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Reduction of Molecular Nitrogen in Molybdenum(III–V) Hydroxide/Titanium(III) Hydroxide Systems[1]

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The stoichiometric reduction of N_2 to N_2H_4 by coprecipitated molybdenum(III–V) hydroxide/titanium(III) hydroxide at room temperature in 95% aqueous CH_3OH proceeds at Mo(IV) active sites, optimally at Mo/Ti ratios of 0.1–0.2. Contrary to previous claims which suggested that N_2 is reduced directly to NH_3 or N_2H_4, the reduction is shown to proceed sequentially. The experimental evidence is consistent with the formation of diazene, N_2H_2, as the initial product. Its subsequent reactions depend on the stationary concentrations at which it is generated. At high concentration, N_2H_2 disproportionates into N_2H_4 and N_2; at low concentrations decomposition into N_2 and H_2 occurs instead, giving rise to a N_2-stimulated evolution of H_2. The reduction of C_2H_4 to C_2H_6 also proceeds at Mo(IV) sites. In addition to acting as a diluting matrix, a specific activating role of $Ti(OH)_3$ on molybdenum(IV) hydroxide is proposed.

Mononuclear oxomolybdenum(IV) species (Mo^{red}) were originally postulated to be the active reduced forms of the catalysts for the reduction of nitrogenase substrates in the "molybdothiol" model systems of nitrogenase[3] and were subsequently shown[4–6] to behave as 2-electron reductants with respect to substrates such as C_2H_2 or N_2. Similiar studies with Mo(III) derivatives, on the other hand, revealed them to be comparatively unreactive. A reduction of C_2H_2 by Mo(III), for example, was in fact only observed after the spontaneous decomposition of Mo(III) into Mo(IV) and H_2 had occurred.[6]

These observations led us to follow with interest the work of Shilov and his co-workers, who reported[7–10] that coprecipitated methanolic suspensions of $Ti(OH)_3$ with $Mo(OH)_3$ reduce molecular N_2 stoichiometrically to N_2H_4 and NH_3 at room temperature and catalytically at 100–140 °C. Nitrogen fixation occurs while $Ti(OH)_3$ undergoes spontaneous decomposition with H_2 evolution and is not directly associated with the Mo-dependent reduction of N_2. Active N_2-reducing systems are also obtained by coprecipitating the molybdenum hydroxide/titanium hydroxide with $Mg(OH)_2$. This has the effect of reducing the rate of $Ti(OH)_3$ decomposition and renders these systems catalytic (with respect to Mo) at elevated reaction temperatures. Under these conditions, $Ti(OH)_3$ acts as the reducing agent and converts oxidized molybdenum sites back into the active reduced forms. Highest catalytic efficiency is observed if a large excess of $Ti(OH)_3$ over $Mo(OH)_3$ is maintained.

The mechanism of N_2 reduction in this remarkable, if intractable, heterogeneous and amorphous system has remained obscure. In weakly alkaline media, the Russian workers believe[9,10] the reduction of N_2 to proceed at binuclear Mo(III) sites in one step to NH_3, as little N_2H_4 is formed. In strongly alkaline suspensions, where more N_2H_4 is formed, the reduction of N_2 to NH_3 is assumed to take place in two steps (via N_2H_4).[10]

Since our work indicated that Mo(IV) rather than Mo(III) species are reactive in other protic N_2-reducing systems,[3–6] we considered it to be unlikely that $Mo(OH)_3$ was the reactive form of molybdenum in the present system. Accordingly, we first decided to reinvestigate the reduction of the Mo(V) stock solutions and then to correlate the N_2-reducing activity of the hydroxide gels with the oxidation states of molybdenum. Denisov et al.[7–9] routinely reduced stock solutions of $MoCl_5$ or $MoOCl_3$ in 95% aqueous methanol with Zn amalgam *in the presence* of $TiCl_3$. Since it is not possible under these conditions to establish whether the reduction of Mo(V) actually produced Mo(III), we instead reduced methanolic solutions of $MoCl_5$ separately before adding $TiCl_3$. To slow down the reduction we also replaced the Zn amalgam by pelletized zinc. Now able to follow the reduction of Mo(V) spectrophotometrically and oxidimetrically, we could perform N_2-fixation experiments with molybdenum species in definite formal oxidation states, ranging from V to III. This led us to observe that Mo(IV)- rather than Mo(III)-containing hydroxide gels exhibit the highest N_2-reducing activity. The N_2-fixation experiments were also conducted over the entire composition range of the binary molybdenum(IV) hydroxide/titanium(III) hydroxide system. Apart from determination of the yields of N_2H_4 and NH_3, the H_2 evolution during N_2 reduction was also monitored; studies with other protic N_2-reducing systems have shown[1,6,11] that the appearance of an "anomalous", i.e. N_2-stimulated, evolution of H_2 during the reaction is indicative of the intermediate formation and decomposition of N_2H_2. Finally, the reduction of C_2H_4 was also investigated. This substrate was used as a molecular probe for 2-electron-reducing sites in the hydroxide gels. Acetylene was also tested but was found to be unsuitable for the intended purpose as it is rapidly reduced to C_2H_4 by $Ti(OH)_3$ in the absence of molybdenum, in accord with earlier observations of Denisov et al.[7]

