16860 (to L. G. Lang). We thank Professor T. G. Traylor for an authentic sample of compound **4**. We also thank Professors J. P. Collman and L. G. Lang for helpful discussions. We acknowledge the assistance of J. L. Desorcie, D. J. Brennan, K. D. Lavin, and N. M. Tollefson in obtaining the spectral data.

**Registry No.** **3**, 77130-40-6; **4**, 96964-15-7; **6**, 5032-39-3; **7**, 96948-52-6; **8**, 96948-53-7; **9**, 96998-68-4; **10**, 96964-16-8; CO, 630-08-0; 3-(methylamino)propionitrile, 693-05-0.

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# Catalytic Reduction of $NO_2^-$ by HCOOH in the Presence of $MoO_2(S_2CNEt_2)_2$ and $MoO(S_2CNEt_2)_2$

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The reduction of $NO_2^-$ to $N_2O$ by HCOOH in *N*,*N*-dimethylformamide (DMF) in the presence of $MoO(S_2CNEt_2)_2$ or $MoO_2(S_2CNEt_2)_2$ as a catalyst has been accomplished for the first time. The reaction of $MoO(S_2CNEt_2)_2$ with $NO_2^-$ in DMF rapidly proceeds to afford $MoO_2(S_2CNEt_2)_2$ and $N_2O_2^{2-}$, the latter of which may be produced by the dimerization of a possible intermediate $NO^-$. Both $MoO_2(S_2CNEt_2)_2$ and $N_2O_2^{2-}$ further react with HCOOH to give $MoO(S_2CNEt_2)_2$ and $N_2O$, respectively. The catalytic reaction obeys first-order kinetics with respect to the concentration of $MoO(S_2CNEt_2)_2$ or $MoO_2(S_2CNEt_2)_2$. The rate-determining step is the reduction of $MoO_2(S_2CNEt_2)_2$ by HCOOH, giving $MoO(S_2CNEt_2)_2$.

## Introduction

Denitrification by anaerobic bacteria refers to the dissimilatory reduction of $NO_3^-$ and $NO_2^-$ to $N_2O$, which is further reduced to $N_2$.[1-3] These processes are of interest in biological removal of $NO_3^-$ and $NO_2^-$ from the water of rivers and lakes. Dissimilatory nitrate reductases contain iron, labile sulfide, and molybdenum[4] and have been purified from several bacteria. The dissimilatory nitrite reductases are divided into two types: one is a hemoprotein of cytochromes *c* and *d*[5-9] and the other is a copper-containing metalloflavoprotein.[10-12] Electrons required in the reduction of $NO_3^-$ and $NO_2^-$ by these reductases can be supplied from formate dehydrogenases, which oxidize HCOOH to $CO_2$.[13,16] The formate dehydrogenases coupled with those reductases are known to involve iron, labile sulfide, selenium, and molybdenum[17]

Previous model studies of nitrate reductases have shown that the reactions of $NO_3^-$ with oxomolybdenum complexes give a variety of products such as $NO_2$, $NO_2^-$, NO, $N_2O$, $NH_3OH^+$, and $NH_4^+$, depending on the reaction conditions.[18-25] It has also been shown that $NO_2^-$, the first reduction product of $NO_3^-$ by nitrate reductases, can be reduced to NO by oxomolybdenum complexes.[26] Catalytic reductions of $NO_3^-$ and $NO_2^-$ by oxomolybdenum complexes have, however, been unsuccessful so far. This paper demonstrates the first catalytic reduction of $NO_2^-$ to $N_2O$ by HCOOH in the presence of $MoO_2(S_2CNEt_2)_2$ or $MoO(S_2CNEt_2)_2$.

