Contribution from the Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322

Electrochemistry of Monomeric Molybdenum(V)–Oxo Complexes in Dimethylformamide

R. D. TAYLOR, J. P. STREET, M. MINELLI, and J. T. SPENCE*

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The electrochemistry of nine monomeric molybdenum(V)–oxo complexes in dimethylformamide has been investigated by cyclic voltammetry and controlled-potential coulometry at a platinum electrode. $MoOCl_3L$ (L = *o*-phenanthroline, α,α'-bipyridyl), $MoOClL_2$ (L = 8-hydroxyquinoline, 8-mercaptoquinoline), and MoOClL (L = disalicylaldehyde *o*-phenylenediimine, *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine, *N,N'*-bis(2-mercapto-2-methylpropyl)ethylenediamine) are facilely reduced by one-electron reductions to Mo(IV) species. $(C_2H_5)_4NMoOCl_2$(salicylaldehyde *o*-hydroxyanil) is reduced in a two-electron step to an Mo(III) species. None of the complexes are oxidizable in the voltage range used (+0.50 to −2.50 V vs. SCE) to Mo(VI) complexes. Comparison with reduction peaks for molybdenum(VI)–dioxo complexes indicates the Mo(V) monomers are not obtainable by electrochemical reduction of the Mo(VI) complexes, and are, in some cases, thermodynamically unstable to disproportionation into Mo(IV) and Mo(VI). Implications for redox states in molybdenum enzymes are discussed.

Introduction

Molybdenum is now well established as a necessary cofactor for a number of redox enzymes,[1,2] and there is considerable current interest in the properties and reactions of its complexes as possible models for these enzymes.[2-4] During catalysis, Mo(V) has been identified by electron spin resonance (ESR) spectrometry for the molybdenum enzymes xanthine oxidase, aldehyde oxidase, sulfite oxidase, and nitrate reductase.[1,2,5] The ESR signal appears to arise from a monomeric Mo(V) center as a result of electron transfer to or from the substrate.[1,2,5] Clearly, a knowledge of the structures, properties, and reactions of monomeric Mo(V) complexes is of importance for an understanding of these enzymes.

The aqueous chemistry of Mo(V) is dominated by ESR inactive oxo-bridged dimers;[2,3] in nonaqueous solvents, however, monomers are reasonably stable, and a number of such complexes have been reported in the literature.[2,6,7] The electrochemistry of a few dioxomolybdenum(VI) complexes and Mo(V) oxo-bridged dimers has been investigated,[8-11] but few data concerning the electrochemical behavior for monomeric molybdenum(V)–oxo complexes are available.[2] Such data are necessary for a proper understanding of the redox behavior of the molybdenum centers of the enzymes.

As part of our model studies for molybdenum enzymes, we have investigated the electrochemistry of the monomeric molybdenum(V)–oxo complexes $MoOCl_3L$ (L = *o*-phenanthroline, α,α'-bipyridyl), $MoOClL_2$ (L = 8-hydroxyquinoline, 8-mercaptoquinoline), MoOClL (L = disalicylaldehyde *o*-phenylenediimine, *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine, *N,N'*-bis(2-mercapto-2-methylpropyl)ethylenediamine), and $(C_2H_5)_4NMoOCl_2L$ (L = salicylaldehyde *o*-hydroxyanil), and the results are reported here.[12]

Results

All the complexes except MoOCl(salphen)[12] can exist in both cis and trans isomers with respect to the donor atom coordinated in the position trans to the MoO (oxo) group. In this work, cis and trans refer to the position of the coordinated chelate ligand with respect to the oxo group. The basis for assignment of cis or trans structures for the complexes has been previously reported;[6,7] it must be pointed out, however, only the structures of *trans*-$MoOCl_3$(bpy),[12] *trans*-MoOCl$(tox)_2$ (N trans to oxo, two S atoms trans to each other), and *trans*-$(C_2H_5)_4$-$NMoOCl_2$(sap) (N trans to oxo)[12,13] have been established by X-ray crystallography, and some of the assignments are tentative.[7]

