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The Chemical Evolution of a Nitrogenase Model. 14. Stoichiometric Reactions of Complexes of Molybdenum(V), Molybdenum(IV), and Molybdenum(III) with Acetylene and Nitrogen

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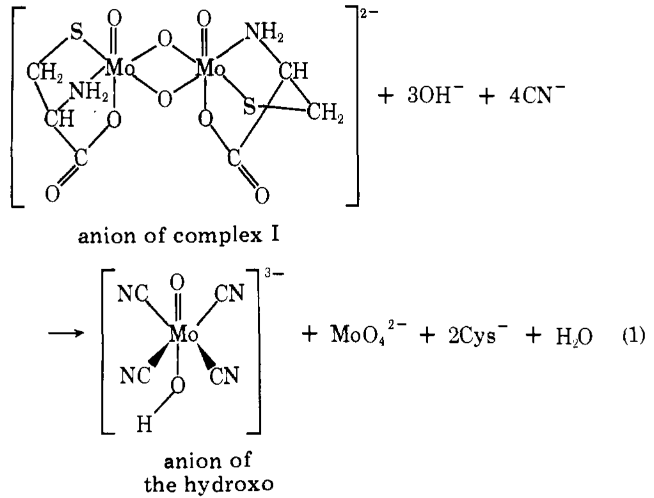
Abstract: The binuclear complex of oxomolybdate(V) with L-(+)-cysteine and related complexes with other ligands disproportionate in alkaline solutions into derivatives of oxomolybdate(IV) and -(VI). The Mo(IV) complexes generated in this fashion act as two-electron reductants with respect to acetylene and nitrogen. Acetylene is reduced exclusively to ethylene at low Mo(IV) concentrations. At higher concentrations of Mo(IV), ethane, 1,3-butadiene, and 1-butene are formed in addition to ethylene. Under the alkaline reaction conditions employed, nitrogen is not reduced to ammonia or hydrazine. However, diimide is formed as evidenced by a marked stimulation of hydrogen evolution, which is inhibited by allyl alcohol; both reactions are characteristic of diimide in strongly alkaline aqueous solution. Reactions of Mo(IV) species generated by the alkali decomposition of the ion $[Mo(O)_2(CN)_4]^{4-}$ with acetylene and nitrogen produced similar results. Reactions of complexes of Mo(III) with acetylene occur with low efficiency and are accompanied by the evolution of copious amounts of hydrogen, in contrast to the behavior of nitrogenase. Hence, the substrate reducing site of nitrogenase more likely contains a mononuclear Mo(IV) rather than a Mo(III) species in the active reduced form.

In recent papers of this series[1,2] we have demonstrated that mononuclear cyano complexes of oxomolybdate(IV) act as two-electron reductants in reactions with acetylene or nitrogen in mildly acidic and alkaline solutions. Because little is known about the behavior of complexes of oxomolybdate(IV), and in view of the continuing discussions concerning the valence changes of molybdenum in functional nitrogenase (N_2-ase), we have continued our studies to include reactions of Mo(IV) species generated in alkaline media, covering base concentrations up to 11 M (NaOH). It is realized that these conditions are no longer "biological", nor does this paper describe further improvements in the development of functional models of N_2-ase. However, since we have previously postulated that Mo(IV) complexes are the active catalysis in the molybdothiol model systems,[3] while other authors have suggested that Mo(III) derivatives are involved,[4] it seemed necessary to further reaffirm our original conclusions. In addition, we also decided to investigate some reactions of Mo(III) complexes to test their behavior under conditions of substrate reduction. The starting point of the present study was our observation[2] that the binuclear complex of oxomolybdate(V) with L-(+)-cysteine ("complex I")[5] reacts with alkaline cyanide to yield salts of the mononuclear cyanocomplexes of oxomolybdate(IV) ["complex II"][6,7] according to reaction eq 1. It thus seemed reasonable to expect that complex I would undergo disproportionation in alkaline solution also in the absence of added cyanide, giving rise to the formation of equilibrium amounts of Mo(IV) complexes whose reactions with substrates of N_2-ase could thus be investigated under stoichiometric conditions. We also studied the reactivity of fragments of the ion $[Mo(O)_2(CN)_4]^{4-}$ generated in strongly alkaline solutions with respect to reducible substrates. Although this ion does not disproportionate, it decomposes in alkali with displacement of coordinated cyanide.[6] Hence, Mo(IV) species from different



anion of complex I

anion of the hydroxo form of complex II

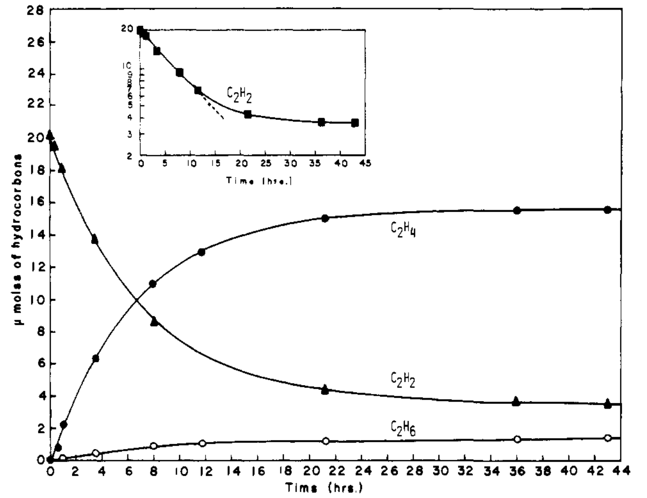


Figure 1. Time dependence of the reduction of C_2H_2 by complex I in alkaline solution. The reaction solution contained 300 μmol of complex I in 5.0 mL of 3.42 M NaOH in 20% ethylene glycol in water. The initial partial pressure of C_2H_2 was 0.017 atm at 23 °C in a total gas-phase volume of 33 mL, corresponding to the addition of 0.5 mL of C_2H_2 gas at 1 atm.