Results

Zinc Reduction of Molybdenum(V) Chloride Solutions in Methanol. On dissolution of molybdenum(V) chloride in CH_3OH, extensive solvolysis occurs with formation of chlorooxomolybdenum(V) species together with substantial amounts of Mo(IV) species generated through secondary reduction or disproportionation reactions.[12] Upon the addition of Zn, chloro complexes of oxomolybdenum(IV) and ultimately of Mo(III) are generated. Following the reduction by optical absorption spectroscopy, we noted a band at 296 nm ($\epsilon = 1.25 \times 10^3$) to be characteristic of Mo(IV) species in solution. This band is weak at $t = 0$ min and reaches its maximum intensity after about 7 min of reduction (Figure 1), at which point the reduction of Mo(V) to Mo(IV) is complete, as evidenced by

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Table I. Yields of NH_3, N_2H_4, and H_2 from N_2 under Various Conditions at 21 °C

A. Dependence on Mo Oxidation State

expt no.	% compn[a] of Mo stock soln			yield, μmol		
	Mo(V)	Mo(IV)	Mo(III)	NH_3	N_2H_4	H_2
1	54.5	45.5[b]	0	2.03	0.02	66.0
2	0	100[c]	0	7.50	2.30	77.5
3	0	71.1	28.9	2.15	2.15	62.5
4	0	0	100	1.14	1.14	7.9

B. Dependence on Mo/Ti Ratios

expt no.	Mo/Ti	yield, μmol		
		NH_3	N_2H_4	H_2
5	0	0	0.05	0
6	0.053	3.05	1.35	111
7	0.11	5.30	2.25	50.4
8	0.25	6.25	1.73	8.8
9	0.43	3.44	1.75	1.8
10	1.0	0.16	0.07	1.3
11	3.0	0	0	0

C. Dependence on N_2 Pressure

expt no.	P_{N_2}, atm	yield, μmol		
		NH_3	N_2H_4	H_2
12	145	5.85	2.36	69.0
13	95	3.63	1.94	34.8
14	14.6	0.95	0.81	4.3
15	4.4	0.80	0.53	1.8
16	1.3	0.23	0.13	1.3

D. Dependence on Reaction Solution Volume

expt no.	soln vol/ 50 μmol of Mo(IV)	yield, μmol		
		NH_3	N_2H_4	H_2
17	20	3.92	2.00	42.5
18	66	1.07	3.10	54.7
19	200	0.36	2.40	68
20	400	0	1.44	108

E. Dependence on KOH Concentration

expt no.	KOH concn, M	yield, μmol		
		NH_3	N_2H_4	H_2
21	0.1	3.13	0.08	12.1
22	0.5	3.63	1.94	34.4
23	2.0	2.73	3.24	45.8
24	0.1[d]	2.40	0.47	16.0

[a] Experimental conditions: solution volume, 20 mL; reaction time, 30 min; KOH concentration, 0.5 M, except where indicated. N_2 pressures: experiments 1–4, 156 atm; experiments 5–11, 120 atm; experiments 17–20, 113 atm; experiments 21–24, 95 atm, or as indicated. Total amount of Mo and Ti = 550 μmol. Mo/Ti ratios: experiments 1–4 and 12–20, 0.11; experiments 21–24, 0.18, or as indicated. Composition of Mo stock solution as determined by optical absorption spectroscopy and oxidimetric titrations of stock solutions prior to addition of $TiCl_3$: experiments 1–4, as indicated; in all other experiments, 100% Mo(IV). [b] Composition of "Mo(V)" stock solution prior to reduction with zinc. [c] After 7 min of reduction with zinc. [d] Experiment run as no. 21 except at 1/3 of total Mo,Ti concentration; yields expressed per 50 μmol of Mo(IV).

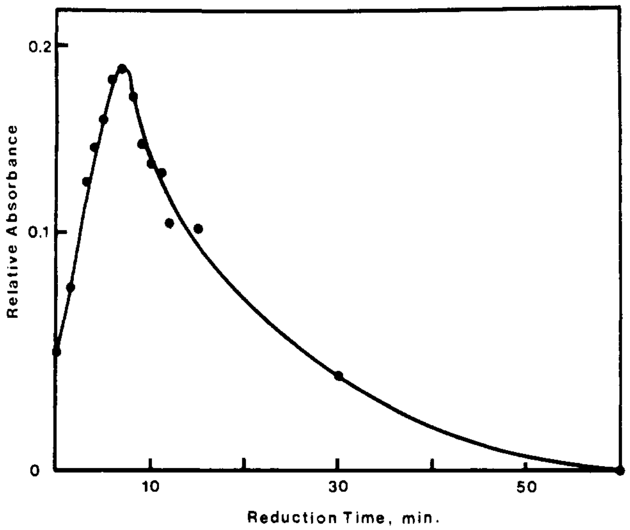

Figure 1. Relative absorbance values at 296 nm in methanol as a function of reduction time with Zn (see Experimental Section for further details).