## Experimental Section

**Materials.** Commercially available guaranteed reagent grade $NaNO_3$, $NaNO_2$, and HCOOH were used without further purification. Tetrabutylammonium nitrate and nitrite were prepare by the reactions of $NaNO_3$ and $NaNO_2$ with *n*-$Bu_4NBr$, respectively, in *N*,*N*-dimethylformamide (DMF). $MoO_2(S_2CNEt_2)_2$,[27] $MoO(S_2CNEt_2)_2$,[28] and $Na_2N_2O_2$[29] were prepared according to the literature methods. Solvent DMF was purified by distillation over CaO under reduced pressure of $N_2$, stored under dry nitrogen, and bubbled with He for at least 1 h right before use. Standard $N_2O$ and $CO_2$ gases used for the quantitative analysis of reaction products were obtained from Gaschro Kogyo Co. Ltd.

**Reactions.** A rubber-septum-capped reaction flask (35 $cm^3$) containing $MoO_2(S_2CNEt_2)_2$ or $MoO(S_2CNEt_2)_2$ ($7.5 \sim 30.0$ μmol) was throughly flushed with He to remove air. A DMF (10 $cm^3$) solution containing $NaNO_2$ (300–600 μmol) and HCOOH (300–600 μmol) was injected into the flask through the septum cap by syringe techniques, and the solution was stirred magnetically at a given reaction temperature (±0.2 °C). At fixed time intervals, 0.1-$cm^3$ portions of gas and the solution were sampled from the gaseous and the liquid phases, respectively, in the flask through the septum cap. The quantitative analysis of the reaction products ($CO_2$ and $N_2O$) in both phases was performed on a Shimazu gas chromatograph GC-7A with a 3-m column filled with Gaschropack 54 (Gaschro Kogyo Co. Ltd.) at 100 °C with use of He (40 $cm^3$/min) as a carrier gas. The amount of $Na_2N_2O_2$ produced in the

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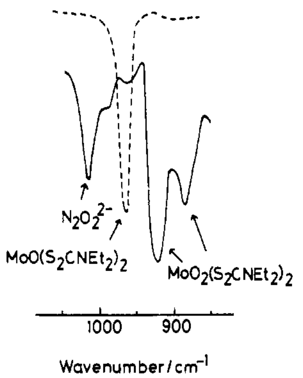

**Figure 1.** IR spectra of $MoO(S_2CNEt_2)_2$ (- -) and the reaction mixture immediately after mixing $MoO(S_2CNEt_2)_2$ with an equimolar amount of $n$-$Bu_4NNO_2$ (–) in $CH_2Br_2$.

reaction of $MoO(S_2CNEt_2)_2$ with $NaNO_2$ in DMF was determined with a Shimazu isotachophoretic analyzer Model IP-2A by using $Cd(NO_3)_2$ (6.0 mmol dm$^{-3}$) and $CH_3(CH_2)_4COOH$ (10.0 mmol dm$^{-3}$) as leading and terminal electrolytes, respectively.

**Spectra.** Infrared and electronic spectra were recorded on Hitachi 215 and Union SM-401 spectrophotometers, respectivley.

## Results and Discussion

**Reactions of $MoO(S_2CNEt_2)_2$ with $NO_3^-$ and $NO_2^-$.** It is well-known that coordinatively unsaturated $MoO(S_2CNEt_2)_2$ is easily oxidized by pyridine *N*-oxide or dimethyl sulfoxide to give $MoO_2(S_2CNEt_2)_2$ and pyridine[30] or dimethyl sulfide,[31] respectively. This reaction may be interpreted as a nucleophilic attack by the oxygen of pyridine N-oxide or dimethyl sulfoxide to molybdenum(IV), followed by cleavage of the N–O or S–O bond. $MoO(S_2CNEt_2)_2$ is known to undergo nucleophilic attack by bases such as pyridine derivatives and tertiary phosphines to form 1:1 adducts.[32] Such an oxygen atom transfer reaction from a labile oxygen-containing molecule to $MoO(S_2CNEt_2)_2$ may be applicable to the reduction not only of $NO_3^-$ but also of $NO_2^-$.

