(III) complexes break the Cr–N bond somewhat more slowly than do the complexes listed in Table III.[24-26]

Scheme I then adequately, but not unambiguously, accounts for the aquation behavior of *trans*-$Cr(en)_2X_2^+$ species. In particular, we have found no H^+ catalysis of the aquation of *trans*-$Cr(en)_2F_2^+$. This result is in conflict with other studies of chromium(III) fluoride complexes.[15,27] In these cases, however, the net aquation process apparently involves the loss of a fluoride ligand (although in the case of $Cr(NH_3)_5F^{2+}$ there have been reports that NH_3 is lost[28]). For *trans*-$Cr(en)_2F_2^+$ the rate of fluoride loss is so slow relative to that of Cr–N bond rupture that even at the highest acid concentration studied an insignificant amount of Cr–F bond cleavage occurs. Hence no H^+ catalysis is observed. (In concentrated $HClO_4$, aquation of fluoride does occur.[10]) The disturbing feature of Scheme I is that there is no evidence[20] for an isolable monodentate species with the structure $Cr(en)(enH)H_2OCl_2^{2+}$ but that $Cr(en)(enH)H_2OF_2^{2+}$ is isolated in solution: $k_N/(k_C + k_L)$ is much greater than 1 for X = F but much less than 1 for X = Cl. This latter system is compatible with some of the other monodentate species that have been investigated: rupture of the first Cr–N bond is faster than that of the remaining Cr–N bonds as in the case of $Cr(dien)(H_2O)_3^{3+}$,[9] $Cr(dienH)(H_2O)_4^{4+}$,[9] and $Cr(en)(H_2O)_4^{3+}$.[8] It is not compatible with others.[26] We are puzzled by this feature but can offer no explanations other than *a posteriori* ones.

The system on which we report shows one other unusual feature compared to previously isolated complexes with monodentate ligands: the monodentate ligand closes in acid solution to re-form a chelated system.[29] Although such processes are found with ligands containing carboxylate groups,[30] they may be suspected to be unusual when the pendant group contains such a weak acid as $-NH_3^+$. (Alexander and Spillert reported only a small amount of ring closure in a monodentate ethylenediamine complex of Co(III) even in basic solutions.[31]) It may be that the hydrogen bonding between coordinated F^- and $-NH_3^+$ facilitates this ring closure; partial transfer of the hydrogen would increase the nucleophilicity of the amine and would enhance the leaving ability of F^-.

Acknowledgment.—This work was supported by a research grant from the Academic Senate, University of California, San Diego, Calif. We also thank Professor J. W. Vaughn for samples of [*trans*-$Cr(en)_2F_2$]Cl.

(24) Another direct comparison is given in the review of Garner and House.[15] *cis*-$Cr(en)_2(H_2O)_2^{3+}$ aquates to $Cr(en)(H_2O)_4^{3+}$ with $k = 2.9 \times 10^{-4}$ sec^{-1} (30°)[25] whereas *cis*-$Cr(en)_2ox^+$ loses one end of an ethylenediame with $k = 1.1 \times 10^{-5}$ (25°).[26]

(25) H. L. Schläfer and R. Kollrack, *Z. Phys. Chem. (Frankfurt am Main)*, **18**, 348 (1958).

(26) H. Gausmann, Thesis, Johann Wolfgang Goethe-Universitat, Frankfurt, Germany, 1964; quoted in ref 16.

(27) T. P. Jones and J. K. Phillips, *J. Chem. Soc. A*, 674 (1968), and references therein.

(28) M. Linhard, *Z. Anorg. Allg. Chem.*, **278**, 24 (1955).

(29) From the limit on the amount of *trans*-$Cr(en)_2F_2^+$ that may be present when chromatographically pure $Cr(en)(enH)H_2OF_2^{2+}$ is allowed to aquate, we estimate that the rate constant for $Cr(en)(enH)H_2OF_2^{2+} \rightarrow$ *trans*-$Cr(en)_2F_2^+ + H^+$ is less than 5×10^{-7} sec^{-1}.

(30) See, for instance, D. H. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965).

(31) M. D. Alexander and C. A. Spillert, *ibid.*, **9**, 2344 (1970).

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The Electrochemistry of Molybdenum(VI,V)–8-Quinolinol Complexes in Dimethyl Sulfoxide

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Received March 29, 1971

The electrochemistry of dioxobis(8-quinolinolato)molybdenum(VI) ($Mo^{VI}O_2Q_2$) and μ-oxo-dioxotetrakis(8-quinolinolato)-dimolybdenum(V) ($Mo^{V}_2O_3Q_4$) has been studied in dimethyl sulfoxide using cyclic voltammetry, chronopotentiometry, and controlled-potential coulometry at a platinum electrode. The reduction of $Mo^{VI}O_2Q_2$ occurs in two one-electron steps, with solvent attack of the reduction intermediates and displacement of the 8-quinolinolate ligands. A Mo(IV) species produced by the reduction of $Mo^{VI}O_2Q_2$ catalytically reduces any excess 8-quinolinol. $Mo^{V}_2O_3Q_4$ is reduced in two reversible one-electron steps. Unimolecular rate constants for the decomposition of the resulting Mo(V)–Mo(IV) and Mo(IV)–Mo(IV) dimers have been determined. The decomposition products are identical with the reduction intermediates of $Mo^{VI}O_2Q_2$. The oxidation of $Mo^{V}_2O_3Q_4$ is an irreversible one-electron process producing a Mo(VI)–Mo(V) dimer which decomposes and is oxidized further to produce $Mo^{VI}O_2Q_2$.

Molybdenum, which is an important trace element in living organisms, occurs in at least four enzymes: xanthine oxidase,[1] aldehyde oxidase,[2] nitrate reductase,[3] and nitrogenase (molybdoferredoxin).[4] Biochemists[5] generally agree that molybdenum alternates between the 6+ and 5+ oxidation states during enzyme catalytic activity. These oxidation states have been identified in nitrate reductase by complexation with 8-quinolinol.[6,7] Molybdenum(V) epr signals have been recorded for the four molybdenum enzymes in the presence

(1) R. C. Bray, P. F. Knowles, and L. S. Meriwether, "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malmstrom, and T. Vanngard, Ed., Pergamon Press, Oxford, 1967, p 249.

(2) H. Beinert and W. H. Orme-Johnson, ref 1, p 221.

(3) A. Nason, "The Enzymes," Vol. 7, P. D. Boyer, H. Lardy, and K. Myrback, Ed., Academic Press, New York, N. Y., 1963, p 587.

(4) K. B. Taylor, *J. Biol. Chem.*, **244**, 171 (1969).

(5) D. J. D. Nicholas and P. J. Wilson, *Biochim. Biophys. Acta*, **86**, 466 (1964).

(6) D. J. D. Nicholas and A. Nason, *J. Biol. Chem.*, **211**, 183 (1954).

(7) D. J. D. Nicholas and H. M. Stevens, *Nature (London)*, **176**, 1066 (1955).

of substrate.[2,3,8,9] Molybdenum(III) is not probable because its common oxidation potential is not ideal for biological systems. Molybdenum(IV) normally is quite unstable, but the possibility of the 4+ or 3+ oxidation states cannot be ruled out. No more than 37% of the total molybdenum has been accounted for in epr experiments of fully reduced enzyme.[2] In fact, recent work on xanthine oxidase has indicated that Mo(VI) is reduced to Mo(III) and possibly even Mo(II). This proposal was necessary to account for the number of electrons transferred to the enzyme.[10]

The importance of molybdenum in flavoproteins has been reviewed from the standpoint of coordination chemistry[11] and has prompted a study of the kinetics of complex formation in aqueous solution between molybdenum(VI) and 8-quinolinol;[12] the latter was proposed as a model for xanthine oxidase (a molybdenum containing flavoprotein). A recent review[13] of the oxo species of molybdenum(VI,V) and their complexes provides a useful background for the electrochemical studies of the interaction between molybdenum(VI,V) and flavin model compounds.