Cyclic Voltammetry. Preliminary work indicated satisfactory voltammograms could be obtained in dimethylformamide (DMF), dimethyl sulfoxide (Me_2SO), or CH_3CN, using $(C_2H_5)_4NCl$ (TEACl), $(n\text{-}C_4H_9)_4NBF_4$ (TBATFB), or $(C_2H_5)_4NClO_4$ (TEAP) as electrolyte. Coulometric experiments, however, indicated Me_2SO and TEAP oxidize the initial reduction products of the complexes to Mo(VI) species, while CH_3CN is not easily dried. In the presence of BF_4^-, Cl^- partially dissociates from the complexes during the coulometric experiments, causing shifts in the reduction peaks. Therefore, DMF and TEACl were used exclusively in all the electrochemical work.

The data from the cyclic voltammograms for the complexes in the range +0.50 to −2.50 V vs. SCE are summarized in Table I. All complexes except $(C_2H_5)_4NMoOCl_2$(sap) have a well-defined reduction peak in the range −0.25 to −0.90 V. This reduction peak is coupled to an oxidation peak and is due to a one-electron reduction (confirmed by controlled-potential coulometry). This reduction is essentially reversible for $MoOCl_3$(bpy), $MoOCl_3$(phen),[12] and MoOCl$(ox)_2$[12] (ΔE_p, the difference in potential for the cathodic and anodic peaks, is 0.0595 V, and i_{p_a}/i_{p_c}, the ratio of the anodic to the cathodic peak heights, is 1.00 for a reversible, one-electron reduction[14,15]). The degree of reversibility varies for the other complexes from quasireversible[14] to highly irreversible for this reduction peak.

Anodic scans, beginning just slightly more positive than the first reduction peak, show no oxidation peaks in the voltage range used, indicating none of the complexes are electrochemically oxidizable to Mo(VI) species under these conditions. Rapid anodic scans extending to +1.00 V vs. SCE in the presence of TBATFB also show no oxidation peaks.

Other reduction peaks at more negative potentials are irreversible, and the number of electrons involved could not be determined with any certainty by controlled-potential coulometry. Cyclic voltammetry of the ligands alone indicates they are reduced only at potentials much more negative than the first reduction peak for the complexes and, therefore, are not involved in this reduction. Representative cyclic voltammograms are shown in Figures 1 and 2.

Controlled-Potential Coulometry. Controlled-potential coulometry at a platinum cathode was used to determine the number of electrons involved in the reduction peaks in the cyclic voltammograms.

All the complexes are sensitive to traces of H_2O in the solvent. While this is no difficulty with cyclic voltammetry, due to the short time scale (scan rates were generally 100 mV/s), it is a significant problem in the coulometric experiments, which required 2–3 h for completion. The monomeric Mo(V) complexes slowly dimerize upon standing, even in the driest DMF, producing oxo-bridged Mo(V) dimers (the ESR signals gradually diminish in intensity), which are only reduced at much more negative potentials.[8] This reaction was con-

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Table I. Cyclic Voltammetric Data for Mo(V) Complexes[a]

complex	first reduction E_{p_c}[b]	E_{p_a}[b]	ΔE_p[b]	i_{p_a}/i_{p_c}[c]	other cathodic peaks E_{p_c}[b]
cis-$MoOCl_3$(bpy)	−0.270	−0.200	0.070	1.10	−1.605
trans-$MoOCl_3$(bpy)	−0.250	−0.180	0.070	1.19	−1.560
cis-$MoOCl_3$(phen)	−0.260	−0.189	0.071	1.18	−1.530
trans-MoOCl$(ox)_2$	−0.520	−0.445	0.075	1.17	−1.780
trans-MoOCl$(tox)_2$	−0.415	+0.240	0.655		−1.380, −1.655
cis-MoOCl(salphen)	−0.535	−0.390	0.145		−1.165
trans-MoOCl(mee)	−0.910 (−0.465)[e]	−0.215	0.695		
trans-MoOCl(mpe)	−0.495	−0.340	0.155		−1.135
trans-$(C_2H_5)_4NMoOCl_2$(sap)	−1.055	−0.050[d]	1.005		−1.600