The reaction of $MoO(S_2CNEt_2)_2$ with $NO_3^-$ and $NO_2^-$ was carried out in DMF. The electronic absorption spectrum of a DMF solution of $MoO(S_2CNEt_2)_2$ was almost unchanged over 6 h at room temperature in the presence of an equimolar amount of $NaNO_3$. In accordance with this, the formation of neither $MoO_2(S_2CNEt_2)_2$ nor $NO_2^-$ has been confirmed in the reaction of $MoO(S_2CNEt_2)_2$ with $NO_3^-$ in $CHCl_3$.[30,33] On the other hand, a pink DMF solution of $MoO(S_2CNEt_2)_2$ was changed to a yellow one in 1 min upon the addition of an equimolar amount of $NaNO_2$ dissolved in DMF.[34] The infrared spectrum obtained immediately after mixing equimolar amounts of $MoO(S_2CNEt_2)_2$ and $n$-$Bu_4NNO_2$ in $CH_2Br_2$ shows that $MoO(S_2CNEt_2)_2$ ($\nu$(Mo=O) 966 cm$^{-1}$) is oxidized to give $MoO_2(S_2CNEt_2)_2$ ($\nu$(Mo=O) 916 and 879 cm$^{-1}$) together with $(n\text{-}Bu_4N)_2N_2O_2$ ($\nu$(N—O) 1040 cm$^{-1}$), as depicted in Figure 1, while no reaction has occurred between $NO_2^-$ and $MoO_2(S_2CNEt_2)_2$ in the same solvent as confirmed by the IR spectrum. It should be noted that $Mo_2O_3(S_2CNEt_2)_4$ ($\nu$(Mo=O) 936 cm$^{-1}$) was absent in the final product. This result suggests that the reaction proceeds almost quantitatively since $MoO_2(S_2CNEt_2)_2$ rapidly attains equilibrium with $MoO(S_2CNEt_2)_2$ affording $Mo_2O_3(S_2CNEt_2)_4$.[35-38] The formation of $N_2O_2^{2-}$ in the reaction of $MoO(S_2CNEt_2)_2$ with $NO_2^-$ may have resulted from the dimerization of $NO^-$ as reported elsewhere.[39]

**Table I.** Amounts of $CO_2$ Evolved and Rate Constants for the Reactions of $MoO_2(S_2CNEt_2)_2$ (300 $\mu$mol) with HCOOH (300 $\mu$mol) in DMF (10 cm$^3$) at Several Temperatures

| temp/°C | amt of $CO_2$$^a$/$\mu$mol | $k$/mol$^{-1}$ dm$^3$ s$^{-1}$ |
|---|---|---|
| 30 | 114$^b$ | $6.11 \times 10^{-5}$ |
| 40 | 287 | $1.28 \times 10^{-4}$ |
| 50 | 300 | $2.33 \times 10^{-4}$ |
| 60 | 302 | $5.00 \times 10^{-4}$ |

$^a$For 24 h. $^b$For 72 h.

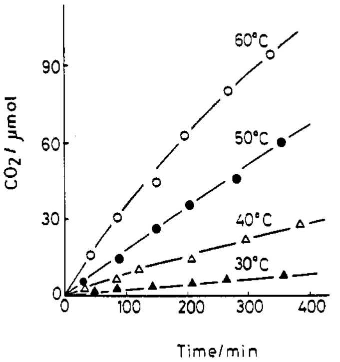

**Figure 2.** Plots of $CO_2$ produced vs. time in the reaction of $MoO_2(S_2CNEt_2)_2$ (300 $\mu$mol) with HCOOH (300 $\mu$mol) in DMF (10 cm$^3$).