sources became available which could be compared with the active forms of molybdenum in the catalytic molybdothiol systems.[3] These forms were previously considered to be derivatives of oxomolybdate(IV) and shown to act as two-electron reductants. To obtain information on the behavior of Mo(III) ions or complexes under comparable conditions, the salt K_3MoCl_6 was subjected to alkaline hydrolysis, both in the presence and absence of complexing agents or ligands such as L-(+)-cysteine or CN^-. Acetylene and nitrogen were employed as the substrates: acetylene, because it is the most frequently used alternate substrate of N_2-ase; nitrogen, because its reduction to ammonia via diimide and hydrazine is of general interest.

Results

Stoichiometric Reduction of Acetylene with Complex I in Alkaline Solutions. Reaction Conditions. When aqueous solutions of complex I are made alkaline by the addition of NaOH, their color changes from orange to brown, and they later become heterogeneous due to the formation of a brown-green precipitate of mixed-valence molybdenum hydroxides and aquated oxides.[8] Homogeneous solutions are obtained, if the same reaction is performed in aqueous solutions containing small amounts of ethylene glycol, glycerol, or of other polyols. Since it was desirable to study these reactions in homogeneous solution, most experiments were carried out in 20% solutions of ethylene glycol in water.

Reaction Products and Stoichiometry. The reduction of C_2H_2 by complex I in water-glycol yields C_2H_4 as the main product at low concentrations of complex ($<10^{-3}$ M), in 4 M NaOH at 40-75 °C and C_2H_2 pressures of up to 1 atm. Under these conditions, the reaction goes to completion within about 2 h, affording C_2H_4 at yields approaching 100% based on the amount of complex I, according to reaction eq 2:

$$C_2H_2 + [Mo(V)]_2 + 2H_2O \rightarrow C_2H_4 + 2Mo(VI) + 2OH^- \quad (2)$$

In addition to C_2H_4, traces of C_2H_6 and of H_2 are formed. A typical yield-time plot of an acetylene reduction experiment is shown in Figure 1. Upon completion of the reaction, the solutions become colorless due to the quantitative formation of Mo(VI). However, in the absence of glycol or other polyols, the reactions do not go to completion due to the formation of unreactive insoluble precipitates.

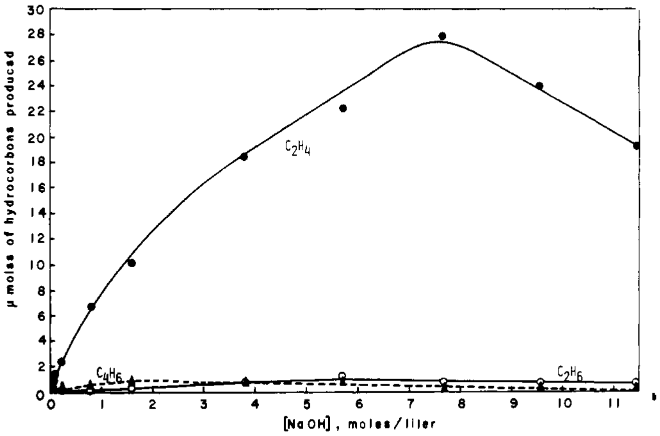


Figure 2. Acetylene reduction by complex I in water-glycol, dependence of the hydrocarbon product yields on the concentration of NaOH. The reaction solutions contained 30 μmol of complex I in a total volume of 5.0 mL. The solvent was 20% ethylene glycol in water; concentrations of NaOH are as indicated. Yields were measured after 21 h of reaction at 60 °C under 1 atm of C_2H_2.

Factors Influencing Reaction Rates and Product Distribution. While C_2H_4 is the main product of C_2H_2 reduction at low concentrations of complex I, increasing amounts of C_2H_6, C_4H_6 (1,3-butadiene), and of C_4H_8 (1-butene) are formed at higher concentrations. The hydrocarbon product distribution is also dependent upon the concentration of base, the pressure of C_2H_2, temperature, and the presence of additives which influence the solubility of the disproportionation products of complex I. In Table I, the results of typical experiments under various conditions are summarized. In Figure 2, the dependence of the hydrocarbon product yields on the concentrations of base is shown for the reaction in water-glycol. Since glycol prevents C_4-hydrocarbon production and stimulates C_2H_4 formation[9] we investigated the effects of other additives as well. These results are summarized in Figure 3. Finally, a number of experiments were performed under catalytic conditions (with $NaBH_4$ as reducing agent) and are summarized in Table II.

Stoichiometric Reduction of Acetylene with Complex II in Alkaline Solutions. The complex anion $[Mo(O)_2(CN)_4]^{4-}$ decomposes in strongly alkaline solution to yield fragments containing Mo(IV) which reduce C_2H_2 at higher rates than those of complex I under comparable conditions (Figures 1 and 4). In aqueous glycol, the reaction solutions remain homogeneous, affording C_2H_4 as the main product. The reaction stoichiometry is given by eq 3:

$$C_2H_2 + [Mo(IV)] + 2H_2O \rightarrow C_2H_4 + Mo(VI) + 2OH^- \quad (3)$$

As with complex I, insoluble products are formed if the experiments are conducted in water instead of water-glycol, and the reactions do not go to completion. The hydrocarbon product distribution depends on the concentration of base as shown in Figure 5.