[a] Scan rate 0.100 V/s; 0.10 M TEACl in DMF. [b] Volts vs. SCE. [c] Calculated according to the method of ref 15. [d] Poorly defined anodic peak. [e] See text.

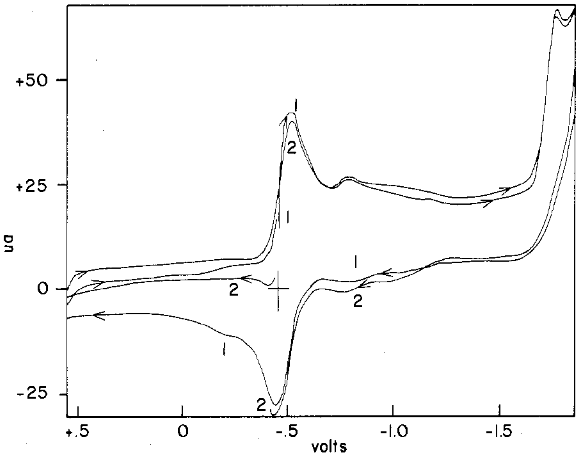

Figure 1. Cyclic voltammograms for MoOCl$(ox)_2$: 1, cathodic scan; 2, anodic scan. Conditions: 6.05 × 10^{-4} M, scan rate, 0.100 V/s, 0.10 M TEACl in DMF, volts vs. SCE.

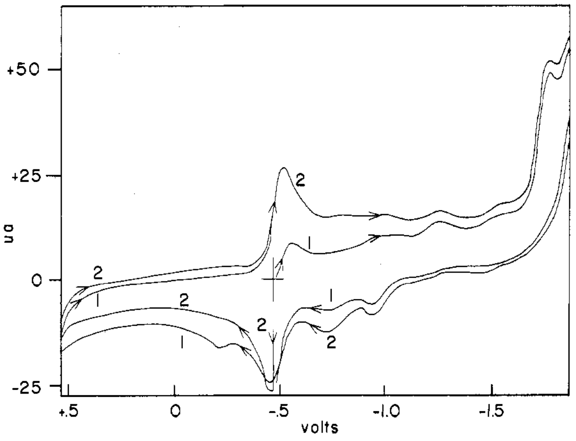

Figure 2. Cyclic voltammograms for MoOCl$(ox)_2$ after one-electron reduction at −0.615 V: 1, cathodic scan; 2, anodic scan. Conditions: 6.05 × 10^{-4} M, scan rate 0.100 V/s, 0.10 M TEACl in DMF, volts vs. SCE.

firmed by comparing the electronic spectra and cyclic voltammograms of solutions of the monomers which had stood for various time periods with the spectra and cyclic voltammograms of solutions of authentic samples of the dimers, where these could be obtained ($Mo_2O_3(ox)_4$, $Mo_2O_3(tox)_4$,[12] $Mo_2O_3(mee)_2$[12]), or with those of solutions containing the other monomers to which small amounts of H_2O had been deliberately added. For MoOCl$(ox)_2$, as an example, this reaction may be written