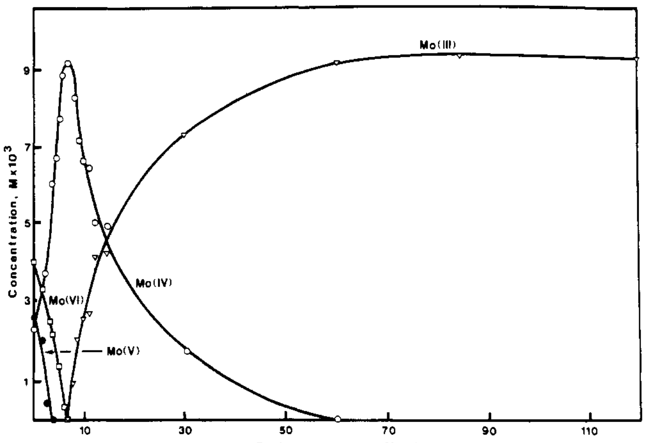

Figure 2. Kinetic reduction curves of $MoCl_5$ stock solutions in methanol. A 0.046 M $MoCl_5$ solution (10 mL) was reduced with 1 g of pelletized zinc at 21 °C. Aliquots were withdrawn at various time points for absorption spectroscopy and oxidimetric titrations.

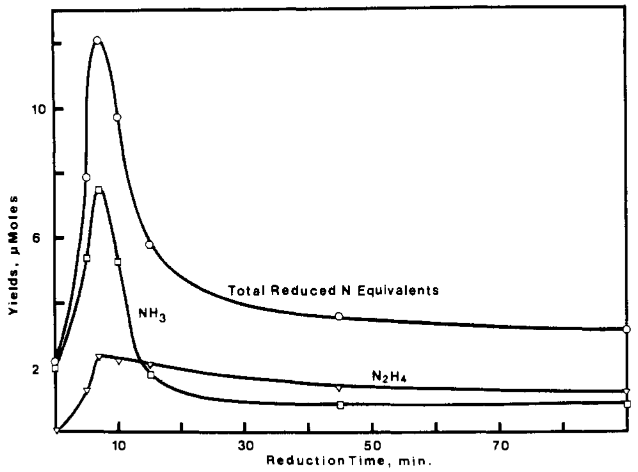

Figure 3. Yields of reduced nitrogen products as a function of $MoCl_5$ stock solution reduction time. Nitrogen-fixation experiments at P_{N_2} = 156 atm, 21 °C and 30-min reaction time. For other experimental details, see Table I, experiments 1–4.

oxidimetry with $KMnO_4$. As reduction is continued to the Mo(III) state, the band declines and eventually disappears (Figure 1). When the results of the oxidimetric determinations and the optical absorption measurements are combined, kinetic curves of the disappearance of Mo(VI), Mo(V), and Mo(IV) and of the appearance of Mo(III) during the reduction can be constructured and are shown in Figure 2.

Reduction of Nitrogen by Molybdenum(III–V) Hydroxide/Titanium(III) Hydroxide. Figure 3 and Table I show that the highest combined yields of NH_3 and N_2H_4 are obtained from molybdenum hydroxide/titanium hydroxide generated from Mo(IV) stock solutions. Although some N_2-reducing activity is observed with molybdenum hydroxide/titanium hydroxide gels prepared from "Mo(V)" stock solutions, this is due to the

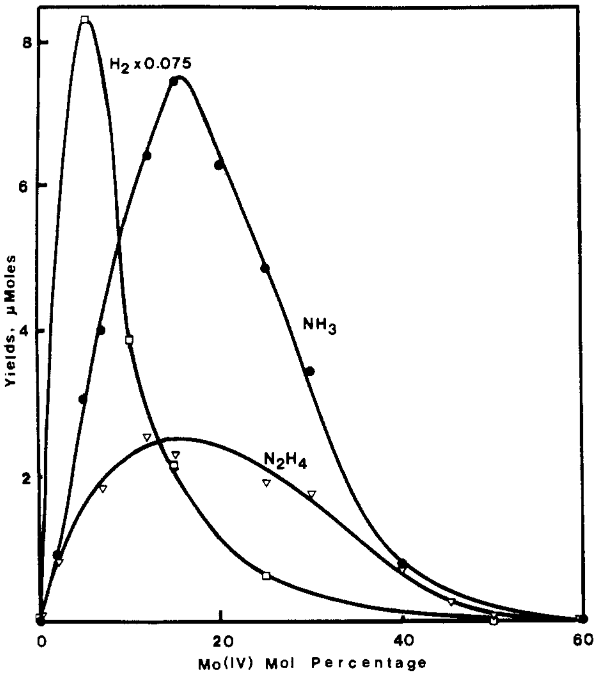

Figure 4. Yields of reduced nitrogen products as a function of molybdenum(IV) hydroxide/titanium(III) hydroxide gel composition. Conditions are as given in experiments 5–11, Table I.

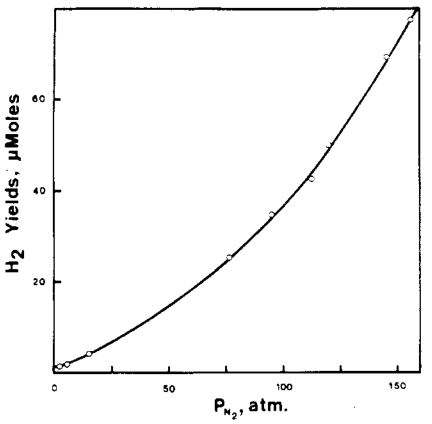

Figure 5. Nitrogen stimulation of H_2 evolution. The hydroxide gel (Ti + Mo = 550 μmol, Mo/Ti = 0.11) was suspended in 20 mL of KOH of initial concentration of 0.5 M, in 95% aqueous CH_3OH. Hydrogen yield measurements were performed after 30 min of reaction.