Most investigators believe that enzymatic molybdenum is involved in the electron-transfer mechanism during the redox process. The electron-transfer path appears to be[2,10,14]

$$\text{substrate} \longrightarrow \text{Mo(VI)–Mo(V)} \longrightarrow \text{FAD–FADH}\cdot \longrightarrow \text{Fe(III)–Fe(II)} \longrightarrow \text{O}_2 \quad (1)$$

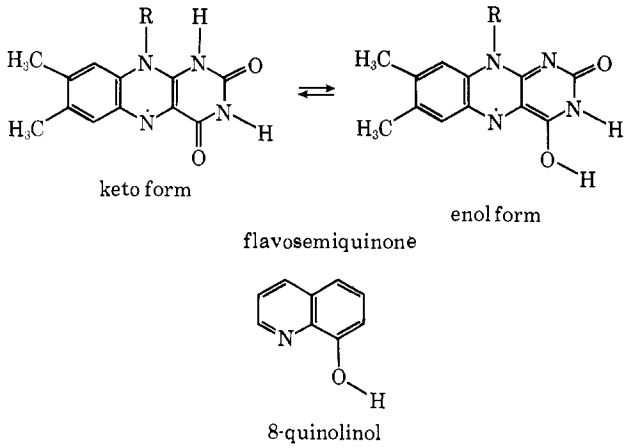
An alternate path may occur in xanthine oxidase, depending on pH and substrate[1]

$$\text{substrate} \longrightarrow \text{FAD–FADH}\cdot \longrightarrow \text{Mo(VI)–Mo(V)} \longrightarrow \text{Fe(III)–Fe(II)} \longrightarrow \text{O}_2 \quad (2)$$

During nitrate reduction catalyzed by nitrate reductase, a Mo(V) epr signal has been reported. The proposed electron-transfer sequence is[6]

$$\text{reduced nicotinamide–adenine dinucleotide} \longrightarrow \text{FAD} \longrightarrow \text{Mo(VI)} \longrightarrow \text{NO}_3^- \quad (3)$$

Few studies of enzymatic molybdenum have considered the electrochemical behavior of molybdenum. Obviously, the investigation of redox properties of actual enzymes is difficult due to their size and complexity. Thus, model systems are attractive as a basis for initial electrochemical investigation. Molybdenum–flavin complexes are relevant because at least two molybdenum enzymes contain FAD as a coenzyme. The epr work of Beinert[14] has indicated that a molybdenum–flavin interaction occurs. An electrochemical study of molybdenum–flavin complexes is logical, but the complexity of flavin electrochemistry[15] makes the choice of a simpler model system desirable. 8-Quinolinol is structurally similar to flavosemiquinone when the isoalloxazine nucleus is in the enol form[16] and several molybdenum–8-quinolinol complexes are known.[13] These



complexes are not water soluble, so an electrochemical study in an aqueous medium is not possible. However, spectroscopic evidence has indicated that the protein fragment of flavoenzymes provides a nonaqueous environment similar to an aprotic medium.[17] Consequently, the present research has been directed to the study of the electrochemical behavior of molybdenum–8-quinolinol complexes in dimethyl sulfoxide.

Experimental Section

Cyclic voltammetry, chronopotentiometry, and coulometry were performed with a three-electrode potentiostat–amperostat constructed with solid-state operational amplifiers.[18] An external input to the integrator circuit was installed to permit the use of a Wenking Model 61RH potentiostat for coulometry. Cyclic voltammograms and chronopotentiograms were recorded on a Hewlett-Packard Moseley Model 7030A X-Y recorder. Coulometry curves were recorded on a Sargent Model SR-strip chart recorder.

A 15-ml gas-tight all-glass electrochemical cell was designed specifically for this research. The cell top had four openings: one opening with a tube extending downward and closed at the bottom end with a fine-porosity glass frit for isolation of the auxiliary electrode, the second with a tube extending upward in which the low surface area working electrode was placed, the third with a 7/15 female ground-glass joint to accept a reference electrode, and the fourth with a 10/18 female ground-glass joint to accept a jointed thermometer or a high surface area working electrode. A miniature Luggin capillary could be suspended from a small glass hook on the side of the auxiliary electrode compartment. A two-position Teflon stopcock, which was connected to the side of the cell body, included a ground-glass ball joint to permit the connection of a source of purging gas. One stopcock outlet was attached to a coarse-porosity glass frit for purging below the solution surface and the other outlet to an opening permitting purging above the solution surface. One side arm has a 10/18 female ground-glass joint to permit the attachment of a one-way liquid bubbler for use during degassing or a ground-glass stopper for sealed-cell experiments. A rubber stopper could be placed in the other side arm for the withdrawal of a sample of solution with a syringe. In addition, a tungsten wire was sealed in the bottom of the cell to provide an electrical connection with a large surface area Hg pool working electrode.

For cyclic voltammetric and chronopotentiometric experiments a Beckman Model 39273 platinum-inlay electrode was employed; a platinum gauze electrode was used for the coulometric and electrolysis experiments. The area of the inlay electrode was determined by chronopotentiometric reduction of ferricyanide ion. The reference electrode consisted of an aqueous Ag–AgCl electrode in 0.4 *F* tetramethylammonium chloride solution in a cracked glass-bead salt bridge (0.000 V *vs.* sce). A Luggin capillary was used in conjunction with the reference electrode in all

(8) C. H. Fewson and D. J. D. Nicholas, *Biochim. Biophys. Acta*, **49**, 335 (1961).
(9) D. J. D. Nicholas, P. W. Wilson, W. Heinen, G. Palmer, and H. Beinert, *Nature (London)*, **196**, 433 (1962).
(10) G. Palmer and V. Massey, *J. Biol. Chem.*, **244**, 2614 (1969).
(11) R. J. P. Williams, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 65.
(12) P. F. Knowles and H. Diebler, *Trans. Faraday Soc.*, **64**, 977 (1968).
(13) P. C. H. Mitchell, *Quart. Rev., Chem. Soc.*, **20**, 103 (1966).
(14) K. V. Rajagopalan, P. Handler, G. Palmer, and H. Beinert, *J. Biol. Chem.*, **243**, 3784, 3797 (1968).
(15) D. T. Sawyer, R. Y. Komai, and R. L. McCreery, *Experimentia*, in press.
(16) A. Albert, *Biochem. J.*, **54**, 646 (1953).
(17) V. Massey and H. Ganther, *Biochemistry*, **4**, 1161 (1965).
(18) A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, **39**, 411 (1967).

cases and the shield tubes were filled with the supporting electrolyte solution used in the same solution.

Vibrational spectra of the synthesized complexes were recorded with a Perkin-Elmer Model 621 spectrophotometer. Spectra for solid samples were recorded in KBr pellets. A Cary 14 spectrophotometer was used to record the electronic spectra of the electrochemical solutions. The epr spectra were recorded with a Varian V4500 spectrometer using a special electrolysis–epr flow cell. The flow rate was controlled with a Harvard 1100 portable infusion–withdrawal pump driving B-D Luer-Lok syringes of various sizes. A Hamilton 10-μl syringe was used to sample the coulometric cell which was fitted with serum caps. The gas chromatographic analysis for ethylene was performed on a 10% Na_3PO_4–Porasil C column at 60° using a Varian Aerograph Series 1200 gas chromatograph.[19] The system was calibrated with CP grade ethylene (Matheson Co.).

Chemicals.—Dimethyl sulfoxide (DMSO) (J. T. Baker Analyzed reagent grade) was obtained in pint bottles to minimize water contamination; the water content varied between 0.02 and 0.05%. Tetraethylammonium perchlorate (TEAP) was prepared by stoichiometric combination of reagent grade perchloric acid and reagent grade tetraethylammonium bromide. The product was allowed to crystallize from the cooled solution and was recrystallized twice from cold water.

The preparation of dioxobis(8-quinolinolato)molybdenum(VI) was accomplished by the method of Stevens.[20] The resulting yellow compound was characterized by comparison with published vibrational[21,22] and electronic[20,21] spectra. The results of a gravimetric analysis[23] for Mo and C and H analyses indicate that the composition is $Mo^{VI}O_2(C_9H_6NO)_2$. *Anal.* Calcd for $MoC_{18}H_{12}N_2O_4$: Mo, 23.05; C, 51.94; H, 2.91. Found: Mo, 23.30, C, 51.61; H, 2.94.