$$2MoOCl(ox)_2 + H_2O \rightarrow Mo_2O_3(ox)_4 + 2H^+ + 2Cl^- \quad (1)$$

Table II. Controlled-Potential Coulometric Reduction Data

complex	E_{redn}[a]	n (electrons/ molecule)[b]
cis-$MoOCl_3$(bpy)	−0.385	0.77 ± 0.04
trans-$MoOCl_3$(bpy)	−0.365	0.86 ± 0.09
cis-$MoOCl_3$(phen)	−0.365	1.00 ± 0.14
trans-MoOCl$(ox)_2$	−0.615	0.93 ± 0.04
trans-MoOCl$(tox)_2$	−0.515	0.96 ± 0.01
cis-MoOCl(salphen)	−0.615	0.98 ± 0.02
trans-MoOCl(mee)	−0.965	0.99 ± 0.01
trans-MoOCl(mpe)	−0.610	0.84 ± 0.04
trans-$(C_2H_5)_4NMoOCl_2$(sap)	−1.250	1.74 ± 0.09

[a] Volts vs. SCE; 0.10 M TEACl in DMF. [b] Averages for two or more reductions.

The rate of this reaction varies somewhat with the complex, but even in the case of MoOCl(mee), which appears to be the most stable to H_2O, significant dimerization occurs in 24 h.

As seen in Table II, controlled-potential reduction at a potential corresponding to the first peak indicates all complexes except $(C_2H_5)_4NMoOCl_2$(sap) are reduced in a one-electron step to what is assumed to be an Mo(IV) species, while $(C_2H_5)_4NMoOCl_2$(sap) requires two-electrons and is most likely reduced to an Mo(III) species. The somewhat low values of n for some of the complexes are due to their slow reaction with traces of H_2O in the solvent during the course of the coulometric determination, as discussed above. Solutions of the complexes, which were allowed to stand under N_2 for the same time as the coulometric experiments, showed changes in their electronic and ESR spectra and their cyclic voltammograms which correlated well with the amount of dimerization expected from the values of n.

As is seen in Figure 2, cathodic cyclic voltammograms of the reduced solutions, beginning at potentials slightly more negative than the oxidation peaks, indicated essentially complete reduction, while anodic scans showed the oxidation peaks due to the reduced species and the coupled reduction peaks characteristic of the original complexes.

Upon reoxidation at potentials corresponding to the coupled oxidation peaks, solutions having the same electronic and ESR spectra and cyclic voltammograms as the original complexes were obtained (with small contributions from the oxo-bridged dimers formed by reaction 1), indicating no irreversible changes occur upon reduction.

The only exception to this behavior was found with MoOCl(mee). After coulometric reduction, an anodic scan for this complex shows a reduction peak at −0.463 V, 0.475 V more positive than for the original complex (Figure 3). Upon reoxidation, however, the original cyclic voltammogram and electronic and ESR spectra were obtained. Cyclic voltammograms for this complex, when scanned in the cathodic direction beginning just before the −0.910-V reduction peak, reveal a small peak at −0.465 V. Furthermore, cyclic volt-

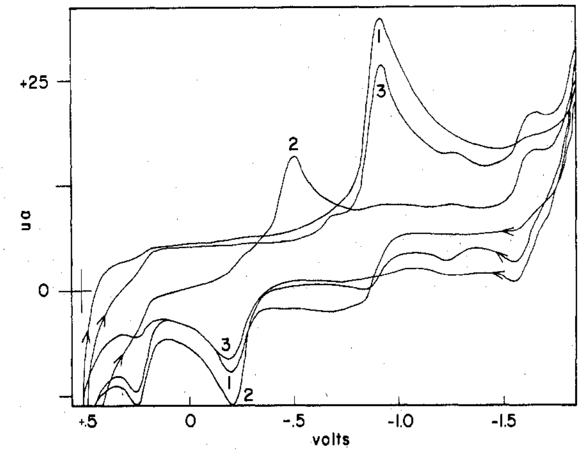

Figure 3. Cyclic voltammograms for MoOCl(mee): 1, before reduction; 2, after one-electron reduction at −0.965 V; 3, after one-electron reoxidation at −0.245 V. Conditions: 5.00 × 10^{-4} M, cathodic scans beginning at +0.50 V, scan rate 0.100 V/s, 0.10 M TEACl in DMF, volts vs. SCE.