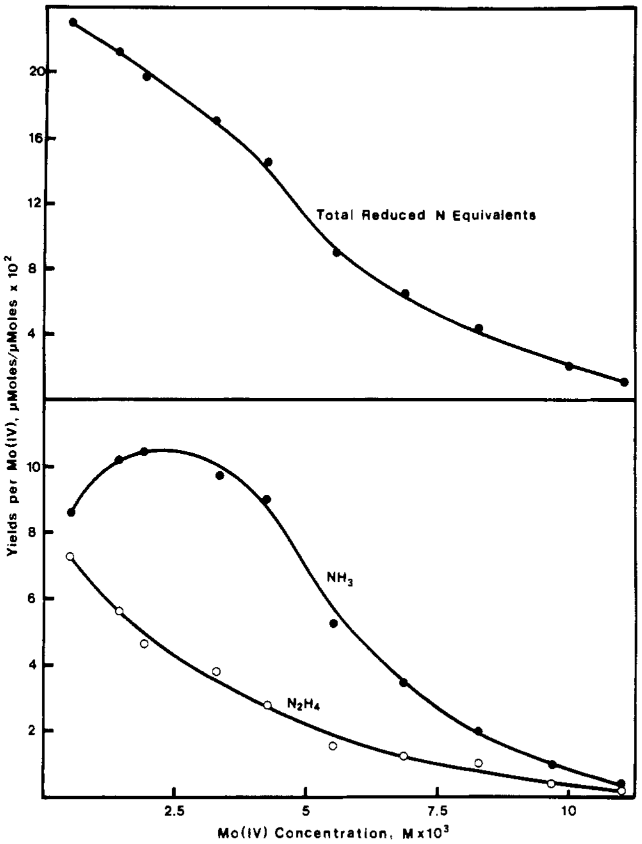

Figure 6. Yields of reduced nitrogen products per mole of Mo(IV) as a function of increasing Mo(IV) concentration in the gels. Reaction conditions are as in experiments 5–11, Table I.

presence of Mo(IV), formed on storage of the stock solutions by secondary reduction or disproportionation reactions (see Figure 2). The apparent slight N_2-reducing activity of Mo(OH)$_3$/Ti(OH)$_3$ gels is similarly attributed to the presence of some Mo(IV), whose formation is possible either by decomposition or disproportionation of molybdenum(III) hydroxide during the precipitation process. In Figure 4, the yields of N_2H_4, NH_3, and H_2 are shown as a function of the Mo/Ti ratios under specified conditions. Maximum yields of both N_2H_4 and of NH_3 were observed at the Mo/Ti ratio of about 0.15. Measurements of the amounts of H_2 produced at different Mo/Ti ratios reveal that N_2-stimulated hydrogen evolution reaches a maximum at the Mo/Ti ratio of about 0.05. This H_2 evolution increases with increasing N_2 pressure (Figure 5). In Figure 6, the dependence of the yields of N_2H_4 and of NH_3 per Mo(IV) is given as a function of the total molybdenum concentration. Table I also shows the dependence of the yields of NH_3, N_2H_4, and H_2 on total reaction solution volume. Neither the individual molybdenum(III), molybdenum(IV), or molybdenum(V) hydroxides nor Ti(OH)$_3$ exhibits substantial N_2-reducing activity at N_2 pressures of 100 atm and reaction temperatures of up to 140 °C. It should be noted, however, that molybdenum(IV) and molybdenum(III) hydroxides reduce N_2H_4 rapidly; with titanium(III) or molybdenum(V) hydroxides, the reduction of N_2H_4 proceeds only very slowly and only at less than 5% of the rate observed with molybdenum(IV) hydroxide.[13]

Reduction of Ethylene. Although C_2H_4 reacts to some extent with Ti(OH)$_3$ itself, it is reduced with highest efficiency at almost the same Mo/Ti ratio as N_2 (Figure 7). At the optimal Mo/Ti ratios, close to 1 mol of C_2H_6/mol of Mo(IV) is formed; in addition to C_2H_6, traces (less than 1%) of CH_4 are also produced, reaching a maximum at Mo/Ti ratios of 0.15–0.2. The H_2 evolution from the molybdenum(IV) hydroxide/titanium(III) hydroxide gels is suppressed by C_2H_4 up to the Mo/Ti ratios of about 0.2. There are no apparent inhibitory effects of C_2H_4 on H_2 production from Ti(OH)$_3$ (see Figure 7).

Discussion

Oxidation State of Molybdenum. Figure 4 strikingly demonstrates that the reactivity of the molybdenum hydroxide/titanium hydroxide gels depends on the duration of the reduction of the Mo(V) stock solutions with Zn: A sharp-yield maximum is observed after 7 min of reduction, which coincides with the reduction of Mo(V) to Mo(IV) (see Figure 2). The apparent slight reactivities at zero reduction time are due to the presence of Mo(IV) in the parent "Mo(V)" stock solutions. The low N_2-fixing activity after long reduction times suggests that some Mo(IV) is produced during the preparation of the molybdenum hydroxide/titanium hydroxide gels.