Stevens also reported the synthesis of a purple Mo(V) complex which he identified as oxohydroxybis(8-quinolinolato)molybdenum(V) [MoO(OH)Q_2], a monomeric Mo(V) complex. Following his synthetic route, a mixture of $Mo^{V}_2O_3Q_4$ and $Mo^{VI}O_2Q_2$ was isolated as determined from the published vibrational and electronic spectra of $Mo^{V}_2O_3Q_4$[24] and $Mo^{VI}O_2Q_2$.[20-22]

Pure $Mo^{V}_2O_3Q_4$, μ-oxo-dioxotetrakis(8-quinolinolato)dimolybdenum(V), was prepared by modifying Stevens' synthetic procedure. Instead of starting with a solution of $MoCl_5$ in concentrated HCl, 0.6 g of $Na_2MoO_4 \cdot 2H_2O$ was dissolved in 5 ml of 3 *F* HCl. A small amount of Hg was added and the solution was shaken until the intensification of the wine red Mo(V) color ceased. This solution was added to a solution of 5 g of 8-quinolinol in 50 ml of ethanol. Twenty milliliters of water was added, and the solution was filtered after 10 min. The filtrate was poured into 400 ml of 0.04 *F* NaOH solution heated to 60°. The solution was stirred and maintained at 60° until a purple precipitate formed and the solution was no longer purple. The precipitate was filtered, washed with water and ethanol, and dried *in vacuo* over P_2O_5.

The vibrational and electronic spectra of the synthesized compound agreed with those published by Mitchell.[23] A gravimetric analysis for molybdenum[25] was difficult because of the stability of the compound toward air oxidation. Oxidation was complete after 12 hr at 480°. The volatility of MoO_3 at 500° results in a weight loss of 0.072% every 2 hr.[24] Therefore, 12 hr at 480° should result in a low molybdenum determination. The results of the Mo determination and C and H analyses indicate that the composition is $Mo^{V}_2O_3(C_9H_6NO)_4 \cdot H_2O$. *Anal.* Calcd for $Mo_2C_{36}H_{26}N_4O_8$: Mo, 22.99; C, 51.81; H, 3.14. Found: Mo, 21.96; C, 51.85; H, 3.27.

Results

The electrochemical behavior of free ligand in solution needs to be known so that electrochemical data for the free ligand can be separated from those for the complex itself. A reduction mechanism for 8-quinolinol (HQ) in *N*,*N*-dimethylformamide (DMF) at a dropping Hg electrode has been reported.[26]

In dimethyl sulfoxide (DMSO) at a Pt electrode the cyclic voltammogram of HQ has an irreversible cathodic peak at −1.95 V followed by anodic peaks at −0.4 V (H_2 oxidation) and +0.05 V. Coulometric reduction at −2.0 V indicates a one-electron reduction. The cyclic voltammogram of reduced HQ has an irreversible anodic peak at +0.05 V. The reduction of H_2Q^+ (HQ + H^+) is similar to the reduction of HQ except that an anodic peak is not observed at +0.05 V; the overall reaction is the catalytic reduction of H^+. The cyclic voltammogram and electronic spectrum of Q^- (HQ + OH^-) are identical with those of reduced HQ. Coulometric oxidation of Q^- at +0.25 V is hindered but results in a one-electron oxidation to a product which has the same cyclic voltammogram as HQ. Therefore, HQ is reduced at −1.95 V, and Q^- is oxidized at +0.05 V.

Dimethyl sulfoxide (DMSO) offers several advantages as an electrochemical solvent for $Mo^{VI}O_2Q_2$; further purification is not necessary, solubility is good, and the electrochemical behavior of $Mo^{VI}O_2Q_2$ is somewhat simpler (Figure 1A) than for DMF or acetonitrile.

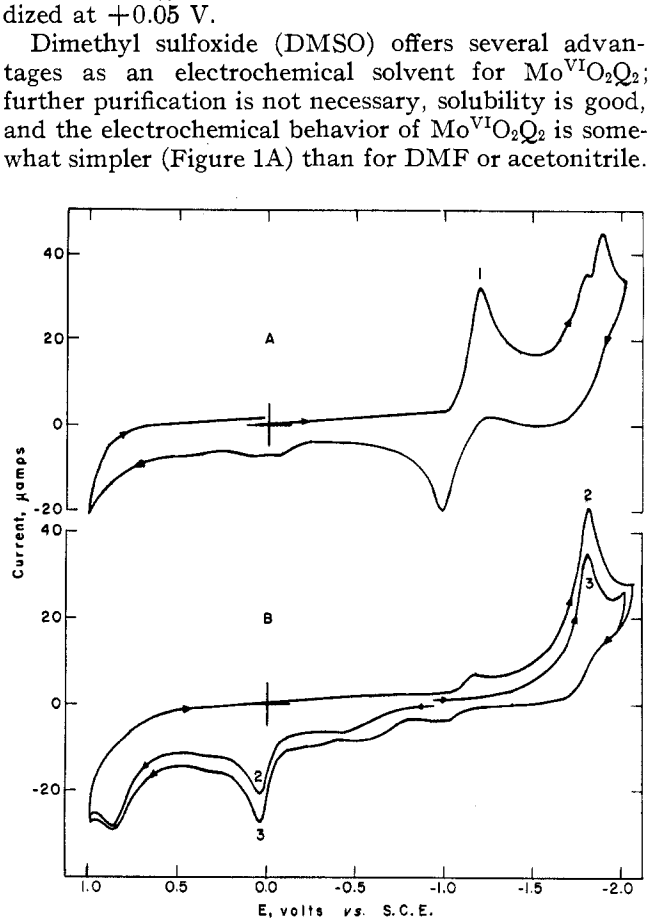


Figure 1—Cyclic voltammograms of 1.0×10^{-3} *F* $Mo^{VI}O_2Q_2$ in 0.1 *F* TEAP in DMSO at a platinum electrode; scan rate, 0.1 V/sec: A, before coulometric reduction at −1.3 V; B, after coulometric reduction at −1.3 V; 1, 3, initial cathodic scan; 2, initial anodic scan.

Cyclic voltammograms for $Mo^{VI}O_2Q_2$ as a function of scan rate indicate that the reduction peak at −1.15 V may consist of two superimposed peaks. However, at a scan rate of 1.0 V/sec this cathodic peak is not distorted and the difference in peak potentials between the cathodic and anodic waves, ΔE_p, is 230 mV (centered at −1.071 V). As the scan rate is decreased, the cathodic wave becomes distorted such that E_p

(19) A. F. Isbell and D. T. Sawyer, *Anal. Chem.*, **41**, 1381 (1969).
(20) H. M. Stevens, *Anal. Chim. Acta*, **14**, 126 (1956).
(21) F. W. Moore and R. E. Rice, *Inorg. Chem.*, **7**, 2510 (1968).
(22) R. J. Magee and A. S. Witwit, *Anal. Chim. Acta*, **29**, 517 (1963).
(23) P. C. H. Mitchell, *J. Chem. Soc. A*, 146 (1969).
(24) F. Pavelka and A. Zucchelli, *Mikrochem. Ver. Mikrochim. Acta*, **31**, 69 (1944).
(25) P. Niericker and W. D. Treadwell, *Helv. Chim. Acta*, **29**, 1472 (1946).
(26) T. Fujinaga, J. Izutsu, and K. Takaoka, *J. Electroanal. Chem.*, **16**, 89 (1968).

measurements are inaccurate. In contrast, the anodic wave remains sharp, so that the difference between its E_p and -1.071 V can be doubled to obtain approximate values for ΔE_p at lower scan rates.