Reduction of Acetylene by Complexes of Mo(III). The stoichiometric reduction of C_2H_2 by molybdenum with the oxidation number of +3 was investigated by hydrolyzing *dilute*[10] solutions of K_3MoCl_6 with aqueous NaOH in the presence or absence of glycol. The reduction of C_2H_2 under these conditions yields C_2H_4 and C_2H_6 as the main products, but the overall electron transfer efficiency is low due to the rapid evolution of large amounts of H_2 and the formation of Mo(IV) and Mo(V) hydroxides, which accumulate even in water-glycol as the solvent. The H_2/C_2H_4 ratios are very large after short reaction times and gradually decline, as may be seen from Figure 6.

Table I. Yields and Distribution of Hydrocarbons Formed in the Stoichiometric Reduction of C_2H_2 by Complex I under Various Conditions

	Parameter varied and exptl conditions[a]							Molar product distribution, %				%
No.		[Complex], M	$[OH^-]$, M	$p(C_2H_2)$	T (°C)	Time, h	Solvent	C_2H_4	C_2H_6	C_4H_6	C_4H_8	conversion[b]
1	[Complex]	0.0005	3.2	0.03	23	54	H_2O/glycol	94.3	5.7	0	0	97.0
2		0.001						93.3	6.7	0	0	100.0
3		0.002						92.9	7.1	0	0	100.0
4		0.005						92.2	7.8	0	0	100.0
5	p-(C_2H_2)	0.006	3.82	0.03	60	24	H_2O/glycol	96.1	3.9	0	0	21.9
6				0.075				99.3	0.7	0	0	76.7
7				0.30				93.5	4.8	1.6	0.1	97.9
8				0.70				93.6	3.6	2.6	0.1	100.0
9				1.00				92.8	3.7	3.3	0.2	100.0
10	Temp	0.006	2.55	1.00	23	23	H_2O/glycol	91.2	0.2	8.2	0.4	18.6
11					40			92.5	2.5	4.7	0.3	96.5
12					60			93.3	3.3	3.2	0.2	96.3
13					100			94.7	3.4	1.8	0.1	100.0
14	Base	0.006	11.46	1.00	60	21	H_2O/glycol	97.0	2.7	0.3	0	97.1
15			3.82					94.6	3.4	1.9	0.1	97.8
16			0.80					92.3	1.2	6.2	0.3	88.8
17			0.20					92.8	0.6	6.3	0.3	55.3
18	[Complex] and solvent	0.00006	3.0	1.00	60	3	H_2O	95.2	0	4.8	0	100.0
19		0.00006					H_2O/glycol	100.0	0	0	0	78.9
20		0.0006					H_2O	76.5	0	22.7	0.8	74.7
21		0.0006					H_2O/glycol	97.0	1.7	1.3	0	100.0
22		0.006					H_2O	67.6	0.7	29.6	2.2	50.2
23		0.006					H_2O/glycol	92.6	3.7	3.5	0.2	98.2
24		0.06					H_2O	58.6	7.0	32.3	2.2	23.4
25		0.06					H_2O/glycol	89.0	7.2	3.8	0	54.7
26	Base	0.006	11.46	1.00	60	21	H_2O	98.6	0	1.4	0	24.3
27			3.82					59.7	0.7	38.5	1.0	43.3
28			0.80					39.7	1.5	54.0	4.8	23.0
29			0.20					29.9	2.2	61.3	6.6	13.2

[a] Concentrations of complex I and of $[OH^-]$ are expressed in mol/L, the initial pressure of C_2H_2 in atmospheres. The total solution volume was 5.0 mL, the total gas volume, 33.0 mL, respectively. [b] Based on the initial concentration of complex I.

Table II. Catalytic Reduction of C_2H_2 with $NaBH_4$ as a Function of Increasing Concentration of Complex I[a]

Complex I, M	Total hydrocarbons produced, μmol	Mole ratios C_2H_4/C_4H_6
1×10^{-4}	64.0	25.2[b]
3×10^{-4}	84.4	11.9
1×10^{-3}	105.2	4.2
5×10^{-3}	266.6	1.8
1×10^{-2}	367.6	1.8
5×10^{-2}	385.4	1.75

[a] Reaction vials of 38-mL capacity contained, in 4.0 mL of 0.2 F pH 9.6 borate buffer: complex I (see concentrations indicated); $NaBH_4$, 0.265 mmol at $T = 0$. The initial pressure of C_2H_2 was 1 atm; hydrocarbon yields were determined after 18 h of reaction at 25 °C. [b] With $NaBH_4$ in the absence of complex I some reduction of C_2H_2 to C_2 and C_4 hydrocarbons occurs presumably due to the presence of trace metal contaminants in the $NaBH_4$. Entries are corrected for this background hydrocarbon production.

The addition of equivalent amounts of L-(+)-cysteine causes a fourfold stimulation of C_2H_2 reduction and lowers the H_2 evolution to about half of the amount observed in the absence of cysteine. Cyanide stimulates C_2H_2 reduction only by a factor of 2 but depresses H_2 production to the same extent as does cysteine. Interestingly, some of the coordinated CN^- is reduced to CH_4 under the reaction conditions, in contrast to the behavior of complex I or complex II in the presence of CN^-. The addition of equimolar amounts of EDTA and NTA has little or no effect on the rates and yields of H_2 from alkaline Mo(III) but significantly diminishes C_2H_2 reduction. This is attributed to the formation of Mo(V) complexes with these ligands; independent experiments indicate that these complexes reduce C_2H_2 only very slowly due to their slow rate of disproportionation in alkaline solutions.