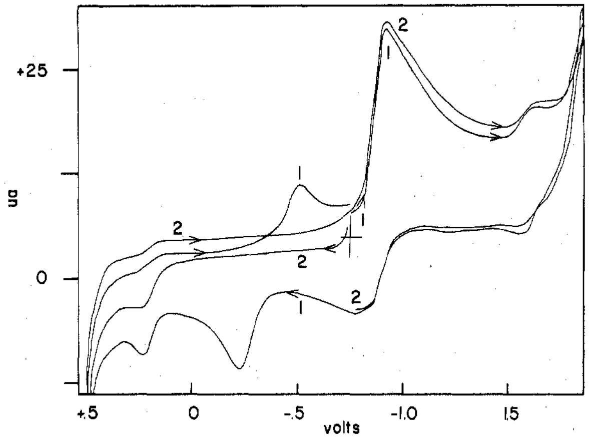

Figure 4. Cyclic voltammograms for MoOCl(mee): 1, cathodic scan; 2, anodic scan. Conditions: scan rate 0.100 V/s, 0.10 M TEACl in DMF, volts vs. SCE.

Table III. Electronic Spectra of Mo(IV) Reduction Products[a]

Mo(V) complex	λ_{max}, nm	log e
cis-$MoOCl_3$(bpy)	682	3.79
	525	3.78
trans-$MoOCl_3$(bpy)	682	3.90
	531	3.72
cis-$MoOCl_3$(phen)	696	3.78
	533	3.52
	429	3.46
trans-MoOCl$(ox)_2$	670	3.54
	579 sh	
trans-MoOCl$(tox)_2$	760	3.73
	648	3.63
	495	3.98
cis-MoOCl(salphen)	425 sh	
trans-MoOCl(mee)	530	3.03
trans-MoOCl(mpe)	463	2.81
trans-$(C_2H_5)_4NMoOCl_2$(sap)	450	2.78

[a] 0.10 M TEACl in DMF.

Table IV. Cyclic Voltammetric Data for Molybdenum(VI)–Dioxo Complexes[a,b]

complex	E_{p_c}[c]	E_{p_a}[c]	ΔE_p[c]
$MoO_2(ox)_2$	−1.220	−0.970	0.251
$MoO_2(tox)_2$	−1.000	−0.905	0.095
MoO_2(mee)	−1.315	−1.215	0.100
MoO_2(mpe)	−1.445	−0.890	0.555
MoO_2(sap)	−1.155	*e*	
MoO_2Cl_2 + phen[d]	−0.595	−0.490	0.105
MoO_2Cl_2 + bpy[d]	−0.735	−0.488	0.247

[a] Scan rate 0.100 V/s; 0.10 M $(C_2H_5)_4NCl$ in DMF. [b] MoO_2(salphen) cannot be prepared, due to necessity of *cis*-dioxo structure, which is prohibited by planar ligand. [c] Volts vs. SCE. [d] 1:1 mixture, MoO_2Cl_2:ligand. [e] No well-defined anodic wave.

ammograms taken during the coulometric reoxidation of the one-electron-reduced species indicate the presence of both reduction peaks. This behavior indicates the one-electron-reduced species is reoxidized to a different MoOCl(mee) complex, which converts to the original complex. This conversion must be reasonably rapid, since the cathodic-scan cyclic voltammogram for the original solution (Figure 4) shows only a small peak at −0.465 V after a scan time of approximately 30 s (scan rate 100 mV/s). The two MoOCl(mee) complexes may be isomers, with the less stable (−0.465 V) isomer being converted rapidly to the more stable (−0.910 V) isomer after being formed by reoxidation of the one-electon-reduced species (there are three possible trans isomers and one cis isomer for this complex).