ΔE_p for an electrochemically reversible system (rapid electron-transfer kinetics) is $57/n$ mV.[27] In contrast, an anodic wave is not observed for a totally irreversible reduction (slow electron-transfer kinetics). Therefore, the reduction of $Mo^{VI}O_2Q_2$ is an intermediate case (quasireversible). Nicholson[28] has derived a relationship between ΔE_p and $-\log \nu$ which permits the evaluation of the simple heterogeneous electron-transfer rate constant, $k_{s,h}$. A plot of ΔE_p *vs.* $-\log \nu$ is superimposed on a working plot of ΔE_p *vs.* $\log \psi$. The analytical term ψ is given by

$$\psi = \frac{(D_O/D_R)^{\alpha/2} k_{s,h}}{(n\pi F \nu D_O/RT)^{1/2}} \quad (4)$$

where O and R refer to the oxidized and reduced species, respectively, D is the diffusion coefficient, F is the faraday, and α is the transfer coefficient (that fraction of the potential which favors the reduction reaction). The assumption that the ratio of diffusion coefficients is unity does not introduce as much error as the determination of D_O (discussed below). The results of this treatment are illustrated by Figure 2 and yield approximate values

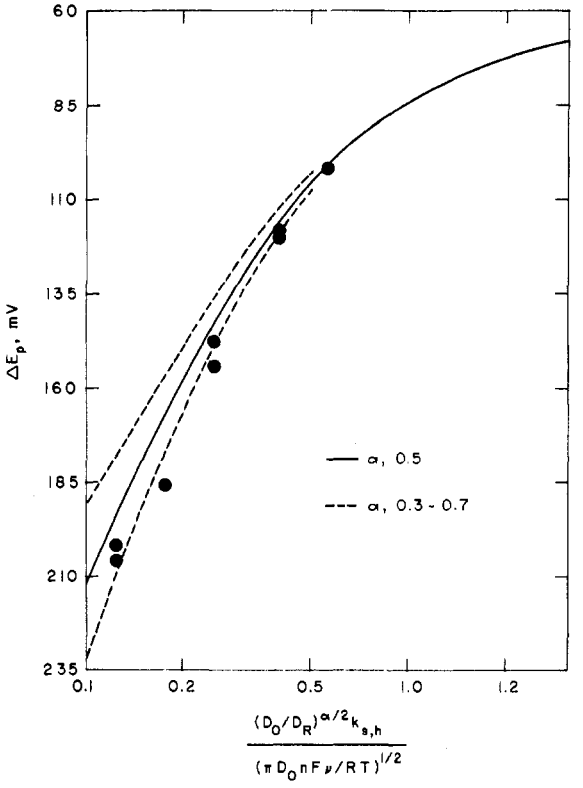


Figure 2.—The variation of cathodic-to-anodic peak potential difference, ΔE_p, as a function of scan rate for the quasireversible reduction of $Mo^{VI}O_2Q_2$. Data points for $E' = -1.071$ V, $D_O = 3.8 \times 10^{-6}$, $n = 1$, $\alpha = 0.7$, and $k_{s,h} = 1.2 \times 10^{-3}$ cm sec^{-1}.

of $k_{s,h}$ (1.2×10^{-3} cm/sec), n (1 electron), and α (0.7). A couple with an α value greater than 0.5 has a sharp cathodic wave and a broad anodic wave, a characteristic which is verified experimentally (Figure 1). The necessity of obtaining ΔE_p values by an indirect method limits the accuracy and reliability of the kinetic parameters. However, the data at high scan rates are obtained directly and smoothly fit the curve in Figure 2.

Chronopotentiometry is a convenient method for the determination of diffusion coefficients. The length of a diffusion-controlled chronopotentiometric wave, τ, is related to the diffusion coefficient, D, by the Sand equation[29]

$$i\tau^{1/2} = 1/2\pi^{1/2} nFAD^{1/2}C \quad (5)$$

where i is the current, τ the transition time, C the bulk concentration of the electroactive species, and A the electrode area.

For the reduction of $Mo^{VI}O_2Q_2$, the $i\tau^{1/2}$ values from chronopotentiometry are not constant, which indicates that the reduction reaction is not a simple diffusion-controlled process. As i increases, $i\tau^{1/2}$ decreases to a constant value of 3.8×10^{-5} A sec$^{1/2}$. This implies that for sufficiently small τ values, the electrochemical reaction goes to completion before chemical complications can occur. Therefore, the value of 3.8×10^{-5} A sec$^{1/2}$ has been used to calculate the diffusion coefficient for $Mo^{VI}O_2Q_2$; the value is 3.8×10^{-6} cm^2/sec.

The value of n for the reduction of $Mo^{VI}O_2Q_2$ depends on the reduction potential, E, at which the coulometric determination is made (Table I). The peak

TABLE I

CONTROLLED-POTENTIAL COULOMETRY OF 1.0×10^{-3} *F* $Mo^{VI}O_2Q_2$ (0.1 *F* TEAP) IN DMSO AT A PLATINUM ELECTRODE AND PEAK CURRENTS FOR THE RESULTING PRODUCT SOLUTIONS

E vs. sce, V	n	i_{pa}(+0.85 V), μA	i_{pa}(+0.85 V), μA	i_{pc}(−1.78 V), μA
−1.1	1.2	20	0	53
−1.2	1.7	21	15	28
−1.3	1.7	22	23	23
−1.4	2.0	24	25	19
−1.5	1.9	23	32	16
−1.9	3.2	22	73	0

currents of the reduction products indicate that the concentration of the product oxidizable at +0.85 V is independent of n. However, the concentration of the product reducible at −1.78 V decreases and the concentration of the product oxidizable at +0.05 V increases as n increases. The addition of H^+ to a solution of reduced $Mo^{VI}O_2Q_2$ increases the cathodic peak current and decreases the anodic peak current; addition of OH^- has the opposite effect. The electronic spectrum of reduced $Mo^{VI}O_2Q_2$ appears to be the sum of the spectra for HQ and Q^-. Because Q^- is oxidized at +0.05 V, the species that is reduced at −1.78 V probably is HQ; addition of HQ to reduced $Mo^{VI}O_2Q_2$ causes an increase in the cathodic peak current. HQ normally is reduced at −1.91 V, but the incremental addition of $Mo^{VI}O_2Q_2$ to a solution of HQ shifts its reduction potential to −1.74 V. Association between HQ and some molybdenum species must be responsible for this anodic shift. In a similar manner, the addition of increments of HQ to a solution of $Mo^{VI}O_2Q_2$ results in the appearance of a reduction wave at −1.73 V.

Interruption of a coulometric experiment periodically to investigate for intermediates by cyclic voltammetry

(27) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(28) R. S. Nicholson, *ibid.*, **36**, 1351 (1964).
(29) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience, New York, N. Y., 1954, Chapter 8.

causes the total analysis time to increase and the final n value to decrease. This indicates that a chemical reaction follows the initial one-electron reduction preventing all of the one-electron reduction product from undergoing a second one-electron step. By decreasing the concentration of the electroactive species, n increases. This indicates that the rate of the competing chemical reaction is concentration dependent.

The addition of HQ to a solution of $Mo^{VI}O_2Q_2$ causes an increase in the cathodic peak current at -1.14 V, which implies a catalytic regeneration of one of the species reduced at -1.14 V. Because the electronic spectrum of a $Mo^{VI}O_2Q_2$–HQ mixture is the sum of the individual spectra of $Mo^{VI}O_2Q_2$ and HQ, there does not appear to be a significant interaction between the two species. Thus, the interaction must occur between reduced $Mo^{VI}O_2Q_2$ and HQ. The n value for the coulometric reduction of $Mo^{VI}O_2Q_2$ at -1.3 V increases as the concentration of HQ is increased, which supports the conclusion that there is catalytic reduction of HQ by reduced $Mo^{VI}O_2Q_2$.

The proposal that HQ is a product of $Mo^{VI}O_2Q_2$ reduction requires a source of H^+. Q^- is not a strong enough base to abstract H^+ from any abundant species in solution because both HQ and Q^- coexist; H^+ must be made available from some other reaction. DMSO is present in abundance but does not have any acidic protons and is not easily reduced or oxidized. TEAP is present in 100-fold excess over $Mo^{VI}O_2Q_2$. The perchlorate ion has no protons to lose, but the tetraethylammonium ion has been shown to lose a proton to a strong base[30]

$$B^- + (C_2H_5)_4N^+ \longrightarrow BH + (C_2H_5)_3N + CH_2{=}CH_2 \quad (6)$$

Coulometric reduction of $Mo^{VI}O_2Q_2$ in a sealed cell followed by gas chromatographic analysis of the gas space above the solution indicates that ethylene is not formed during any stage of the reduction. The sensitivity of the analytical method is more than adequate to detect the levels of ethylene that would be formed by reaction 6. Therefore, TEAP can be eliminated as a proton source.