Our results suggest that the Mo(III) species first react with water to yield H_2 and complexes of Mo(V). The latter in turn disproportionate into derivatives of Mo(IV) and Mo(VI). Accordingly, the stoichiometry of C_2H_4 production can only be expressed approximately, especially since in addition to C_2H_4 larger than usual amounts (up to 30%) of C_2H_6 are formed. Disregarding the formation of unreactive insoluble products, the production of C_2H_4 is expressed by reaction eq 4-7.

$$2\mathrm{Mo(III)} + 4H_2O \rightarrow 2\mathrm{Mo(V)} + 4OH^- + 2H_2 \quad (4)$$

$$2\mathrm{Mo(V)} \rightleftarrows \mathrm{Mo(IV)} + \mathrm{Mo(VI)} \quad (5)$$

$$\mathrm{Mo(IV)} + 2H_2O + C_2H_2 \rightarrow \mathrm{Mo(VI)} + C_2H_4 + 2OH^- \quad (6)$$

$$2\mathrm{Mo(III)} + C_2H_2 + 6H_2O \rightarrow 2H_2 + C_2H_4 + 2\mathrm{Mo(VI)} + 6OH^- \quad (7)$$

According to eq 7, the ratio of the number of electrons used for H_2 production and C_2H_2 reduction should ultimately approach the value of 2.00. The observed value is 3.0 after 24 h (see Figure 6) and reaches 2.30 after 48 h.

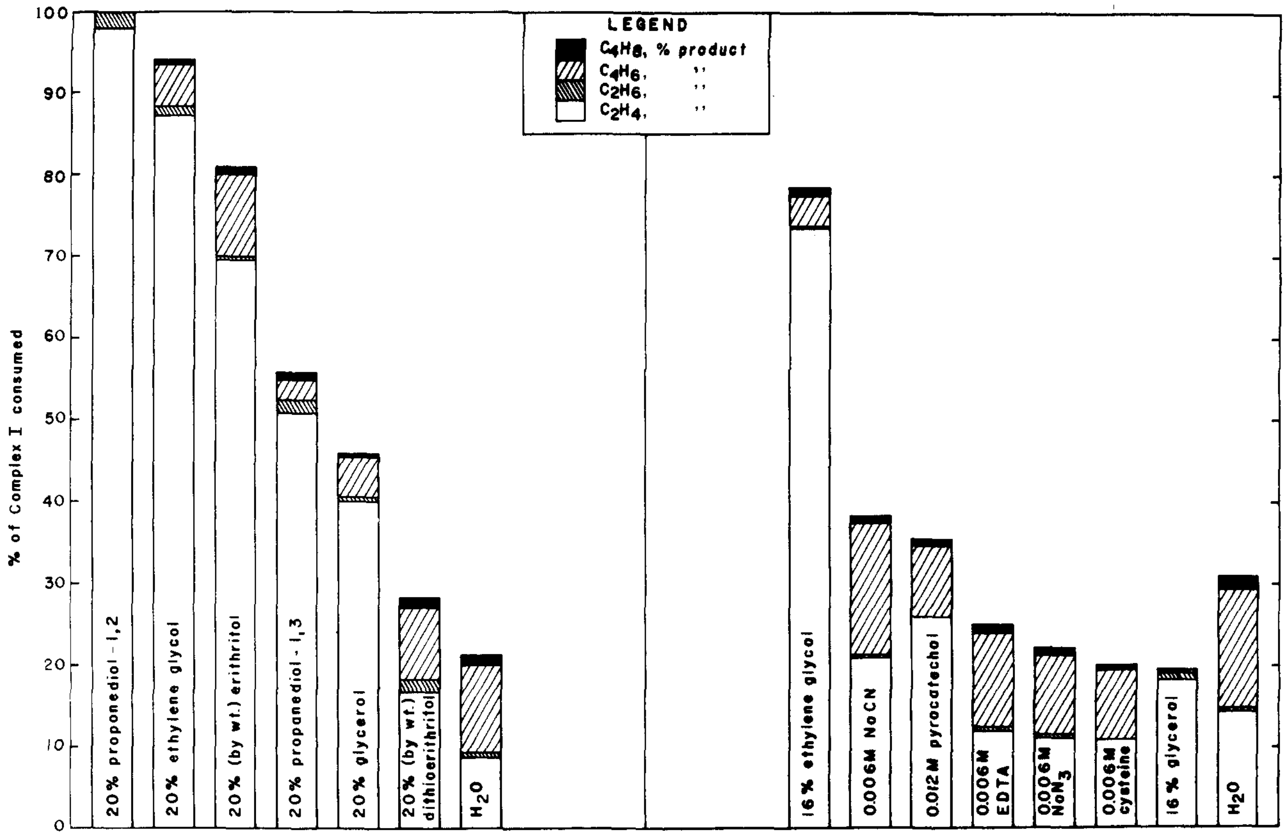


Figure 3. Effects of various additives on the yields and distribution of hydrocarbons in the stoichiometric reduction of C_2H_2 by complex I. Results are shown for two sets of experimental conditions. Experimental series A was run at the initial C_2H_2 pressure of 1 atm, the base concentration of 0.80 M, and the hydrocarbon yields were measured after 21 h. Experimental series B was carried out at 0.5 atm of C_2H_2 at the base concentration of 2.98 M, with yields measured after 90 min of reaction. In both series, the reaction temperature was 60 °C, the initial concentration of complex I 0.006 M, the total gas volume 33 mL, and the solution volume 5.0 mL.