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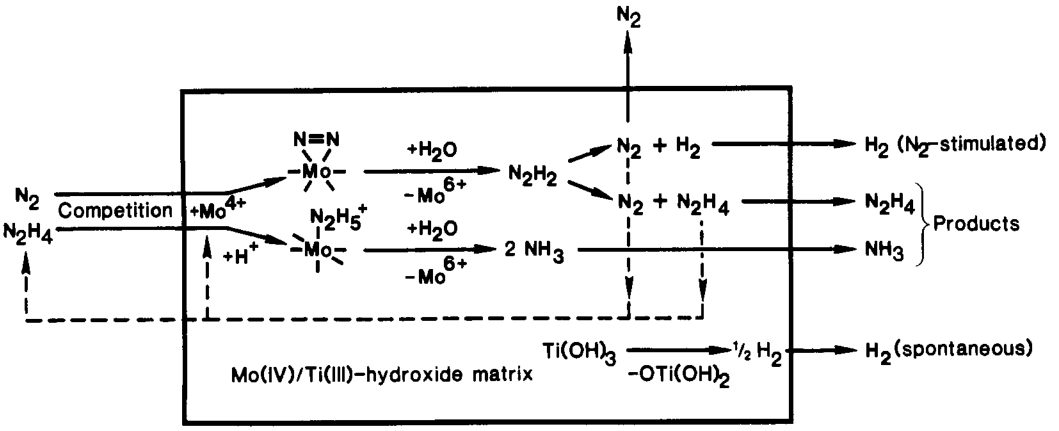
(13) Relative rates of N_2H_4 reduction by molybdenum(III), molybdenum(IV), molybdenum(V), and titanium(III) hydroxides at 21 °C: 100/70/3/2. Metal hydroxides, 50 μmol each, were precipitated in 20 mL of 0.5 M KOH in 95% aqueous methanol (reduction time 30 min, initial N_2H_4 concentration, 10 μmol).

Scheme I. Reactions of N_2 in the Molybdenum(IV) Hydroxide/Titanium(III) Hydroxide System



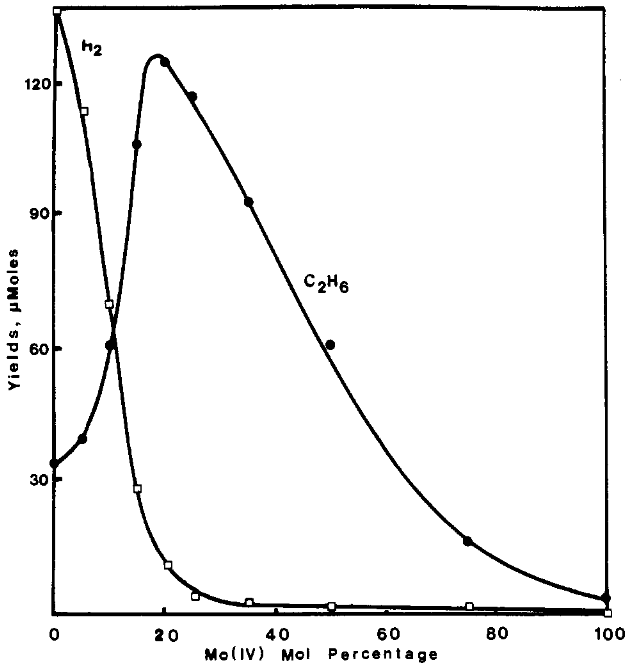


Figure 7. Yields of C_2H_6 and H_2 from reductions of C_2H_4 at 1 atm, as a function of molybdenum(IV) hydroxide/titanium(III) hydroxide gel composition (yield measurements after 16 h of reaction at 21 °C; Ti + Mo = 550 µmol; suspended in 20 mL of 95% aqueous CH_3OH; initial concentration of KOH, 0.5 M).

Mechanism of Nitrogen Reduction. The "diazene mechanism" of N_2 reduction was first formulated in 1974[14] on the basis of studies with molybdothiol systems. This mechanism has since been further substantitated and was shown to operate in other protic N_2-reducing systems.[3,15,18] The results of the present work are consistent with the diazene mechanism of Scheme I and rule out any direct 6- or 4-electron-reduction schemes.

The reduction of N_2 to N_2H_2 occurs at Mo(IV) centers. The subsequent reactions of N_2H_2 are dependent on the stationary concentrations at which it is formed. At low Mo/Ti ratios, N_2H_2 is formed at low concentrations and decomposes predominantly into N_2 and H_2. Accordingly, the N_2-stimulated evolution of H_2 reaches a maximum and little N_2H_4 or NH_3 is formed. At intermediate Mo concentrations in the gels, more N_2H_2 is generated and its disproportionation into N_2H_4 and N_2 is favored, although the concurrent decomposition of N_2H_2 is never fully eliminated.