The quantitative analysis of $N_2O_2^{2-}$ was conducted by the use of isotachophoresis. The reaction of 300 $\mu$mol of $MoO(S_2CNEt_2)_2$ with an equimolar amount of $NaNO_2$ in DMF for 60 min gave 101 $\mu$mol of $Na_2N_2O_2$ with a small amount of unreacted $NO_2^-$. Moreover, the reaction evolved 22 $\mu$mol of $N_2O$ altogether in the gaseous and liquid phases, as determined by gas chromatography. The formation of $N_2O$ may come from the hydrolysis of $N_2O_2^{2-}$.[40] In fact, 300 $\mu$mol of $Na_2N_2O_2$ obtained according to the literature[29] reacted with an equimolar amount of HCOOH as a proton source in DMF (10 cm$^3$) at 30 °C for 90 min quantitatively, affording 148 $\mu$mol of $N_2O$ without evolving $CO_2$. Thus, the reaction of $NO_2^-$ to $N_2O$ in the present study can be expressed by eq 1-3. It should be mentioned that both $NO^-$ and $N_2O_2^{2-}$

$$MoO(S_2CNEt_2)_2 + NO_2^- \rightarrow MoO_2(S_2CNEt_2)_2 + NO^- \tag{1}$$

$$NO^- \rightarrow {}^1/_2N_2O_2^{2-} \tag{2}$$

$$N_2O_2^{2-} + 2H^+ \rightarrow N_2O + H_2O \tag{3}$$

produced in eq 1 and 2, respectively, have been proposed as precursors of $N_2O$ in the reduction of $NO_2^-$ by nitrite reductases.[41-44]

**Reduction of $MoO_2(S_2CNEt_2)_2$ by HCOOH.** As expected from eq 1-3, the reduction of $NO_2^-$ to $N_2O$ may proceed catalytically when $MoO_2(S_2CNEt_2)_2$ formed in eq 1 can successfully be reduced to regenerate $MoO(S_2CNEt_2)_2$. Trialkyl- and triphenylphosphines have widely been used as reducing agents for the oxygen abstraction from $MoO_2(S_2CNEt_2)_2$ in homogeneous systems, giving $MoO(S_2CNEt_2)_2$,[45-48] and these reactions have been applied to

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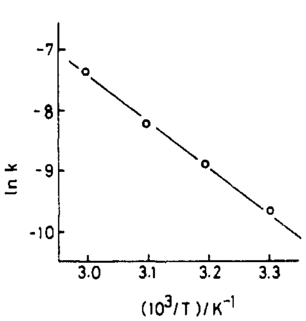

**Figure 3.** Arrhenius plot for the reaction of $MoO_2(S_2CNEt_2)_2$ (300 μmol) with HCOOH (300 μmol) in DMF (10 $cm^3$).

the catalytic oxidation of $PPh_3$ with dioxygen.[37,49,50] Moreover, $PPh_3$ has recently been utilized for a catalytic reduction of $Me_2S{=}O$ affording $Me_2S$ by a $MoOL/MoO_2L$ (L = tridentate ligand) system.[51,52] In the present study, however, formic acid was utilized not only for the smooth evolution of $N_2O$ by the reaction of $N_2O_2^{2-}$ with protons (eq 3) but also to model the chemistry of formate dehydrogenases by means of $MoO_2(S_2CNEt_2)_2$. Thus, the reaction of $MoO_2(S_2CNEt_2)_2$ with an equimolar amount of HCOOH in DMF at various temperatures was followed by monitoring the amount of $CO_2$ evolved (eq 4).

$$MoO_2(S_2CNEt_2)_2 + HCOOH \rightarrow MoO(S_2CNEt_2)_2 + CO_2 + H_2O \quad (4)$$

The reaction conducted at 30 °C was very slow, as shown in Figure 2; the amount of $CO_2$ evolved for 72 h is about half of that expected from the amount of HCOOH used (Table I). At 40 °C or higher temperatures, however, the reaction proceeds quantitatively in 24 h (Table I). The crude product obtained by evaporation of the solvent after the reaction at 40 °C for 24 h was $MoO(S_2CNEt_2)_2$ contaminated with small amounts of both $MoO_2(S_2CNEt_2)_2$ and $Mo_2O_3(S_2CNEt_2)_4$, as confirmed by the infrared spectrum; the formation of $Mo_2O_3(S_2CNEt_2)_4$ may come from the rapid dimerization equilibrium between $MoO_2(S_2CNEt_2)_2$ and $MoO(S_2CNEt_2)_2$[35-38] (eq 5), the latter of which