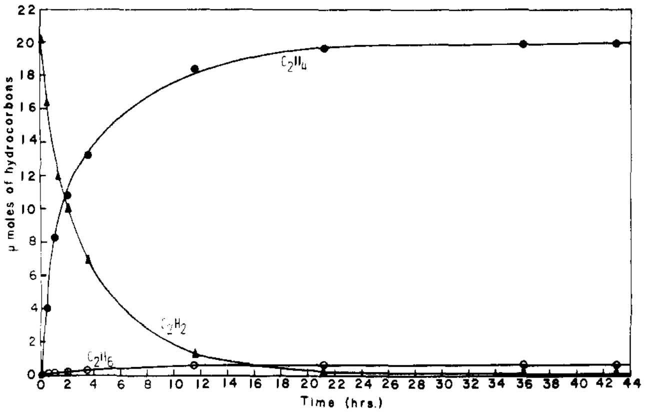
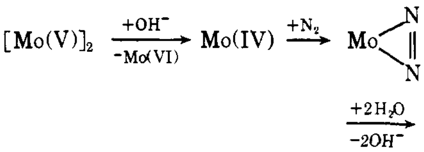


Figure 4. Time dependence of the reduction of C_2H_2 by complex II in alkaline solution. The reaction solution contained 300 μmol of complex II in 5.0 mL of 3.42 M NaOH in 20% ethylene glycol in water. The initial partial pressure of C_2H_2 was 0.017 atm at 23 °C in a total gas-phase volume of 33 mL (corresponding to an addition of 0.5 mL at 1 atm).

Reactions with Molecular Nitrogen. Alkaline solutions of complex I evolve hydrogen slowly at room temperature and more rapidly upon heating to 95 °C under 1 atm of argon (Figure 7). In the presence of nitrogen a significant stimulation of H_2 evolution is observed and is also shown in Figure 7. Since diimide undergoes base-catalyzed decomposition into N_2 and H_2[11] we concluded that N_2 was reduced to diimide, and that the stimulation of H_2 production was due to *decomposing diimide*. Allyl alcohol is an efficient diimide trapping agent[12] and has recently been employed for the detection of diimide in the $V(OH)_2$–$Mg(OH)_2$-nitrogen-fixing system.[13] Figure 8 shows that the H_2 evolution is inhibited by allyl alcohol in the present system as well. Due to its alkali lability, virtually all the N_2H_2 produced decomposes into N_2 and H_2 instead of disproportionating into N_2 and N_2H_4. Accordingly, experiments with $^{15}N_2$ as the substrate revealed that only traces of N_2H_4 or NH_3 are formed.[14] The overall reaction with N_2 is thus formulated in terms of reaction eq 8 and 9.



(8)

$$N_2H_2 \xrightarrow{\text{base catalysis}} N_2 + H_2 \tag{9}$$

The evolution of H_2 from alkaline solutions of complex II is also stimulated by N_2, but the results of individual experiments will not be shown, since N_2 stimulates the reduction of coordinated CN^- as well. This gives rise to the formation of CH_4 which is not detected under argon. Attempts were made to demonstrate a stimulation of H_2 production by Mo(III) complexes in alkaline solutions. However, no significant differences in the rates of H_2 evolution under nitrogen or argon were observed, presumably because the absolute rate of H_2 evolution from Mo(III) complexes in base is about ten times faster than that observed with complex I or complex II.

Discussion

Disproportionation Reactions of Complex I. Complex I is known to decompose into ESR-active mononuclear complexes of Mo(V) in aqueous solutions at pH 10–12.[15] The concentration of ESR-active species amounts to only 1–2% of the total molybdenum present. The ESR signals disappear in more

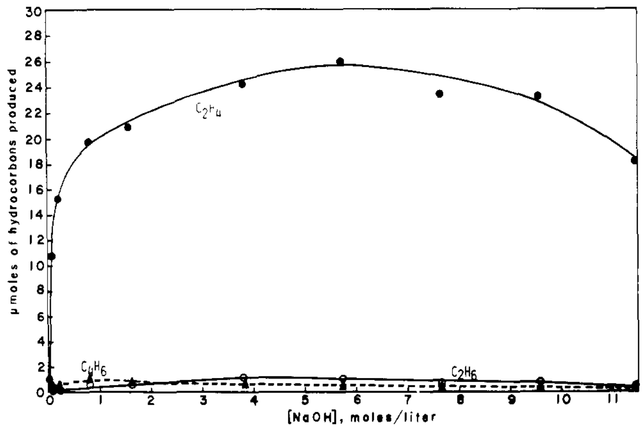


Figure 5. Acetylene reduction by complex II in water–glycol, dependence of the hydrocarbon product yields on the concentration of NaOH. The reaction conditions were the same as in Figure 2 with complex II replacing complex I.

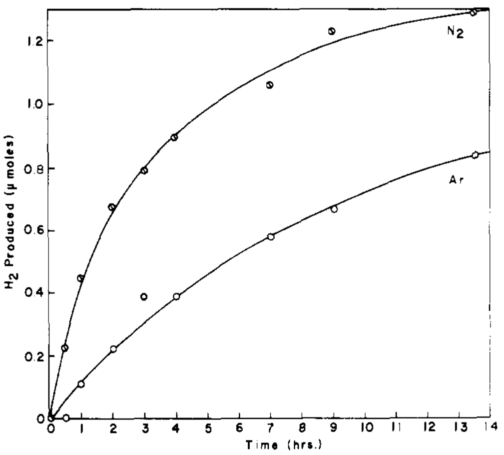


Figure 7. Time dependence of the evolution of H_2 from solutions of complex I in 3.82 M NaOH in 20% ethylene glycol in water. The reaction solution contained 30 μmol of complex I in a total volume of 5.0 mL. Experiments were run under 1 atm of argon or N_2 at 95 °C.

