11: $R_1, R_2, R_3, R_4 = H$
14: $R_1, R_4 = H; R_2, R_3 = CH_3$
15: $R_1, R_4 = CH_3; R_2, R_3 = H$

12: $R_1, R_2, R_3, R_4 = H$
16: $R_1, R_4 = CH_3; R_2, R_3 = H$
17: $R_1, R_4 = H; R_2, R_3 = CH_3$

13: $R_1, R_2, R_3, R_4 = H$
18: $R_1, R_4 = CH_3; R_2, R_3 = H$

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that may be important in other thermal reactions do not seem to be detectable here.

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Kinetics and Mechanism of Nitrate Reduction by a Dimeric Aquamolybdenum(III) Complex in Aqueous Solution. Direct Evidence for an Oxo-Group Transfer

Karl Wieghardt,* Maria Woeste, Partha S. Roy, and Phalguni Chaudhuri

Lehrstuhl für Anorganische Chemie I
*Ruhr-Universität, D-4630 Bochum, FRG*

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The molybdoenzyme *E. coli* nitrate reductase catalyzes the reduction of nitrate to nitrite at an active site of mononuclear Mo(IV) (or Mo(V)) center.[1] In the past a number of monomeric oxomolybdenum(V) complexes have been found to reduce nitrate to NO_2 in nonaqueous solvents.[2] The formation of a (nitrato)-molybdenum(V) precursor complex has been proposed in the rate-determining step with subsequent intramolecular one-electron transfer and oxo-group transfer to produce dioxomolybdenum(VI) species and NO_2. The mononuclear hexaaquamolybdenum(III) cation has been shown to reduce NO_3^- to NO_2^- in aqueous solution generating the aquamolybdenum(V) dimer, $[Mo_2O_4(H_2O)_6]^{2+}$.[3] Formally, this reaction involves a two-electron transfer which could be an oxo-transfer reaction. The transfer of an oxygen atom from the inert nitrate ion to the respective molybdenum centers has not been previously demonstrated experimentally.

We here wish to report the kinetics and mechanism of the reaction of the diamagnetic, green bis(μ-hydroxo)bis[aqua-(1,4,7-triazacyclononane)molybdenum(III)](4+) cation[4,5] with

nitrate in acidic aqueous solution.

The reaction of the bis(μ-hydroxo)bis[aqua(1,4,7-triazacyclo-nonane)molybdenum(III)](4+) cation[4,5] with nitrate under strictly oxygen-free conditions yields quantitatively *purple anti*-$[L_2Mo_2O_4]^{2+}$[4a] and nitrite (eq 1).
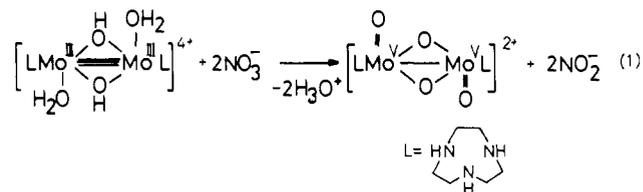
The formation of NO_2^- during the above reaction was proven in situ when the reaction was carried out in the presence of sulfanilic acid and α-naphthylamine in acidic aqueous solution both of which do not react with either the Mo(III) dimer or the Mo(V) dimer in the absence of nitrate. The generation of the known deep-red azo dye is good evidence for the presence of NO_2^-. The stoichiometry of the above reaction was determined spectrophotometrically (Job's method) using amidosulfonic acid as effective nitrite scavenger (eq 2)[6] and quantitative determination

$$H_2NSO_3H + NO_2^- \xrightarrow{\text{fast}} HSO_4^- + N_2 + H_2O \qquad (2)$$
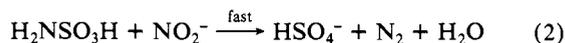
of the gaseous nitrogen evolved. One nitrate is consumed per molybdenum(III) center.