$$MoO_2(S_2CNEt_2)_2 + MoO(S_2CNEt_2)_2 \rightleftharpoons Mo_2O_3(S_2CNEt_2)_4 \quad (5)$$

is produced in the reaction of eq 4. The formation of $Mo_2O_3(S_2CNEt_2)_4$ was confirmed from the color change of the reaction mixture in DMF; the initial yellow solution of $MoO_2(S_2CNEt_2)_2$, upon the addition of HCOOh, gradually changed to deep violet due to $Mo_2O_3(S_2CNEt_2)_4$, which was formed according to eq 4 and 5. As the reaction proceeded, however, the solution faded in color owing to the shift of the equilibrium (eq. 5) to the left resulting from the consumption of $MoO_2(S_2CNEt_2)_2$, and finally a pink solution was obtained. It should be mentioned that no reaction occurred between $MoO(S_2CNEt_2)_2$ (300 μmol) and HCOOH (300 μmol) in DMF (10 $cm^3$) at 30 °C for 24 h.

Recently, Holm et al.[38] reported a simulation method for the kinetics of an irreversible oxygen abstraction reaction from $MoO_2(S_2CNEt_2)_2$ with tertiary phosphines followed by the rapid dimerization equilibrium of eq 5. In the present study, however, the oxygen abstraction reaction from $MoO_2(S_2CNEt_2)_2$ with HCOOH (eq 4) is quite slow (Figure 2). In early stages of the reaction, therefore, the concentration of $MoO(S_2CNEt_2)_2$ may be very small, and hence the amount of $MoO_2(S_2CNEt_2)_2$ consumed in the reaction of eq 5 may be neglected. Thus, the rate of the reaction of eq 4 can safely be determined from the amount of $CO_2$ evolved in the initial stages. In fact, the reaction of $MoO_2(S_2CNEt_2)_2$ (300 μmol) with HCOOH (300 μmol) in DMF (10 $cm^3$) obeyed second-order kinetics within the amount of $CO_2$ evolved, being less than 20 μmol. The rate constants thus obtained are collected in Table I. A plot of the constant against the reciprocal temperature gives a straight line, as shown in Figure 3, from which the activation energy for the reaction of eq 4 has been determined as 57.8 kJ $mol^{-1}$.

**Table II.** Reactions of $NaNO_2$ with HCOOH in the Presence of $MoO_2(S_2CNEt_2)_2$ in DMF (10 $cm^3$) at 50 °C for 24 h

| | starting material[a] | | | product[a] | |
|---|---|---|---|---|---|
| entry | $MoO_2$-$(S_2CNEt_2)_2$ | HCOOH | $NaNO_2$ | $CO_2$ | $N_2O$ |
| 1 | 30.0 | 300 | 300 | 197 | 89 |
| 2 | 30.0 | 600 | 300 | 197 | 90 |
| 3 | 30.0 | 300 | 600 | 197 | 104 |
| 4 | 30.0 | 600 | 600 | 316 | 151 |
| 5 | 22.5 | 300 | 300 | 188 | 90 |
| 6 | 15.0 | 300 | 300 | 187 | 91 |
| 7 | 7.5 | 300 | 300 | 170 | 75 |

[a] In μmol.

**Table III.** Reactions of $NaNO_2$ (300 μmol) with HCOOH (300 μmol) in the Presence of $MoO_2(S_2CNEt_2)_2$ (30 μmol) or $MoO(S_2CNEt_2)_2$ (30 μmol) in DMF (10 $cm^3$) for 24 h

| temp/ °C | $MoO_2$-$(S_2CNEt_2)_2$ | | $MoO(S_2CNEt_2)_2$ | |
|---|---|---|---|---|
| | $N_2O$[a] | $CO_2$[a] | $N_2O$[a] | $CO_2$[a] |
| 30 | 82 | 151 | 88 | 115 |
| 40 | 89 | 194 | 95 | 155 |
| 50 | 89 | 197 | 100 | 184 |
| 60 | 105 | 210 | 104 | 192 |

[a] In μmol.