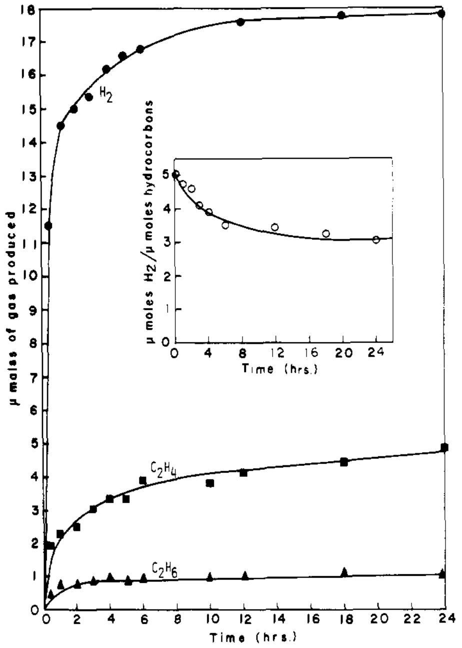


Figure 6. Yields of H_2 and of hydrocarbons in the reduction of C_2H_2 by Mo(III) species generated by the hydrolysis of $MoCl_6^{3-}$ in alkaline solution. The reaction solutions contained 100 μmol of K_3MoCl_6 in 15.0 mL of 2.0 M NaOH in H_2O. The total gas volume was 45.0 mL; the initial partial pressure of C_2H_2 was 0.022 atm at 23 °C.

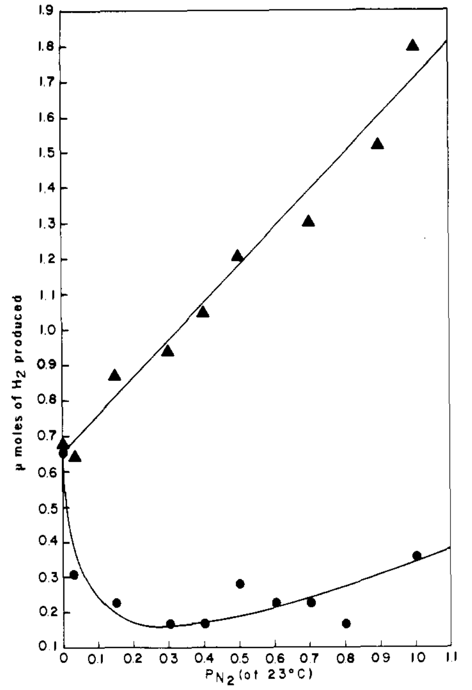
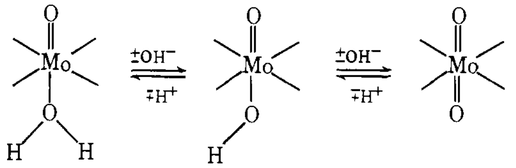


Figure 8. Hydrogen evolution as a function of the partial pressure of N_2 in the presence (●) and absence (▲) of allyl alcohol. H_2 yields were measured after 14 h of reaction at 95 °C. The reaction solutions contained 30 μmol of complex I in 5.0 mL of 3.82 M NaOH dissolved in 20% ethylene glycol in water. The concentration of allyl alcohol was 0.015 M.

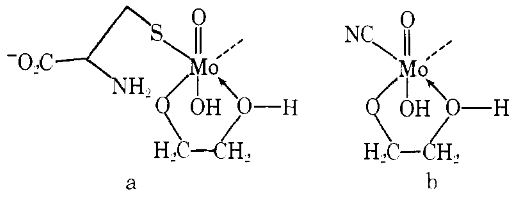
strongly alkaline solutions. It is reasonable to assume that complex I disproportionates into derivatives of Mo(IV) and Mo(VI) which would be ESR silent; a disproportionation into Mo(III) and Mo(VI) can be ruled out since Mo(III)-cysteine complexes have been shown[15] to give ESR signals differing from those of mononuclear Mo(V) species mentioned above. Further evidence against the formation of Mo(III) disproportionation products follows from the fact that Mo(III) complexes evolve H_2 spontaneously and more rapidly than Mo(IV) species generated under the same conditions, as will be outlined below. Other authors have also suggested that binuclear complexes of oxomolybdate(V) can disproportionate into derivatives of Mo(IV) and Mo(VI).[16] Nucleophilic attack by OH^- represents one mechanistic pathway. Although defined Mo(IV)-cysteine complexes have not yet been isolated from our reaction solutions,[17] reaction eq 1 as well as the experiments with C_2H_2 provide good indirect evidence that disproportionation occurs and that the Mo(IV) species generated are two-electron reducing agents. Their behavior may thus be compared to that of "Mo^{red}", the active catalytic species in the molybdothiol model systems,[3] but since the disproportionation requires strongly alkaline conditions, differences in reactivity with the catalytically produced Mo^{red} exist which we attribute mainly to shifts in protonation-deprotonation equilibria of molybdenum-bound hydroxyl groups. Such shifts are well known in the chemistry of cyano complexes of oxomolybdate(IV)[6] and are schematically represented in eq 10.



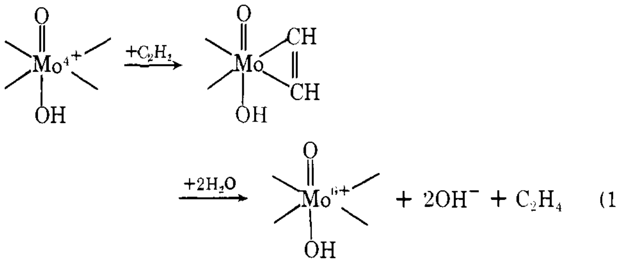
(10)

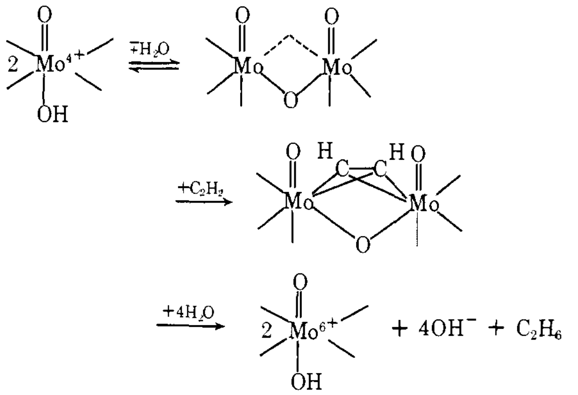
The presence of coordinated cysteine in the Mo(IV) species derived from complex I introduces further complications.