The kinetics of the reaction between $[L_2Mo_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ and nitrate (pseudo-first-order conditions; excess NO_3^-) were determined spectrophotometrically at 380 nm using eight different solutions containing varying amounts of NO_3^- ($[NO_3^-]$ = 0.01–0.40 M; $[Mo^{III}_2] = 4 \times 10^{-4}$ M), methanesulfonic acid ($[H^+]$ = 0.1 M), and amidosulfonic acid ($[H_2NSO_3H] = 5.2 \times 10^{-3}$ M). The ionic strength was adjusted to 0.5 M by using sodium methanesulfonate as innocent electrolyte. Plots of absorbance changes, log $(A_t - A_\infty)$, against time, t, were linear for at least 4 half-lives.[7] The final spectrum, after the reaction with nitrate was complete, corresponded exactly to that of *anti*-$[L_2Mo_2O_4]^{2+}$.[8] Scan spectra recorded during the reaction revealed the presence of two isosbestic points at 335 and 473 nm. Variation of $[Mo^{III}_2]$ ($(1.4–4.0) \times 10^{-4}$ M) did not affect the pseudo-first-order rate constants, k_{obsd}. Values of the second-order rate constant, k (M^{-1}

$$-d[Mo^{III}_2]/dt = d[Mo^V_2]/dt = k[Mo^{III}_2][NO_3^-] \qquad (3)$$

s^{-1}), obtained by a least-squares treatment of data are 0.023 (10 °C), 0.042 (17 °C), and 0.10 (25 °C). Activation parameters for k are $\Delta H^\ddagger = 69 \pm 4$ kJ mol^{-1} and $\Delta S^\ddagger = -33 \pm 12$ J mol^{-1} K^{-1}. It is noted that a small but reproducible linear dependence of the rate on $[H^+]$ is observed. Thus in going from $[H^+] = 0.05$ to 0.30 M ($[NO_3^-] = 0.05$ M, $[Mo^{III}_2] = 2 \times 10^{-4}$ M, $[H_2NSO_3H]$ = 5×10^{-3} M, 25 °C, $I = 0.5$ M ($NaCH_3SO_3$)) the value of k_{obsd}

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(5) In all experiments described here solid samples of diamagnetic, green $[L_2Mo_2^{III}(\mu\text{-}OH)_2(OH)_2](PF_6)_2 \cdot H_2O$ were used as starting material (L = 1,4,7-triazacyclononane). This salt was prepared from $[L_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]I_2 \cdot H_2O^{4a}$ (2.5 g) in deoxygenated aqueous HPF$_6$ (0.5 M, 50 mL) at room temperature. Desired product 1.5 g, precipitated slowly at 0 °C. Anal. Calcd for $C_{12}H_{34}O_4N_6Mo_2P_2F_{12}$: C, 17.44; H, 4.39; N, 10.77. Found: C, 17.3; H, 4.1.; N, 9.9.

(6) Oxygen-free aqueous solutions of the Mo$^{III}_2$ dimer do not react with H_2NSO_3H.

(7) Kinetic runs performed in the absence of H_2NSO_3H under otherwise identical conditions were not found to follow strictly first-order kinetics and the final absorption spectrum indicated the presence of small amounts of other products than *anti*-$[L_2Mo_2O_4]^{2+}$. In a few preliminary, separate experiments it was confirmed that the Mo(III) dimer reacts rapidly with nitrite and NO generating *yellow* solutions, from which yellow-greenish solids were obtained (IR bands at 1780 and 1630 cm^{-1} are indicative of dinitrosylmolybdenum species).

(8) The rate of the previously reported irreversible, H$^+$-catalyzed anti → syn isomerization[9] of the product *anti*-$[L_2Mo_2O_4]^{2+}$ is much slower under our experimental conditions and does not interfer with the spectrophotometric product analyses measured directly after the reduction of nitrate is complete.

increases from 4.8×10^{-3} to 7.2×10^{-3} M^{-1} s^{-1}. We cannot offer at present a reasonable explanation for this effect, since in this range of [H$^+$] the Mo(III) dimer is fully protonated (aqua ligands) whereas the nitrate anion is fully deprotonated.