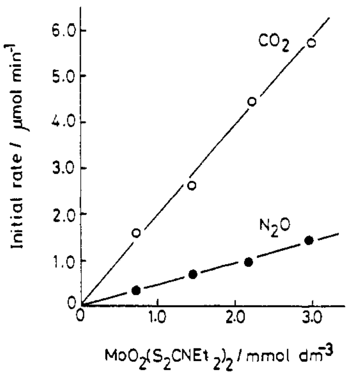

**Figure 4.** Plots of the initial rates of formation of $N_2O$ and $CO_2$ vs. the concentration of $MoO_2(S_2CNEt_2)_2$ in the reaction of $NaNO_2$ (300 μmol) with HCOOH (300 μmol) in DMF (10 $cm^3$).

**Catalytic Reduction of $NO_2^-$ to $N_2O$.** Since no reaction occurs between $NaNO_2$ and HCOOH,[53] the reaction of $NO_2^-$ to $N_2O$ can be constructed as a catalytic cycle by combining eqs. 1–4; the overall reaction is represented by eq 6.[54] The reaction of 300 μmol of $NaNO_2$ with 300 μmol of HCOOH in the presence of 30 μmol of $MoO_2(S_2CNEt_2)_2$ at 50 °C for 24 h produced 89 μmol of $N_2O$ and 197 μmol of $CO_2$ (entry 1 in Table II). The amounts of $N_2O$ and $CO_2$ produced are almost unchanged upon increasing the amount of either HCOOH or $NaNO_2$ (entry 2 or 3) but increase if both reactants are increased (entry 4). It should be noted that the amounts of $N_2O$ and $CO_2$ produced were essentially independent of the amount of $MoO_2(S_2CNEt_2)_2$ used (entry 1, 5, 6, and 7). There are found, however, good linear relations between the initial rates of formation of $N_2O$ and $CO_2$ and the concentration of $MoO_2(S_2CNEt_2)_2$ as depicted in Figure 4, which

$$2HCOOH + 2NO_2^- + 2H^+ \rightarrow 2CO_2 + N_2O + 3H_2O \quad (6)$$

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(53) Neither $CO_2$ nor $N_2O$ was evolved in the reaction of $NaNO_2$ (300 μmol) with HCOOH (300 μmol) in DMF (10 $cm^3$) at 30 °C for 24 h.

(54) Protons arising from $H_2O$ as well as HCOOH also participate in the reaction of eq 6 since $N_2O_2^{2-}$ decomposes to $N_2O$ even in the absence of HCOOH (eq 3).

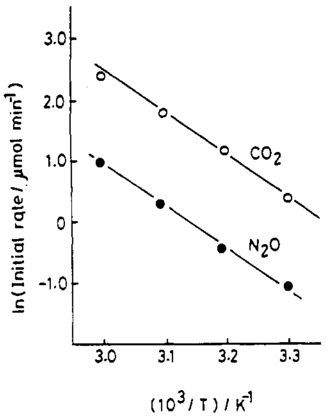
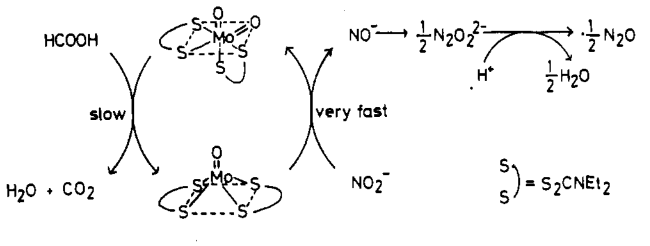


**Figure 5.** Arrhenius plots for the initial rates of formation of $CO_2$ and $N_2O$ in the reaction of $NaNO_2$ (300 μmol) with HCOOH (300 μmol) in the presence of $MoO_2(S_2CNEt_2)_2$ (30 mmol) in DMF (10 $cm^3$).