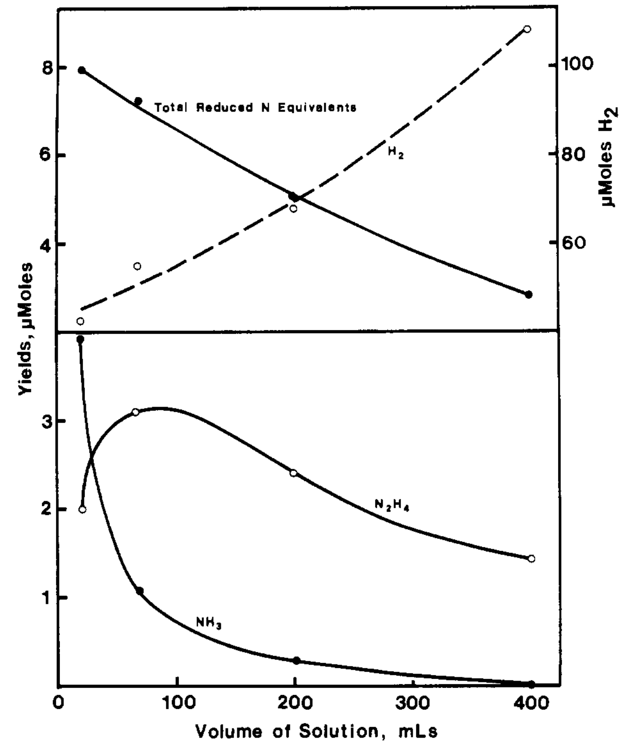


Figure 8. Yields of reduced nitrogen products as a function of the reaction solution volume per 50 µmol of Mo. Reaction conditions are as given in experiments 17–20, Table I.

Effect of Reaction Solution Volume/Hydroxide Gel Ratio. The disproportionation of N_2H_2 undoubtedly occurs to a large extent within the hydroxide gel where it is initially formed and present at the highest local concentrations. However, some N_2H_2 apparently also diffuses into the homogeneous phase where it becomes subject to base-catalyzed decomposition into N_2 and H_2. Product N_2H_4 also diffuses out of the gel before it is reduced to NH_3. This explains why the yields of N_2H_4, NH_3, and H_2 are dependent on the solution volume/gel ratio. Figure 8 shows that the total yields of reduced nitrogen products decline continuously with increasing solution volume/gel ratio; this is equivalent to an increase of the reaction solution volume.

On the other hand, there is an initial increase of the yields of N_2H_4, while NH_3 actually declines. This is because N_2H_4 competes with N_2 for Mo(IV) reducing sites. If the reaction solution volume is large, the reduction of N_2 is favored over

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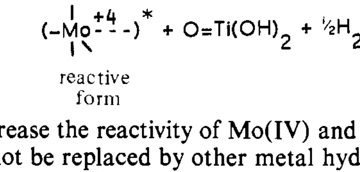
that of N_2H_4. Hence, more N_2H_4 is formed and remains in the reaction solution. However, at very large solution volumes, N_2H_2 diffusion into the homogeneous phase becomes important and results in an increased H_2 evolution due to N_2H_2 decomposition and a decline of the yields of both N_2H_4 and NH_3 (Figure 8). The dilution effect is more noticeable under strongly alkaline reaction conditions. In weakly alkaline suspensions, NH_3 is the main product and only traces of N_2H_4 are formed. This led Denisov et al. to suggest[10] that N_2 is reduced directly to NH_3. However, in weakly alkaline media, N_2H_4 is more firmly absorbed by the acidic metal hydroxides; it is also more readily protonated and thus is reduced to NH_3 more efficiently. Increasing the reaction solution volume nevertheless produces an increase of the yields of N_2H_4. Table I shows that a threefold increase of the reaction solution volume causes a sixfold increase of the yields of N_2H_4 and an equivalent decline of the yields of NH_3. This is consistent only with a stepwise mechanism of N_2 reduction.

Reduction of Ethylene. As for N_2, an initial side-on interaction of C_2H_4 with Mo(IV) is proposed, affording an organomolybdenum(VI) intermediate from which C_2H_6 is released on subsequent Mo–C bond protolysis. In addition, another (possibly carbenoid) organomolybdenum intermediate is apparently formed with cleavage of the ethylenic C═C bond, as evidenced by the formation of traces of CH_4. Since C_2H_4 and N_2 are reduced with maximum efficiency at almost the same Mo/Ti ratios (see Figures 4 and 7), it may be concluded that the reactions occur at the same 2-electron-reducing sites.

Constitution of the Mo(IV) Active Sites and the Role of Titanium(III) Hydroxide. Figure 6 shows that the combined yields of reduced nitrogen products as well as those of N_2H_4, expressed per mol of Mo, *decrease* with increasing Mo/Ti ratios. This is consistent with reactions occurring at mononuclear rather than binuclear Mo(IV) sites. Ammonia yields per mole of Mo initially increase with increasing Mo concentrations. This is due to the sequential nature of N_2 reduction: At very low Mo concentrations, virtually all Mo(IV) sites react with N_2, thus preventing the subsequent reduction of N_2H_4 to NH_3. In homogeneous, Mo-based nitrogen-fixing systems, catalytic activity is similarly associated with mononuclear Mo(IV) species.[3-6] On coprecipitation of molybdenum(IV) hydroxide with $Ti(OH)_3$, amorphous mixed polymers are formed in which the Mo(IV) is likely to be mononuclear as long as $Ti(OH)_3$ is held in considerable excess. Assuming octahedral coordination geometry, a sixfold molar excess of Ti over Mo is hypothetically required to prevent the formation of associated molybdenum species. This would correspond to the Mo/Ti ratio of 0.17, which comes close to the gel composition of maximum reactivity. It appears, however, that $Ti(OH)_3$ is required for functions other than keeping Mo(IV) monomeric. It may also be expected to protect N_2H_2 against base-catalyzed decomposition, just as is known for $Mg(OH)_2$ or $ZrO_2{\cdot}H_2O$ in the corresponding V(II) systems.[15,18] It is finally possible that $Ti(OH)_3$ has a secondary activating effect on Mo(IV). It can be envisaged that the decomposition of $Ti(OH)_3$ to $Ti(O)(OH)_2$ and H_2 generate a coordinative vacancy on Mo(IV), as is schematically represented in eq 1.