The kinetic data suggest that substitution of a coordinated aqua ligand of the Mo(III) dimer by NO$_3^-$ is the rate-determining step (rds) of the redox reaction.[10] An associative mechanism (I_a) is most probably operative.[9]

In order to gain insight into what happens after the rds we have investigated the reaction using ^{18}O-enriched potassium nitrate (60% and 90%) as oxidant.[11] After the reaction of the Mo(III) dimer with NO$_3^-$ in unlabeled water was complete the very insoluble salt, *anti*-[L$_2$Mo$_2$O$_4$]I$_2$, was rapidly precipitated by addition of sodium iodide to the reaction mixture. The solid material was analyzed by infrared spectroscopy. This was readily accomplished because the terminal Mo=O$_t$ stretching frequency and the ν_{as}-(Mo—O) of the bridging oxo groups in the unlabeled Mo(V) dimer are observed as strong, sharp bands at 918 and 730 cm^{-1}, respectively. The IR spectrum of the Mo(V) dimer obtained from such a reaction mixture using ^{18}O-enriched NO$_3^-$ (60%) exhibits then two additional strong bands at 887 and 868 cm^{-1} which are assigned to ν(Mo=O$_t$) stretching frequencies. Most importantly, *no* additional bands are observed at wavenumbers <730 cm^{-1}. This indicates that during the course of the redox reaction no bridging oxygen atoms are incorporated that stem from the nitrate anion; i.e., terminal oxo groups only are transferred from the nitrate to the molybdenum centers. Thus three different products were obtained.

The semiquantitative analysis of respective relative intensities of these ν(Mo=O) stretching frequencies reveals that the amount of ^{18}O-labeled products (II and III) is always 1.4 times more than

	V (Mo=O$_t$)	ν_{as}(Mo–O$_b$)
1	918 cm^{-1}	730 cm^{-1}
II	887 cm^{-1}	730 cm^{-1}
III	868 cm^{-1}	730 cm^{-1}
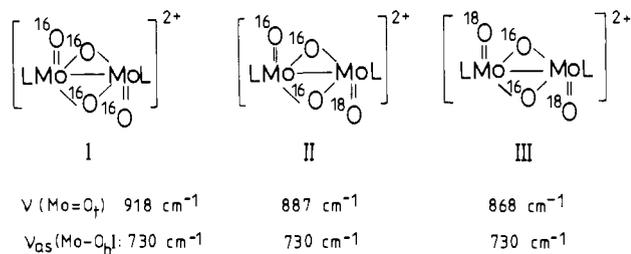
that of I. By use of 90% ^{18}O-enriched nitrate only small amounts of I and II were detected whereas III represents the dominating species. These results can most readily be accounted for if it is considered that only the two terminal oxo groups in *anti*-[L$_2$Mo$_2$O$_4$]$^{2+}$ are transferred from ^{18}O-enriched nitrate and that all the oxygens of the terminal Mo^V = O groups stem from the nitrate; i.e., at least 90% (as a lower limit) of the reduction of NO$_3^-$ by [L$_2$Mo$_2$(μ-OH)$_2$ (H$_2$O)$_2$]$^{4+}$ in acidic aqueous solution in the presence of an NO$_2^-$ scavenger, proceeds via an oxo-group transfer.

(9) Hahn, M.; Wieghardt, K. *Inorg. Chem.* **1984**, *23*, 3977.

(10) Kinetic data for the anation reaction of [L$_2$Mo^{III}$_2$ (μ-OH)$_2$ (H$_2$O)$_2$]$^{4+}$ and chloride ions[9] are comparable.