**Scheme I**



clearly indicates that the catalytic reduction (eq 6) is first-order with respect to the concentration of $MoO_2(S_2CNEt_2)_2$, while the evolution of $N_2O$ may be expected to obey second-order kinetics with respects to the concentration of $MoO_2(S_2CNEt_2)_2$ from the consideration of eq 1–3. Thus, the reactions responsible for the evolution of $N_2O$ (eq 1–3) may not be involved in the rate-determining step in the catalytic cycle.

The differences between $MoO(S_2CNEt_2)_2$ and $MoO_2(S_2CNEt_2)_2$ as catalysts toward the reduction of $NO_2^-$ were examined at various temperatures. The results are collected in Table III, which reveals that there is essentially no difference in the amount of $N_2O$ formed between those two catalysts at each temperature. On the other hand, the amount of $CO_2$ evolved when $MoO(S_2CNEt_2)_2$ was used as a catalyst is appreciably smaller than that evolved when $MoO_2(S_2CNEt_2)_2$ was used. This may be due to the additional evolution of $CO_2$ in the first catalytic cycle by $MoO_2(S_2CNEt_2)_2$ (eq 4). Thus, the actual catalyst for the reduction of $NO_2^-$ would be $MoO(S_2CNEt_2)_2$. The plots of the initial rates of formation of $N_2O$ and $CO_2$ vs. the reciprocal reaction temperatures give two straight lines with the same slope as shown in Figure 5, which suggests that the rate-determining step in the reduction of $MoO_2(S_2CNEt_2)_2$ by HCOOH. This is consistent with the fact that the activation energy (54.8 kJ $mol^{-1}$) obtained from the slope of the two straight lines in Figure 5 is almost the same value of 57.8 kJ $mol^{-1}$ determined from the initial rates of the reduction of $MoO_2(S_2CNEt_2)_2$ by HCOOH (eq 4) at various temperatures.

The most plausible mechanism for the present denitrification of $NO_2^-$ is shown in Scheme I. The initial process is the slow reduction of $MoO_2(S_2CNEt_2)_2$ by HCOOH affording $MoO(S_2CNEt_2)_2$ and $CO_2$, the former of which then is oxidized rapidly by $NO_2^-$ to give an unstable intermediate $NO^-$ with the regeneration of $MoO_2(S_2CNEt_2)_2$. The resulting $NO^-$ spontaneously dimerizes to form $N_2O_2^{2-}$,[39] which reacts with protons to afford $N_2O$ and $H_2O$. It is worthwhile to note that the rate of the reduction of $MoO_2(S_2CNEt_2)_2$ by HCOOH is much slower than that of the oxidation of $MoO(S_2CNEt_2)_2$ by $NO_2^-$, resulting in the extreme lowering of the $MoO(S_2CNEt_2)_2$ concentration in the reaction mixture. Thus, the formation of $Mo_2O_3(S_2CNEt_2)_4$ with a deep violet color (eq 5) was effectively depressed, and a yellow solution due to $MoO_2(S_2CNEt_2)_2$ was maintained throughout the catalytic cycle. Dissimilatory nitrite reductases are known to reduce $NO_2^-$ with evolution of $N_2O$ and $N_2$, the former of which is believed to be a precursor of the latter. No evolution of $N_2$ has, however, been detected in the present study. This is consistent with the fact that no oxygen-transfer reaction occurs between $MoO(S_2CNEt_2)_2$ and $N_2O$.[45]

**Registry No.** $MoO(S_2CNEt_2)_2$, 25395-92-0; $MoO_2(S_2CNEt_2)_2$, 18078-69-8; $NO_2^-$, 14797-65-0; $HCO_2H$, 64-18-6; $N_2O$, 10024-97-2; nitrite reductase, 9080-03-9.