$$-\overset{+4}{Mo}\leftarrow \overset{H}{O}-\overset{OH}{Ti}-OH \longrightarrow (-\overset{+4}{Mo}---)^{*} + O{=}Ti(OH)_2 + \tfrac{1}{2}H_2 \quad (1)$$

This could increase the reactivity of Mo(IV) and explain why $Ti(OH)_3$ cannot be replaced by other metal hydroxides; one exception is $Cr(OH)_2$,[16] which also decomposes with H_2 evolution and thus could have similar activating effects. At elevated temperatures, $Ti(OH)_3$ participates directly in the reaction by reducing oxidized molybdenum sites back to the active reduced form. Due to the concurrent decomposition of $Ti(OH)_3$, the catalytic efficiency is low and noticeable only if $Ti(OH)_3$ is held in large excess over Mo.[7] Moreover, because of the irreversibility of $Ti(OH)_3$ decomposition, the reaction cannot be conducted continuously. Although the decomposition of $Ti(OH)_3$ may be slowed down by coprecipitation with $Mg(OH)_2$,[10] it cannot replace $Ti(OH)_3$, again suggesting that $Ti(OH)_3$ exerts specific activating effects on molybdenum(IV) hydroxide.

Experimental Section

Reagents and Chemicals. All reagents and chemicals were of analytical grade purity and were used without further purification. The Mo(IV) solutions were prepared from methanolic solutions of $MoCl_5$ by reduction with Zn pellets. Typically, 10 mL of a methanolic solution containing 50 μmol of $MoCl_5$ was reduced with 1 g of zinc for 7 min. The solution was withdrawn by means of syringe and stored under argon. The Ti(III) solutions were 0.5 M and prepared by dissolving crystalline $TiCl_3$ in argon-flushed CH_3OH and stored under argon.

Assays and Product Identification. Hydrogen was determined by GLC at 21 °C, using a column of 6-ft length filled with 5A molecular sieves, with thermal conductivity detection and Ar as the carrier gas. Hydrazine was determined spectrophotometrically according to Watt and Chrisp[17] as modified by us.[18] Ammonia was assayed according to the method of Kruse and Mellon.[19] Hydrocarbons were analyzed by GLC with a Varian 1200 aerograph instrument, with He as the carrier gas and a 6-ft Porapack phenyl isocyanate–Porasil, 80–100-mesh column, with flame-ionization detection. For quantitative determinations, propane was used as the internal standard; corrections for solubility of the hydrocarbons in the liquid phase were applied.

Standard Nitrogen-Reduction Technique. Experiments using N_2 pressures *above 4 atm* used a high-pressure stainless-steel autoclave with a glass insert. Its total capacity was 31 mL, solution volumes of 20 mL were typically used. The glass insert had two compartments into which the base and the mixed solutions of Mo(IV) and Ti(III) were placed separately. At $t = 0$ s, the reaction solutions were thoroughly mixed by inverting the apparatus and shaking for 15 s. Slow mechanical shaking was continued usually for 30 min, after which the reactions were terminated. Prior to the analysis of the autoclave reaction solutions, the total amount of gas in the vessel was determined first by collecting the gas over water in a gasometer. The hydrogen content in the gas was subsequently determined by GLC in gas samples withdrawn from the gasometer.

In typical experiments, 1 mL each of the 0.5 M Ti(III) and the 0.05 M Mo(IV) methanolic stock solutions were dissolved in mixture of 14.5 mL of CH_3OH and 1 mL of H_2O. This mixture was injected into one compartment of the autoclave glass insert. Into the other, 2.5 mL of 4 M methanolic KOH was added. The autoclave was assembled and flushed twice with N_2 to remove traces of oxygen. The pressure was brought up to the desired level, and the reaction was initiated as indicated above.

Experiments at N_2 pressures *below 4 atm* were run in glass bottles of 38-mL capacity. These were first rubber serum capped and flushed with N_2 (or Ar) for 15 min. The bottles were then injected with 14.5 mL of methanol, 1 mL of H_2O, and 1 mL each of Mo(IV) solution and Ti(III) solution. For experiments run at 1 atm, the N_2 pressure in the bottles was equilibrated with the outside atmospheric pressure. In experiments run at N_2 pressures up to 4 atm, more N_2 was injected into the bottles, as required. At $t = 0$ s, 2.5 mL of 4 M methanolic KOH was injected. During the addition of KOH, the bottles were consistently shaken for 15 s to ensure complete mixing. For hydrogen determinations, gas samples were taken at stated time points.

For N_2H_4 and NH_3 analysis, the reaction suspensions were acidified with 10 mL of 6 M HCl and vacuum distilled until all methanol was removed. The solution at this point was used for N_2H_4 analysis. For NH_3 determinations, the solutions were made alkaline by adding 10 mL of 12 M NaOH and Kjeldahl distilled into pH 3.7 acetic acid buffer. Ammonia was determined in this solution as described in ref 17 and 18.

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Standard Ethylene-Reduction Technique. Experimental conditions were identical with that described for N_2 reduction except that ethylene-filled glass bottles of 160-mL capacity were employed. For analysis of hydrocarbons by GLC, gas samples were withdrawn at stated time points.