Water comprises 0.05% of Baker reagent grade DMSO. Converting to concentration, 0.05% water is roughly 30 mM or a 30-fold excess over $Mo^{VI}O_2Q_2$. In spite of this, the reduction and oxidation of water are difficult in DMSO due to strong hydrogen bonding. Because of this hydrogen bonding, DMSO normally can be used as an electrochemical solvent directly from the bottle without prior drying. However, molybdenum in high oxidation states has a strong affinity for oxygen-containing species, especially if the primary coordination sites are not occupied by an oxygen atom. In the case of the reduction product of $Mo^{VI}O_2Q_2$, this affinity may be sufficiently strong to abstract an OH^- group from hydrogen-bonded water in DMSO and thereby release a proton to the solution. Although no direct evidence exists to support this proposal, the absence of alternative sources of protons leads to the conclusion that water is their source during the reduction of $Mo^{VI}O_2Q_2$.

The peak potentials and currents of the reduction waves for H^+ and $Mo^{VI}O_2Q_2$ are not affected when either species is added to a solution of the other species. However, addition of OH^- decreases the peak currents of the $Mo^{VI}O_2Q_2$ reduction waves, increases the peak current for the oxidation of Q^-, and causes the appearance of a new anodic peak at $+0.9$ V. With continued addition of OH^-, the $Mo^{VI}O_2Q_2$ reduction waves disappear completely leaving one anodic wave corresponding to the oxidation of 2 mol of Q^- per mole of $Mo^{VI}O_2Q_2$ and a second anodic peak at $+0.9$ V. Neutralization of the basic solution leads to the slow formation of $Mo^{VI}O_2Q_2$ as shown by cyclic voltammetry.

Three cathodic peaks are observed around -1.8 V during cyclic voltammetry of $Mo^{VI}O_2Q_2$. For a scan rate of 1.0 V/sec, overlapping peaks are observed at -1.72 and -1.85 V. As the scan rate is decreased, a new peak appears at -1.78 V while the peak at -1.72 V disappears and the peak at -1.85 V shifts anodically to -1.82 V. After coulometry between -1.1 and -1.5 V, only the cathodic peak at -1.78 V remains. Because evidence indicates that HQ is reduced at -1.78 V in the presence of reduced $Mo^{VI}O_2Q_2$, further coulometric reduction at -1.9 V corresponds to the reduction of free HQ. Coulometry at -1.3 and -1.9 V successively gives a total n value of 3.4 electrons. The resulting solution has a cyclic voltammogram identical with that observed after the addition of OH^- to a solution of $Mo^{VI}O_2Q_2$. The peak current of the anodic wave at $+0.05$ V and the electronic spectrum indicate that both of the Q^- ligands originally complexed with Mo(VI) are free in solution.

Coulometric oxidation at $+0.9$ V is so hindered that an accurate determination of n is impossible. The oxidation appears to be a one-electron process producing $Mo^{VI}O_2Q_2$ as determined from the cyclic voltammogram of the oxidized solution.

Electron paramagnetic resonance (epr) spectroscopy provides a means of studying $Mo^{VI}O_2Q_2$ reduction intermediates. Monomeric Mo(V) is a d^1 ion coupled with nuclear spins of 0 for the 75%-abundant isotopes and $^5/_2$ for the remaining isotopes. The resulting spectrum is a large singlet and six small satellites. The d^2 Mo(IV) ion in high-spin complexes has a triplet epr signal but no signal in low-spin complexes.[31] The d^3 Mo(III) ion has three unpaired electrons in an octahedral field, resulting in severe line broadening. No epr signal has been reported for Mo(III) in solution.[32]

An epr signal is not observed for the coulometric reduction product of $Mo^{VI}O_2Q_2$. However, two overlapping singlets are observed during the reduction of $Mo^{VI}O_2Q_2$ in an epr-electrolysis flow cell. These singlets have the appropriate g values and peak widths expected for Mo(V) species. Exact g values have not been measured for these signals, but under the experimental conditions employed, their resonance fields are approximately 3412 and 3424 G. These signals appear to originate from two different monomeric Mo(V) intermediates. The $^5/_2$ spin satellites were not observed due to low signal intensity.

The cyclic voltammogram of μ-oxo-dioxotetrakis-(8-quinolinolato)dimolybdenum(V) ($Mo^V_2O_3Q_4$) is complicated (Figure 3). For a cathodic scan, peaks are observed at -1.21, -1.57, and -2.0 V followed by anodic peaks at -1.15, -0.98, and $+0.59$ V. The

(30) A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, **40**, 83 (1968).

(31) E. P. Guymon and J. T. Spence, *J. Phys. Chem.*, **71**, 1616 (1967).

(32) J. T. Spence, *Coord. Chem. Rev.*, **4**, 475 (1969).

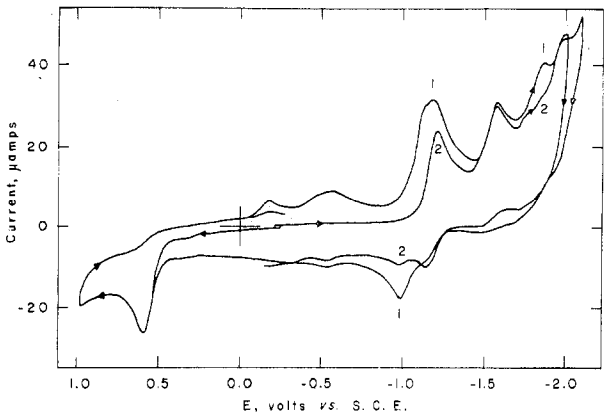


Figure 3.—Cyclic voltammograms of 0.98×10^{-3} *F* $Mo^{V}_2O_3Q_4$ in 0.1 *F* TEAP in DMSO at a platinum electrode; scan rate, 0.1 V/sec: 1, initial anodic scan; 2, initial cathodic scan.

same waves are observed for an initial anodic scan together with small cathodic waves at −0.17 and −0.56 V; the cathodic waves at −1.15 and −1.86 V are larger as is the anodic peak at −0.98 V. The peaks at −1.15, −1.86, and −0.98 are identical with those observed for cyclic voltammetry of $Mo^{VI}O_2Q_2$. The oxidation of $Mo^{V}_2O_3Q_4$ at +0.59 V appears to produce $Mo^{VI}O_2Q_2$ and is a totally irreversible process.

of $(E_p - E')n$ *vs.* log $(k_fRC/nF\nu)$, the combination of E', n, and k_f can be determined (see Figure 4). The initial reduction of $Mo^{V}_2O_3Q_4$ has an n value of 1 and an E' value of −1.187 V. Using these values, the postchemical reaction has a value for k_f of 7.2×10^{-2} sec^{-1}.

A study of the cathodic wave at −1.57 V as a function of scan rate indicates that a small anodic wave appears at −1.52 V at rates of 1.0 V/sec. This second reduction of $Mo^{V}_2O_3Q_4$ also agrees with the treatment of a reversible electron-transfer step followed by a chemical reaction. By assuming n is 1 and E' is −1.560 V, the value for k_f is 1.7 sec^{-1} (see Figure 4).