Whereas cysteine acts as a tridentate ligand relative to oxomolybdate(V) in neutral solution, this type of coordination is unlikely to persist in strongly alkaline media or in the presence of other ligands such as glycols. It must be assumed that coordination sites on the Mo(IV) species are available for the side-on attachment of one molecule of C_2H_2 prior to its reduction to C_2H_4. However, with unidentate ligands, reactive complexes capable of interacting with two molecules of C_2H_2 can be formed. Such species may be responsible for the reduction of C_2H_2 to C_4H_6, as will be outlined below. Glycols and other ligands prevent not only C_4H_6 production but also the formation of precipitates during the reaction. Formulas a and b depict two possible structures of reactive Mo(IV) species derived from complex I and II, respectively, in the presence of ethylene glycol. It is suggested that glycol blocks one or two coordination sites on molybdenum and thus prevents the interaction of a second molecule of C_2H_2, which accounts for the predominant C_2H_4 production.[18] To simplify the following discussion, we shall refer to Mo(IV) species without specifying the presence of glycol, cysteine, or other ancilliary ligands. We shall also not mention equilibria or reactions of the molybdenum complexes with water or hydroxyl ions, even though it is recognized that particularly the latter are also likely to block coordination sites and thus influence the hydrocarbon product distribution.

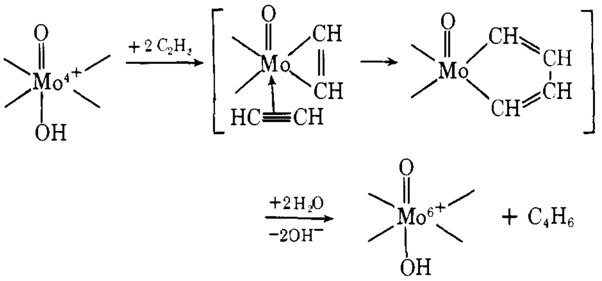


Stoichiometric Reduction of Acetylene to Ethylene and Ethane. The stoichiometry of reduction of C_2H_2 by complex I to C_2H_4 in alkaline solution proceeds formally as expressed by eq 2 but actually involves Mo(IV) species which are oxidized to Mo(VI) according to reaction eq 3, which also applies to the reduction of C_2H_2 by the alkali-decomposition product(s) of complex II. Mononuclear Mo(IV) complexes generated under stoichiometric conditions behave as two-electron reductants, and since the stereochemical course of such reactions has been shown to be exclusively cis, ethylene is evidently generated via a side-on bonded organomolybdenum intermediate as shown in eq 11. The reduction of C_2H_2 to C_2H_6 has been demonstrated to involve binuclear forms of the molybdothiol catalysts.[3,20] We therefore assume that the Mo(IV) species generated by the alkali decomposition of complex I or complex II may also have a tendency to dimerize, giving rise to reactive complexes which are capable of reducing C_2H_2 directly to C_2H_6 in terms of reaction eq 12.


(11)


(12)

Formation of Unsaturated C_4-Hydrocarbons from C_2H_2. Our work shows that C_2H_4 is the main product of the reduction of C_2H_2 under stoichiometric conditions at low molybdenum concentrations and/or low partial pressures of C_2H_2 (see Table I). At high molybdenum concentrations and C_2H_2 pressures, significant amounts of 1,3-butadiene as well as traces of 1-butene are formed in aqueous solutions, but not if glycol or other diols or polyols are added (Table I). The diols or polyols presumably block coordination sites on molybdenum that would otherwise be available for the binding of a second molecule of C_2H_2, and since 1,3-propanediol has a weaker effect than 1,2-propanediol (see Figure 3) we conclude that cis positions on Mo(IV) are blocked. A possible mechanism of C_4H_6 production is shown in eq 13. Under catalytic conditions (i.e., with complex I, and $NaBH_4$ as the reductant) 1,3-butadiene is formed in significant yields at high catalyst concentrations and C_2H_2 pressures in borate, but not carbonate buffer.[19] As the concentration of molybdenum catalyst is decreased, less, and ultimately insignificant amounts, of C_4H_6 are formed relative to C_2H_4 (see Table II). Hence, under conditions approaching those of enzymic assays, particularly at the same low concentrations of molybdenum, molybdothiol catalysts exhibit the desired resemblance in catalytic selectivity with N_2-ase. In view of the problems experienced by Corbin et al.,[19] we emphasize that comparative N_2-ase model studies should preferably be performed at low catalyst concentrations. 1-Butene is invariably formed only in trace amounts. We believe that this four-electron reduction product is formed from binuclear Mo(IV) complexes in which one additional coordination site is available for interaction with two molecules of C_2H_2 but defer detailed discussion of the mechanism. The selective production of C_2H_4 in the reduction of C_2H_2 by N_2-ase thus reaffirms our previous conclusion that the molybdenum atom at the enzymic active site is mononuclear and that its coordination sphere has only two accessible sites for the side-on interaction with one molecule of C_2H_2.