Reduction of MoCl$_5$ Solutions. The freshly prepared, 0.05 M $MoCl_5$ solutions in methanol were reduced with Zn pellets as outlined above. At various time points, aliquots of the reaction solution were withdrawn and placed into argon-filled, serum-capped test tubes for storage. These solutions were diluted with deaerated CH_3OH to 1.5×10^{-4} M. UV spectra were recorded with a Beckman DB-C UV grating spectrophotometer using quartz cells of 1-cm path length. The cells were serum capped and flushed with Ar prior to the injection of the solutions. The reduction of the Mo(V) solutions was also followed by oxidimetric titrations of aliquots withdrawn at various time points. The $KMnO_4$ solution was prepared and standardized by the method of Elwell and Wood;[20] the titrations were performed under argon.

Registry No. $Ti(OH)_3$, 12026-77-6; $Mo(OH)_3$, 60414-57-5; C_2H_4, 74-85-1; N_2, 7727-37-9; Mo, 7439-98-7.

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Oxidation of Cysteine, Cysteine Methyl Ester, and Penicillamine by Copper(II)-2,9-Dimethyl-1,10-phenanthroline Complexes

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A stopped-flow kinetic study of the oxidations of excess cysteine, cysteine methyl ester, and penicillamine by copper(II)-2,9-dimethyl-1,10-phenanthroline (dmp) complexes is reported (25 °C, $I = 0.2$ M, pH 4-7). These reactions were found to be first order with respect to Cu(II), in contrast to the second-order behavior typical of weaker Cu(II) oxidants. Rate variations with mercaptan (RSH) and dmp concentration are consistent with two parallel pathways in which oxidation of coordinated sulfur occurs within 1:1 mercaptan complexes of $Cu(dmp)_2^{2+}$ (rate constant k_0) and $Cu(dmp)^{2+}$ (rate constant k_1). Redox decay of the Cu(II)-S bond proceeds with rate constants of 4.8×10, 3.0×10, 8.3×10 s^{-1} (k_1) and 4×10, 5, 2.4×10^2 s^{-1} (k_0) for cysteine, penicillamine, and cysteine methyl ester, respectively, at pH 6.0. The pH dependence of kinetic precursor complex formation constants showed that both coordinated RS^- and RSH are oxidized in the k_1 pathway, while RSH is the predominant reductant of $Cu(dmp)_2^{2+}$. Formation constants pertaining to the reactions of RS^- (K_{c1}) and RSH (K_{c0}) with $Cu(dmp)^{2+}$ show little effect of β,β-dimethyl substituents or esterification of the amino acid carboxylate group on thermodynamic stability; for cysteine, $K_{c0} = 2 \times 10^4$ M^{-1} and $K_{c1} = 1.2 \times 10^7$ M^{-1}.

Introduction

The electronic and geometric structures of compounds containing a mercaptide sulfur-copper(II) bond are of considerable interest,[1] as this unit occurs in all blue copper proteins.[2] Comparatively little is known about the kinetic and thermodynamic stabilities of RS^--Cu(II) complexes in solution, as internal electron transfer generally is facile. We recently described a remarkably stable S-bonded adduct of cysteine (cys-SH) with the (tris(2-pyridylmethyl)amine)copper(II) ion ($Cu(tmpa)^{2+}$) in aqueous solution and reported both equilibrium and kinetic measurements on its formation and redox decay to give $Cu(tmpa)^+$ and the disulfide cystine.[3] This study of the $[(tmpa)Cu\text{-}S\text{-}cys]^+$ system suggested several contributions to the kinetic stability of the Cu(II)-S bond, including steric crowding about the coordinated sulfur atom, chelation (S,O or S,N) of copper by the mercaptan, and small redox thermodynamic driving force.

Reduction of copper(II) by mercaptans typically is second order with respect to inner-sphere S-bonded intermediates,[4,5] as S-S bond formation and electron transfer may be concerted within a binuclear Cu(II) activated complex.[4] A unimolecular RS^--Cu(II) redox decay pathway may be anticipated, however, in complexes where the oxidizing strength of Cu(II) is substantially enhanced relative to that of $Cu^{2+}(aq)$ ($E° = +153$ mV),[6] permitting the formation of thiyl radicals. We report here kinetic studies of the oxidation of cysteine, cysteine methyl ester, and penicillamine by copper(II)-2,9-dimethyl-1,10-phenanthroline (dmp) complexes. Steric repulsions between the 2,9-dimethyl substituents and the π-accepting capability of phenanthroline ligands both contribute to the exceptionally positive reduction potential of $Cu(dmp)_2^{2+}$ (+615 mV).[8] Although outer-sphere electron transfer pertains in the reactions of substituted hydroquinones[9,10] and transition-metal reductants[11-13] with $Cu(dmp)_2^{2+}$, mixed outer- and inner-sphere reactivity may be anticipated for reductants with sulfur electron donor atoms.[14]

As inner-sphere electron transfer involving displacement of dmp from $Cu(dmp)_2^{2+}$ is kinetically distinguishable from pathways involving intact $Cu(dmp)_2^{2+}$, we concentrate here on redox rate variations linked to the concentration of dmp. The contributions of S,O chelation and the steric environment of the thiolate sulfur atom to inner-sphere rate parameters are probed through the use of cysteine methyl ester and penicil-

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