The chemical reaction following the reduction of $Mo^{V}_2O_3Q_4$ at −1.187 V is so slow that the chronopotentiometric reduction approximates a simple reversible electron transfer for high currents (where $i\tau^{1/2}$ is independent of i) such that[33]

$$E = E' + \frac{RT}{nF} \ln\left[\left(\frac{\tau}{t}\right)^{1/2} - 1\right] + \frac{RT}{2nF} \ln\left(\frac{D_R}{D_O}\right) \quad (7)$$

with E the potential at t seconds after constant current is applied. When t is $\tau/4$, eq 7 reduces to

$$E_{\tau/4} = E' + \frac{RT}{2nF} \ln\left(\frac{D_R}{D_O}\right) \quad (8)$$

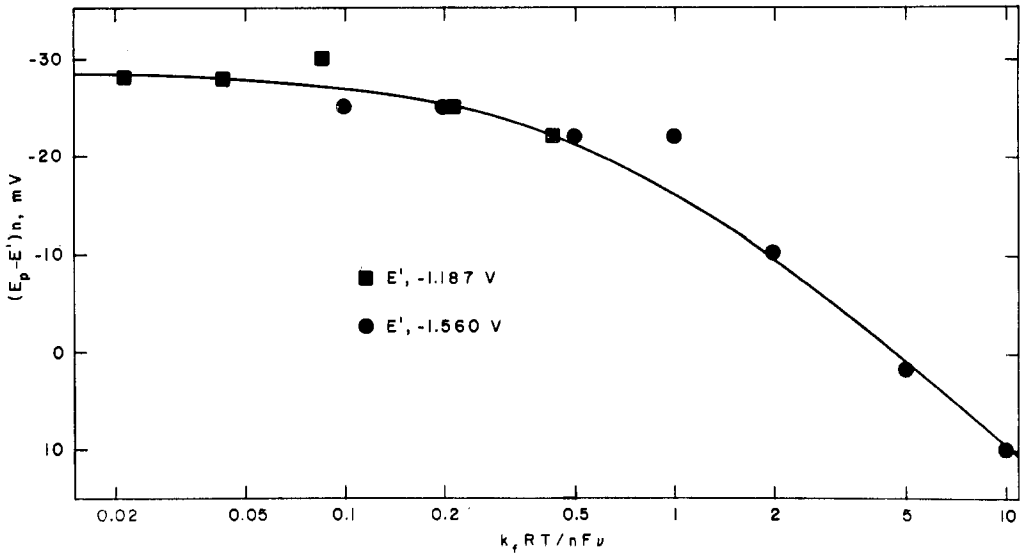


Figure 4.—The variation of peak potential, E_p, as a function of scan rate for the reduction of $Mo^{V}_2O_3Q_4$. Data points for $E' = -1.187$ V, $n = 1$, and $k_f = 7.2 \times 10^{-2}$ sec^{-1} (Mo^{V}–Mo^{V}/Mo^{V}–Mo^{IV}) and for $E' = -1.560$ V, $n = 1$, and $k_f = 1.7$ sec^{-1} (Mo^{V}–Mo^{IV}/Mo^{IV}–Mo^{IV}).

The cathodic peak at −1.21 V, which is coupled with the anodic peak at −1.15 V, remains constant for scan rates from 1.0 to 0.1 V/sec but begins to shift anodically at lower scan rates. The value for ΔE_p at high scan rates is 60 mV compared with the theoretical value of $57/n$ mV for a reversible electron transfer. This implies that n is 1. The formal potential, E', which is 28.5 mV anodic of the cathodic peak potential for a reversible process, can be determined from Figure 3 to have a value of −1.187 V. Nicholson and Shain's treatment[27] of a reversible electron-transfer step followed by an irreversible chemical reaction permits calculation of the first-order rate constant, K_f, for the following chemical reaction. If the experimental points for E_{pc} *vs.* −log ν are superimposed on a working curve

From a plot of E *vs.* ln $(\tau/t)^{1/2} - 1$, n can be calculated. For the reduction of $Mo^{V}_2O_3Q_4$, n is 1.1 electrons per $Mo^{V}_2O_3Q_4$ molecule and $E_{\tau/4}$ is −1.167 V. Although D_R/D_O is not known, E' must be approximately equal to $E_{\tau/4}$.

The diffusion coefficient for $Mo^{V}_2O_3Q_4$ can be calculated from its chronopotentiometric reduction wave; the value is 2.2×10^{-6} cm^2/sec. The chronopotentiogram for the oxidation of $Mo^{V}_2O_3Q_4$ is poorly shaped because of the overlapping oxidation of an impurity, which precludes its use for another determination of the diffusion coefficient.

The coulometric reduction of $Mo^{V}_2O_3Q_4$ at −1.3 V indicates that n is 2.3 electrons. The coulometric curve

(33) W. H. Reinmuth, *Anal. Chem.*, **32**, 1514 (1960).

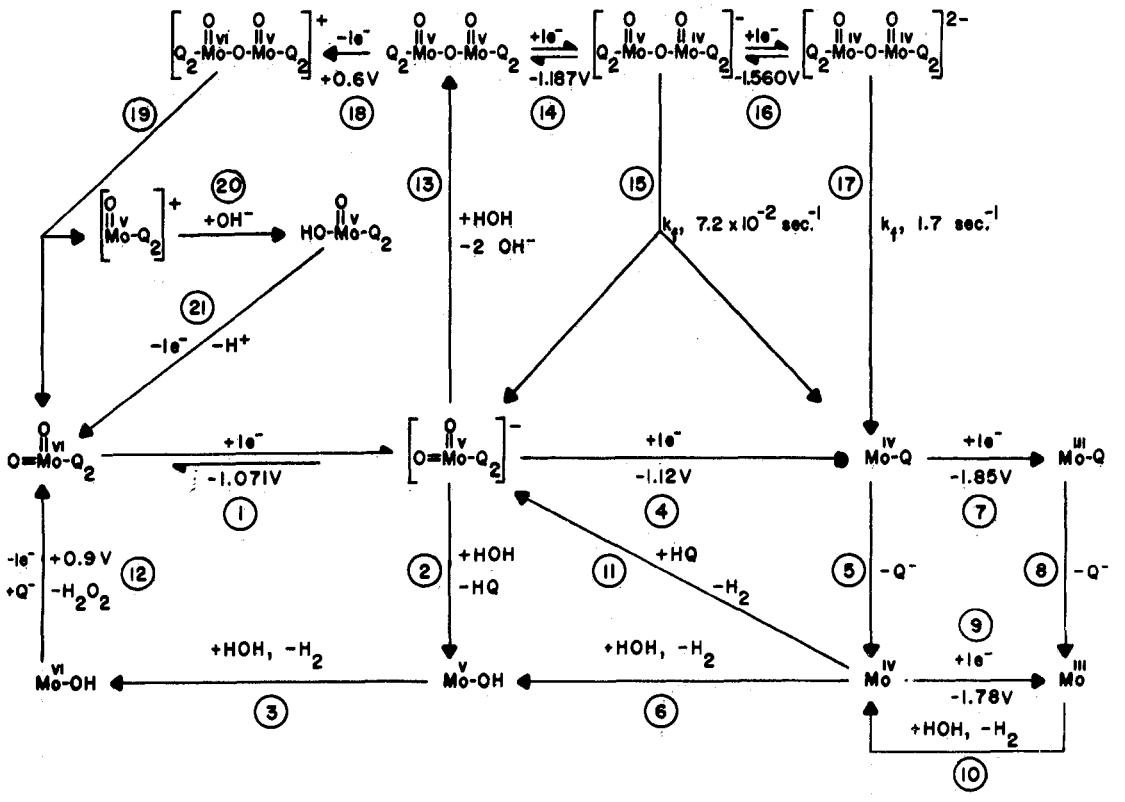


Figure 5.—Redox mechanism for the molybdenum(VI,V)–8-quinolinol complexes in aprotic media.

begins to plateau at n equal to 1 but then continues to increase almost linearly until it plateaus at n equal to 2.3. The cyclic voltammogram of the reduced solution is identical with that of a solution of reduced $Mo^{VI}O_2Q_2$ except for a small cathodic wave at -1.57 and a small anodic wave at $+0.60$ V. The electronic spectrum of the reduced solution appears to be the same as the spectrum of Q^-.

The epr spectrum taken during the reduction of $Mo^{V}_2O_3Q_4$ at -1.3 V indicates that a signal initially appears at a field of 3403 G followed by a second signal at 3410 G. When the applied potential is turned off, the signal at 3403 G decays faster than the signal at 3410 G. The signal at 3403 G must be due to the initial reduction product of $Mo^{V}_2O_3Q_4$ while the signal at 3410 G must be due to a secondary product.

The cyclic voltammogram of a solution produced by the coulometric oxidation of $Mo^{V}_2O_3Q_4$ at $+0.7$ V is identical with that for $Mo^{VI}O_2Q_2$ except for a cathodic wave at -0.65 V. The i_p of the $Mo^{VI}O_2Q_2$ reduction wave indicates that 2 mol of $Mo^{VI}O_2Q_2$ is produced for every mole of $Mo^{V}_2O_3Q_4$ oxidized. The cathodic wave at -0.65 is identical with that for H^+ reduction.

