13] has verified the coupling of two nitrosyl ligands in the cis hyponitrito complex Pt(N$_2$O$_2$)(Ph$_3$P)$_2$ in which the hyponitrito ligand is bound through the oxygen atoms. This complex reacts with CO to give N$_2$O and CO$_2$.[14] An N,O bridging cis hyponitrite is also known[15] in [{Co-(NH$_3$)$_5$}$_2$-μ-N$_2$O$_2$]$^{4+}$.

The temperature dependence studies (Figure 7) permit the calculation of $\Delta H^{\ddagger}$ as 91 ± 4 kJ mol^{-1} and $\Delta S^{\ddagger}$ as −29 ± 12 J deg^{-1} mol^{-1} for the k_1 path. There are large errors which arise from the extrapolation procedure used to get k_2 so that similar calculations for the azide-independent path have not been made. With the exception of the benzyl group, substituents had little effect on the rates (Table IV). It seems probable that the increased rates for the dibenzyldithiocarbamato complex are due to a combination of electronic and

steric effects. The dibenzyldithiocarbamate ligand is the least electron donating of the series studied[16] and also the most bulky. These properties would be expected to act in opposition but the increased rates do suggest that the electronic effect is dominant and the metal center has become more positive for the benzyl substituent. Figure 4 indicates a systematic difference between NaN_3 and KN_3 as reagent. Variations in rate constants were found also for other salts when present in the cis-$Mo(Et_2dtc)_2(NO)_2$–NaN_3 reaction in amounts comparable to the NaN_3. The variation is shown in parentheses: CsBr (+40%); $Ba(NO_3)_2$ (unchanged); MgF_2 (+8%); $CaBr_2$ (–12%). It is likely that different ion clusters are responsible for all these effects in the aprotic solvent employed. In addition, both water and dioxygen affected the rates. For example, if the cis-$Mo(Et_2dtc)_2(NO)_2$–NaN_3 reaction solution in $(CH_3)_2SO$ was made 0.57 M with respect to water, the rate constant was reduced by 20%. In a dioxygen-saturated solution a 50% retardation was observed. A reduction in rate in the presence of water is understood in terms of increased solvation of the anion but the effect of dioxygen is not clear. The presence of nitrogen oxide similarly leads to a decrease in the reaction rate.

Stoichiometry of the Reactions of cis-$Mo(Et_2dtc)_2(NO)_2$ with Azide and Cyanate. The mechanistic studies reported here may be combined with the previously described synthesis and characterization of products[7] in the equations

$$Mo(Et_2dtc)_2(NO)_2 + L^- \rightarrow$$
$$[MoL(Et_2dtc)_2(NO)_2]^- \quad (L = N_3^- \text{ or } NCO^-) \quad (1)$$

$$2[MoL(Et_2dtc)_2(NO)_2]^- \rightarrow [\{MoL(Et_2dtc)_2NO\}_2\text{-}\mu\text{-}N_2O_2]^{2-} \quad (2)$$

$$[\{MoL(Et_2dtc)_2NO\}_2\text{-}\mu\text{-}N_2O_2]^{2-} + (CH_3)_2SO \rightarrow$$
$$MoL(Et_2dtc)_2(CH_3)_2SO\cdot NO + N_2O + Mo \text{ complexes} \quad (3)$$

$$MoL(Et_2dtc)_2(CH_3)_2SO\cdot NO + L^- \rightarrow$$
$$[MoL_2(Et_2dtc)_2NO]^- + (CH_3)_2SO \quad (4)$$

Decomposition of the hyponitrito-bridged complex accounts for the formation and yields of N_2O (see Experimental Section) as well as the isolation of $[Mo(NCO)_2(Et_2dtc)_2NO]^-$ in about 40% yield as the tetraethylammonium salt. Equation 3 is an attempt to account for the decomposition reaction. When $L = N_3^-$ there is evidence for greater lability in the products. Not only is the yield smaller (about 10%) but also the known $Mo(Et_2dtc)_3NO$ complex is obtained in moderate amounts. For this reason the preferred synthetic route for $MoN_3(Et_2dtc)_2(CH_3)_2SO\cdot NO$ is by substitution in the corresponding cyanato complex.[7] Although the oxygen atom left

after the breakdown of the hyponitrito bridge could be transferred to the solvent giving dimethyl sulfone, all attempts to detect this product were unsuccessful. However current work involving thin-layer chromatographic separation of the cyanate reaction product mixture followed by infrared measurements has permitted recognition of molybdenum oxo groups in an otherwise unidentified species.[17]

Similar chemistry to that described for cis-$Mo(Et_2dtc)_2$-$(NO)_2$ in this paper is also found with cis-$W(Et_2dtc)_2(NO)_2$. However, the reactions with azide or cyanate are much too slow but may be accelerated by irradiation with light from a xenon lamp. Complexes of the type $(Et_4N)[WL_2(Et_2dtc)_2NO]$ ($L = N_3^-$, NCO^-, or NCS^-) have been isolated and will be described fully elsewhere. In the reactions involving light, activation of the nitrosyl groups is suggested to take place by charge transfer from metal to the nitrosyl, attended by coordination of the anion to give a hyponitrito-bridged complex analogous to that shown in Figure 6.

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Electrochemical Properties of Aquomolybdenum Ions in Noncomplexing Acidic Electrolytes

PURUSH CHALILPOYIL and FRED C. ANSON*

The electrochemistry of molybdenum in oxidation states III–VI in trifluoromethanesulfonic acid is examined. The electrochemical oxidations of both the monomeric and dimeric forms of aquomolybdenum(III) are irreversible and are preceded by rate-limiting chemical reactions. Oxidation of both monomeric and dimeric Mo(III) leads to dimeric Mo(V) but there is evidence of the intermediacy of unstable monomeric Mo(V) during the oxidation of monomeric Mo(III). The reduction of Mo(IV) is quasi-reversible and diffusion controlled. The product of the reduction is a new form of (probably) dimeric Mo(III). The stable, dimeric form of Mo(V) is reduced to the previously described dimeric form of Mo(III). The reduction of Mo(VI) produces differing sets of products depending upon the potentials where the electrolysis is carried out. At –0.2 V vs. SCE, the monomeric form of Mo(V) appears to be formed initially but it dimerizes rapidly.

The aqueous chemistry of molybdenum in oxidation states II,[1,2] III,[1-7] IV[7-15] and V[7,10,16-20] has attracted considerable

recent attention. Both monomeric and dimeric forms of oxidation state III are now well characterized[1-7] and there is