(13)

Reactions of Mo(III) Complexes. Our studies with Mo(III) complexes as reductants in stoichiometric reactions with C_2H_2 show clearly that the major product is H_2 and that C_2H_4 and other hydrocarbons are produced with much lower efficiency than with Mo(IV) complexes. We infer from these results that the enzymatic reduction of C_2H_2 occurs at a Mo(IV) rather than a Mo(III) active site. On the other hand, the reduction of substrates such as CN^-, of isocyanides, or of nitriles, *does not occur with Mo(IV) alone.* In these reactions, Mo(IV) species merely bind the substrates, and additional electrons must be provided to achieve reduction of the coordinated ligands. The formation of complex II by the reaction of Mo(IV) species with CN^- is a particularly good example for this behavior. The reduction of these substrates may be described in terms of intermediate substrate-catalyst complexes in which the oxidation state of molybdenum is *formally* either +3 or +2.

Reactions with Molecular Nitrogen. The reaction of the Mo(IV) complexes with N_2 indicates that diimide is formed as the initial product, but since these experiments were carried out in strongly alkaline solution, diimide decomposition into the elements according to reaction eq 9 is favored over the disproportionation into N_2 and N_2H_4. The observed stimulation of H_2-evolution by N_2 and its inhibition by allyl alcohol provides convincing evidence for the formation of N_2H_2 from N_2 even though only traces of N_2 are actually reduced completely to N_2H_4 and NH_3. A nitrogen stimulated evolution of H_2 also occurs with $V(OH)_2$ unless it is coprecipitated with $Mg(OH)_2$ or aqueous ZrO_2.[13] Under these conditions, N_2H_2 is generated within the less alkaline environments of the $Mg(OH)_2$ or aqueous ZrO_2 host lattices and hence undergoes disproportionation into N_2H_4 and N_2. We have thus far been unable to find an appropriate lattice for the incorporation of Mo(IV) species. Judging from the amounts of H_2 produced during the enzymatic reduction of N_2 it has been concluded[3] that N_2-ase reduces N_2 via diimide under conditions where only 33% decompose into the elements. This necessitates the further assumption that the immediate environment of the site of N_2-reduction is free of strongly basic groups that would otherwise induce diimide decomposition.

Summary

The binuclear complex of oxomolybdate(V) with L-(+)-cysteine disproportionates in alkaline solutions to yield species capable of reducing C_2H_2 and N_2. The stoichiometry of the reactions indicates that two-electron reducing agents are generated, which are derivatives of mononuclear oxomolybdate(IV). Similar species are generated by the alkali decomposition of cyano complexes of oxomolybdate(IV). The reactivity pattern of the substrate-reducing site of N_2-ase is more consistent with the known chemistry of Mo(IV) than that of molybdenum in any other oxidation state. Finally, the experiments with N_2 show that diimide is formed and subsequently decomposes into N_2 and H_2. Hence the present work again illustrates the *stringent* requirements for the efficient reduction of N_2 via N_2H_2 in protic media.

Experimental Section

Reagents and Chemicals. Complexes I and II were prepared according to the procedures outlined in ref 5 and 6. All standard reagents and chemicals were commercially available and were of Reagent or Analytical Grade purity unless otherwise indicated. Cylinder acetylene (Matheson, purity 99.8%) was acid-washed prior to use. Argon and nitrogen (both from Matheson and of 99.99% purity) were washed with alkaline pyrogallol solution to remove traces of oxygen.

Standard Techniques for Stoichiometric Acetylene Reduction Experiments. The stoichiometric C_2H_2 reduction experiments were performed in reaction vessels of 38 mL total capacity, manufactured by Pierce Chemical Company, Rockford, Ill. After capping with silicone rubber seals, the reaction bottles were flushed with the respective gasses, i.e., argon or acetylene. Subsequently, measured amounts of freshly prepared solutions of complexes I or II in water were injected by means of a syringe, followed by the similar addition of appropriate amounts of ethylene glycol or other solubilizing additives. After temperature equilibration, the reactions were initiated by the addition of solutions of NaOH (usually 6–10 M), to bring the final base concentration to 3.82 M. In the experiments with complexes of Mo(III), freshly prepared dilute aqueous solutions of the salt K_3MoCl_6 must be injected into the reaction vessels immediately since they undergo decomposition with evolution of H_2 even in neutral aqueous solution at room temperature. In typical experiments, the total solution volume was 5.0 mL, and the initial concentration of complexes I or II was 0.006 M; further details of experimental conditions are given in the tables and figure legends.

The hydrocarbon products were measured on a Varian Aerograph Model 2000 GLC instrument, employing a 6 ft column packed with phenyl isocyanate on Porasil C (80–100 mesh), with helium as the carrier gas. The measurements were performed with flame-ionization detection with a column temperature of 40 °C. The hydrocarbon products were identified by cochromatography and by GLC-mass spectrography, using an LKB Model 9000 GC-mass spectrograph. Absolute hydrocarbon yields were determined by comparison of peak areas with those of known amounts of the respective hydrocarbons.

Reactions with Molecular Nitrogen. The experiments with molecular nitrogen as the substrate yield H_2 as the main gaseous product. For H_2 determination, a Hewlett-Packard dual column Model 700 GLC instrument was employed which was equipped with a thermal conductivity detector. The 6 ft column used was packed with Linde Molecular Sieve 5 A, with argon as the carrier gas. Samples for H_2 determination were taken by means of a gas-lock syringe. Experimental details are outlined in the legends of Figure 8.

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(8) The precipitates were collected by centrifugation. The oxidation state of molybdenum was determined by titration with $KMnO_4$ and was 5.2 ± 0.4.

(9) Traces of C_2H_4 are generated if solutions of complex I in water–ethylene glycol are heated to 60 °C. The yields are negligibly small (0.1%) relative to the C_2H_4 formed from C_2H_2.

(10) The initial concentration of K_3MoCl_6 was usually 0.006 M. At concentrations >0.01 M, brown precipitates are formed, less H_2 per molybdenum is generated, and the efficiency of C_2H_2 reduction is quite low, i.e., <10%.

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