The epr spectrum of the oxidation intermediates of $Mo^{V}_2O_3Q_4$ has an initial signal at 3394 G followed by a weak signal at 3384 G and finally a larger signal at 3373 G. The signal at 3394 G must be due to the original one-electron oxidation product of $Mo^{V}_2O_3$ while the other signals are due to secondary products.

Discussion and Conclusions

Figure 5 summarizes a redox mechanism for the molybdenum–8-quinolinol complexes that has been derived from the experimental data. In the absence of any structural information, only molybdenum oxidation states and the type of ligands are inferred in this figure. Reactions 1–12 comprise the mechanism starting with $Mo^{VI}O_2Q_2$. The purple intermediate observed during the coulometric reduction of $Mo^{VI}O_2Q_2$ in acetonitrile and DMF necessitates inclusion of reactions 13–15.

The increase of n from 1 to 2 as the coulometric reduction potential is made more cathodic indicates that a chemical reaction is competing with the second one-electron reduction (reactions 1, 2, and 4). The products of reactions 1 and 2 account for the two singlets in the epr spectrum.

The products obtained during the coulometric reduction at -1.1 V yield a species oxidizable at $+0.9$ V plus the HQ produced in reaction 2 when water attacks the initial $Mo^{VI}O_2Q_2$ reduction product. The addition of OH^- to $Mo^{VI}O_2Q_2$ results in a species oxidizable at $+0.9$ V. If both species are identical, $Mo^{V}OH$ must be oxidized chemically. The Mo(V) species produced at -1.07 V is a good reducing agent and has a strong affinity for oxygen-containing species. Hence, water appears to be reduced to give a $Mo^{VI}OH$ product (reaction 3). If a diamagnetic monooxo- or dioxo-bridged Mo(V) dimer were the final reduction product, the solution color would be expected to be orange-brown or deep purple, respectively. Instead, the solution is the yellowish color of Q^- indicating that the molybdenum-containing species is the characteristic pale color of Mo(VI). The oxidation potential of free OH^- ion is $+0.75$ V.[30] Thus, the complexation of OH^- by Mo(VI) causes the oxidation of OH^- to be more difficult. As reaction 12 indicates, $Mo^{VI}OH$ is oxidized at $+0.9$ V in the presence of free Q^- to give $Mo^{VI}O_2Q_2$.

As the coulometric reduction potential is made more cathodic, reaction 4 becomes faster than reaction 2. The amount of $Mo^{VI}OH$ produced is independent of

the coulometric reduction potential, so the Mo(IV) product of reaction 4 must be chemically oxidized. If Mo(V) is a sufficiently strong reducing agent to reduce water, then Mo(IV) should also reduce water (reaction 6). Reaction 5 is necessary to explain the cathodic waves at −1.85 and −1.78 V during the cyclic voltammetry of $Mo^{VI}O_2Q_2$ and to account for the free Q^- in solution after the coulometric reduction of $Mo^{VI}O_2Q_2$. Coulometry at −1.9 V does not appear to produce any molybdenum-containing species other than the one oxidizable at +0.9 V, so reactions 8 and 10 are necessary to account for the oxidation of Mo(III). The assignment of potentials to reactions 7 and 9 is based on the fact that the peak current at −1.78 V increases relative to that at −1.85 V as the scan rate decreases; a lower scan rate allows more time for reaction 5 to occur.

Reaction 11 is necessary to explain the catalytic reduction of HQ by a Mo(IV) species. Investigators have reported that Mo(IV) catalyzes the reduction of dimethylglyoxime,[34] perchlorate ion,[35,36] nitrate ion,[37,38] oxalate ion,[39] triiodide ion,[31] and oxygen.[31]

Figure 5 also includes the redox mechanisms for $Mo^{V}_2O_3Q_4$ because there is evidence for common redox products from $Mo^{VI}O_2Q_2$ and $Mo^{V}_2O_3Q_4$. Because the reduction of $Mo^{V}_2O_3Q_4$ occurs in two reversible one-electron steps, a mixed-oxidation-state dimer must exist as an intermediate. The Mo(V)–Mo(IV) dimer resulting from the one-electron reduction of $Mo^{V}_2O_3Q_4$ (reaction 14) is relatively stable; its epr spectrum is intense and long-lived. Cyclic voltammetry indicates that its decomposition proceeds by a first-order process whose rate constant is 7.2×10^{-2} sec^{-1} (reaction 15). Because coulometry indicates that n is 2.3 electrons for reduction at −1.3 V, the decomposition product of the Mo(V)–Mo(IV) dimer is reducible at −1.3 V (reaction 4). The epr signal initially seen at 3403 G is due to the Mo(V)–Mo(IV) dimer while the signal observed subsequently at 3410 G is the decomposition product of the Mo(V)–Mo(IV) dimer. This secondary signal occurs at the same field as one of the signals observed during the reduction of $Mo^{VI}O_2Q_2$. The final reduction product of $Mo^{V}_2O_3Q_4$ is identical with that for $Mo^{VI}O_2Q_2$, so the mechanisms for the reduction of both complexes interlock.

Cyclic voltammetry indicates that the decomposition of the Mo(IV) dimer produced by the one-electron reduction of the Mo(V)–Mo(IV) dimer is faster than that of the Mo(V)–Mo(IV) dimer (reaction 17). Mo(V) forms stable dimeric species whereas no stable Mo(IV) dimers are known.

The irreversible oxidation of $Mo^{V}_2O_3Q_4$ proceeds by a one-electron mechanism on the cyclic-voltammetric time scale (reaction 18) and by a two-electron mechanism on the coulometric time scale. Therefore, the initial oxidation product is a Mo(VI)–Mo(V) dimer whose epr signal occurs at the same field as the Mo(V)–Mo(IV) dimer. The decomposition rate of this dimer is not known (reaction 19), but the initial Mo(V) decomposition product reacts further to produce another epr-active Mo(V) species. This final Mo(V) species is oxidized to $Mo^{VI}O_2Q_2$. The resonance fields of the two secondary Mo(V) products are lower than those of other Mo–Q reduction intermediates. Therefore, these intermediates are unique to the oxidation of $Mo^{V}_2O_3Q_4$, and their compositions are unknown. The apparent production of H^+ during the oxidation implicates water in the mechanism and makes reactions 20 and 21 necessary.

The complexity of the redox mechanism for $Mo^{VI}O_2Q_2$ and $Mo^{V}_2O_3Q_4$ does not indicate that molybdenum–8-quinolinol complexes in aprotic media are poor models for enzymatic molybdenum. If the redox properties required of the metal in metal-containing redox enzymes were simple, then many other metals would be satisfactory for enzymatic systems. Possibly, the catalytic behavior of Mo(IV) is the key to its necessity in certain enzymes. The synthesis of tris(8-quinolinolato)molybdenum(III) has been reported.[40] Electrochemical oxidation of this complex might provide additional information about the catalytic nature of Mo(IV) and the types of compounds reduced by it.

The range of redox potentials available from the Mo–Q system is extreme for a two-component system. With redox potentials ranging from +0.9 to −1.9 V, the Mo–Q system offers a series of species which vary from reducing to oxidizing agents. This versatility may be an additional property which makes Mo ideal for enzymatic systems.