(11) ^{18}O-Labeling experiments: In a typical experiment an aqueous solution (10 mL) of H$_2$NSO$_3$H (0.19 g, 1.8 mmol) and [L$_2$Mo$_2$(μ-OH)$_2$ (HO)$_2$](PF$_6$)$_2$ (0.05 g, 0.06 mmol) was reacted with ^{18}O-enriched (60% or 90%) potassium nitrate (0.096 g, 0.9 mmol) under strictly anaerobic conditions (argon atmosphere) at room temperature. Within 40 min the original green color of the solution turned red. Addition of sodium iodide (0.08 g) initiated the precipitation of *anti*-[L$_2$Mo$_2$O$_4$]I$_2$, which was recovered in 96% yield with respect to Mo(III) dimer substrate.

(12) Under our experimental conditions both the oxo groups of the nitrate[13] and of the product *anti*-[L$_2$Mo$_2$O$_4$]$^{2+}$ do not undergo oxygen-exchange reactions with the solvent water. The latter observation is in excellent agreement with Murman's ^{18}O-exchange studies on syn-[Mo$_2$O$_4$(edta)]$^{2-}$.[14]

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On the Nucleophilic Nature of a TMM–PdL$_2$ Intermediate: A Direct Palladium-Catalyzed Addition of Trimethylenemethane to Heteroatom Unsaturation

Barry M. Trost* and Peter J. Bonk

McElvain Laboratories of Organic Chemistry Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706

The chemistry of trimethylenemethane, an intensely studied area from a mechanistic and theoretical point of view,[1] appears poised to have an impact on complex synthesis. Two seemingly related approaches use a metal-catalyzed cycloaddition—one employing 2-[(trimethylsilyl)- or 2-[(trialkylstannyl)methyl]allyl carboxylates[2] and the other alkylidenecyclopropanes.[3] Such
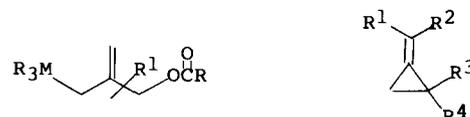
reactions are, however, quite different in many respects such as chemo- and regioselectivity. Clearly the same intermediates cannot be involved in both reactions. In order to try to determine which reaction, if either, proceeds through a TMM–PdL$_2$ species, we have been examining the reactivity profile of the intermediate in the silyl and stannyl carboxylate reaction. Theory indicates that a TMM–PdL$_2$ intermediate should behave as a zwitterion as illustrated in **1**.[4] While the known behavior of the silyl-carboxylates seemingly are in accord with a zwitterionic intermediate,[2,5] carbonyl additions (see eq 1), a classic test of nucleophilicity, have heretofore given poor results.

(1)
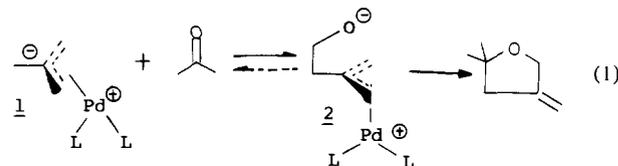
In analogy to the Diels–Alder reaction which can cycloadd to both olefins and carbonyl groups, the extension of the [3 + 2] cycloaddition reaction to carbonyl groups would greatly expand its scope in an important direction since (1) substituted tetrahydrofurans are important structural units of many natural products, especially ionophores, (2) the exocyclic methylene group serves as a versatile handle for structural elaboration, and (3) the 3-methylenetetrahydrofuran is easily oxidized to α-methylene-γ-butyrolactones,[6] another important structural feature of many natural products. The obvious importance of such a process led us to develop a two-step approach using a Lewis acid catalyzed addition of 2-[(trialkylstannyl)methyl]allyl acetate (3) followed by cyclization.[7] We wish to report that such tin conjunctive reagents directly add to aldehydes with excellent chemo- and regioselectivity mediated by a Pd catalyst.

The reaction involves mixing approximately equimolar amounts of an aldehyde and the tin acetate 3 in dioxane with 3 mol % of

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