Ehman[41] has shown that the Fe(II)–Fe(III) redox potential varies with the structure and type of Fe complex. Likewise, a comparison of the redox behavior of Mo–EDTA[42] and Mo–Q complexes indicates that the Mo(VI)–Mo(V) redox potential is dependent on structure. The electrochemical versatility of the flavins[15] and their occurrence in enzymatic systems indicates that the molybdenum–flavin system would be a logical extension of the present investigation. In addition, the extreme range of the Mo–Q redox potentials prob-

TABLE II

FORMAL POTENTIALS AND PEAK POTENTIALS (ν, 0.1 V/SEC) OF FLAVIN-RELEVANT REDOX COUPLES IN DMSO (0.1 F TEAP)[a]

Couple	Potentials *vs.* sce, V: E'	E_{pc}	E_{pa}
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	+0.23		
$FeOx_3 + e^- \rightleftarrows FeOx_3^-$	−0.59		
$O_2 + e^- \rightleftarrows O_2^-$	−0.75		
3-MeFl + $e^- \rightleftarrows$ 3-MeFl$^-$	−0.80		
Rib + $e^- \rightarrow$ Rib$^-$		−0.82	
Rib$^-$ → Rib + e^-			−0.55
$Fe^{II}Rib^- \rightarrow$ Rib + Fe(II) + e^-			−0.42
$MoO_2Ox_2 + e^- \rightleftarrows MoO_2Ox_2$	−1.07		
$MoO_2Ox_2^- + e^- \rightarrow$ Mo(IV)		−1.12	
$Mo_2O_3Ox_4 + e^- \rightleftarrows Mo_2O_3Ox_4^-$	−1.19		
$Mo_2O_3Ox_4^- + e^- \rightleftarrows Mo_2O_3Ox_4^{2-}$	−1.56		
Rib$^-$ + $e^- \rightarrow$ Rib^{2-}		−1.3	
RibH$^-$ → Rib + H^- + 2e^-			−0.55
3-MeFl$^-$ + $e^- \rightarrow$ 3-MeFl^{2-}		−1.62	
3-MeFlH$^-$ → 3-MeFl + H^+ + 2e^-			−0.78

[a] Abbreviations: Rib, riboflavin; 3-MeFl, 3-methyllumiflavin; Ox, 8-quinolinol anion.

(34) A. Narayanan and P. R. Subbaraman, *Indian J. Chem.*, **6**, 265 (1968).

(35) G. P. Haight, Jr., and W. F. Sager, *J. Amer. Chem. Soc.*, **74**, 6056 (1952).

(36) G. P. Haight, Jr., *Anal. Chem.*, **23**, 1505 (1951).

(37) G. P. Haight, Jr., P. Mohilner, and A. Katz, *Acta Chem. Scand.*, **16**, 221 (1962).

(38) G. P. Haight, Jr., and A. Katz, *ibid.*, **16**, 659 (1962).

(39) E. W. Zahnow and R. J. Robinson, *J. Electroanal. Chem.*, **3**, 262 (1962).

(40) Q. W. Choi, J. S. Oh, K. W. Lee, and W. Lee, *Daehan Hwahak Hwoejee*, **12**, 146 (1968); *Chem. Abstr.*, **71**, 24048 (1969).

(41) D. L. Ehman and D. T. Sawyer, *Inorg. Chem.*, **8**, 900 (1969).

(42) F. A. Schultz and D. T. Sawyer, *J. Electroanal. Chem.*, **17**, 207 (1968).

ably will be enhanced by the substitution of a flavin radical for Q^-.[43]

Consideration of the total collection of nonaqueous electrochemical data permits tabulation of a set of formal potentials, E', for oxidation–reduction couples that are relevant to the chemistry of the flavoproteins; Table II summarizes such potentials (*vs.* sce) in DMSO with 0.1 *F* TEAP as the supporting electrolyte. The values represent the average between the cathodic and anodic peak potentials (from cyclic voltammetry) and $E_{\tau/4}$ values (from chronopotentiometry). In addition, the peak potentials at a scan rate of 0.1. V/sec are presented for several irreversible couples. Reference to the potentials in Table II indicates that the electron-transfer mechanism of metalloflavins, in the absence of other factors, probably occurs by the path

$$\text{substrate} \longrightarrow \text{Mo(VI)–Mo(V)} \longrightarrow \text{FAD–FADH}\cdot \longrightarrow \text{Fe(III)–Fe(II)} \quad (9)$$

This is in agreement with the proposals by several investigators of the flavin enzymes[1,2,10,14] and lends support to the proposal that the electron-transfer steps occur in an aprotic environment. Additional studies of the molybdenum–flavin system are in progress to further elucidate the detailed mechanism of electron transfer for the metalloflavin enzymes.

Acknowledgments.—This work was supported by the National Science Foundation under Grant No. GP-16114. We are grateful for an NSF traineeship awarded to A. F. I., Jr.

(43) L. S. Meriwether, W. F. Marzluff, and W. A. Hodgson, *Nature (London)*, **212**, 465 (1966).

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Kinetic Studies on the Formation of a Cyanide-Bridged Adduct of Two Cationic Metal Complexes[1a]

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Received February 25, 1971

Kinetic studies have been carried out on the formation of Cr–NC–Hg^{4+} by the reaction of $CrCN^{2+}$ with Hg^{2+}, which occurs at a rate given by

$$\frac{d[\text{Cr–NC–Hg}^{4+}]}{dt} = \frac{A + B[\text{Hg}^{2+}]}{1 + C[\text{Hg}^{2+}]}[\text{CrCN}^{2+}]_T$$

with values $A = 2.8 \times 10^{-3}$ sec^{-1}, B (M^{-1} sec^{-1}) $= 0.62 + 0.25/[H^+]$, and $C = 24.2 \pm 2.2$ M^{-1} at 25.0° and $\mu = 2.0$ M. The rate constant A represents a correction for a minor pathway; the proposed mechanism for the main pathway involves a rapid association between the two cations, followed by an internal rearrangement or isomerization to yield the final product. Spectrophotometric measurements on the solutions immediately after mixing gave independent evidence for the prior association complex, whose stability constant is represented by C. These studies permit the independent evaluation of C as 28.4 ± 2.5 M^{-1} and generate the visible absorption spectrum of the intermediate. The steps in the mechanism are discussed, and some conjectures are made concerning the structure of the rapidly formed association complex.

Introduction

Polyvalent cationic complexes do not commonly associate with one another to an appreciable extent in aqueous solution. Not only do their like charges destabilize the interaction, but the coordinating strength of a polar solvent which is capable of dissolving and ionizing the parent compounds usually outweighs the stability of a $[MXM']^{m+}$ dinuclear species. Stable association can occur, however, when an ambidentate ligand having both hard base and soft base donor atoms simultaneously associates with a hard and a soft metal ion. This is the case[2–5] with adducts of metal–isothiocyanate complexes and mercury(II), as in eq I.

$$\text{M–NCS}^{2+} + \text{Hg}^{2+} \rightleftharpoons \text{M–NCS–Hg}^{4+} \quad (I)$$

The equilibrium quotients at 25° are 1.7×10^4 M^{-1} for $CrNCS^{2+}$ ($\mu = 1.0$ M)[4] and 9.8×10^4 M^{-1} for $Co(NH_3)_5NCS^{2+}$ ($\mu = 0.10$ M).[5b] The driving force for reaction I resides in the hard acid–hard base interaction, Cr–N, and (especially) the soft–soft interaction, Hg–S. This reaction occurs "instantaneously"; a further reaction slowly takes place,[4] which preserves all the features of stability associated with reaction I, while relieving the electrostatic repulsions associated with the 4+ adduct, as in the reaction

$$(H_2O)_5\text{Cr–NCS–Hg}^{4+} + H_2O \longrightarrow \text{Cr}(H_2O)_6^{3+} + \text{HgSCN}^+ \text{ (slow)} \quad (II)$$

A somewhat different sequence of events transpires when the reactant with Hg^{2+} is the cyano complex $Cr–CN^{2+}$. A stable association occurs[6] accompanied by a rearrangement reaction, linkage isomerization of cyanide ion. This process (reaction III) does not occur

$$\text{Cr–CN}^{2+} + \text{Hg}^{2+} = \text{Hg–CN–Cr}^{4+} \quad (III)$$

instantaneously, unlike reaction I. In the present paper we report the results of kinetic and spectrophotometric studies in the mechanism of reaction III.

(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2799. (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

(2) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966).

(3) M. Orhanović and N. Sutin, *ibid.*, **90**, 538, 4286 (1968).

(4) J. N. Armor and A. Haim, *ibid.*, **93**, 867 (1971).

(5) (a) K. Schug and B. Miniatas, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p M136; (b) L. C. Falk and R. G. Linck, *Inorg. Chem.*, **10**, 215 (1971).

(6) J. P. Birk and J. H. Espenson, *ibid.*, **7**, 991 (1968).