Attempts to determine the number of electrons involved in the reductions at the more negative peaks (<−1.20 V) in the cyclic voltammograms (Table I) were unsuccessful. In all cases, high final currents were observed, greatly above the background levels of the preelectrolyzed solvent, indicating some secondary process was occurring (possibly reduction of the ligands or catalytic reduction of the solvent or traces of H_2O). Similar results have been reported by others.[8]

The Mo(IV) complexes produced in the controlled-potential reductions are probably pentacoordinate oxo complexes,[2] although this is not certain. The only Mo(IV) complex with any of these ligands reported in the literature is $MoO(ox)_2$; it was poorly characterized, however, and its oxidation state and structure are in doubt.[16] The Mo(IV) products have distinctive electronic spectra in most cases, differing considerably from those of the original complexes and from the Mo(V) oxo-bridged dimers (Table III). These Mo(IV) species are sensitive to traces of H_2O or O_2 in the system, being slowly oxidized to the Mo(V) oxo-bridged dimers upon standing under N_2 for prolonged periods in the solvent. Upon admission of air, they are almost instantly reoxidized to the monomers, indicating they are extremely sensitive to O_2 in solution.

Discussion

With the exception of $(C_2H_5)_4NMoOCl_2$(sap), the Mo(V) complexes are facilely reduced to Mo(IV) species at a platinum cathode. In the case of $(C_2H_5)_4NMoOCl_2$(sap), the only anionic complex, the two-electron reduction may be due to a shift in the one-electron reduction peak to a more negative potential, as a consequence of the charge, where it possibly overlaps a second reduction peak for reduction to the Mo(III) state.

The inability to oxidize the Mo(V) complexes to molybdenum(VI)–dioxo complexes ($MoO_2(ox)_2$, e.g.) is most likely due to the necessity of replacement of a Cl^- by a second oxo group, which could only come from H_2O, in the coordination sphere. Oxidation to a molybdenum(VI)–monooxo species, such as $MoOCl(ox)_2^+$, is also quite unlikely, since $MoOCl_4$ is known to be unstable, and the MoO group is extremely rare for Mo(VI) complexes.[2] In this respect, it is significant that $Mo_2O_3(ox)_4$ is oxidized to $MoO_2(ox)_2$ only at a very positive potential in Me_2SO.[8]

An important conclusion of these studies is that the monomeric Mo(V) state is clearly unobtainable for these complexes by electrochemical reduction of the corresponding molybdenum(VI)–dioxo complexes under the conditions used, since the Mo(VI) complexes are reduced only at potentials considerably more negative than those required for reduction of the Mo(V) monomers (Table IV) ($MoO_2(ox)_2$ is reduced to $Mo_2O_3(ox)_4$ at −1.07 V and to an Mo(IV) complex at −1.12 V in Me_2SO;[8] the other molybdenum(VI)–dioxo complexes in Table III are presumed to be reduced to similar products, although the details of these reductions have not been investigated).

Because of the irreversible nature of many of these reductions, caution must be exercised in drawing conclusions concerning thermodynamic stability. With those reductions which may be classified as reversible or quasi-reversible,[14] however, it appears the Mo(V) monomer state is thermodynamically unstable, and the Mo(V) monomers should disproportionate into Mo(VI) and Mo(IV) species. While there is no direct evidence to support this, it may be the mechanism whereby the Mo(V) oxo-bridged dimers are formed by reaction with H_2O:

$$H_2O + 2MoOCl(ox)_2 \rightleftarrows MoO_2(ox)_2 + MoO(ox)_2 + 2Cl^- + 2H^+ \quad (2)$$

$$MoO_2(ox)_2 + MoO(ox)_2 \rightleftarrows Mo_2O_3(ox)_4 \quad (3)$$

Newton et al. have recently reported equilibrium 3 strongly favors the product.[17]

Since the majority of the substrates of the molybdenum enzymes are oxidized by two electrons (xanthine to uric acid, e.g.),[2] it is likely enzymatic Mo(VI) is reduced directly to the Mo(IV) state. The observed Mo(V) ESR signal would then arise during reoxidation of Mo(IV) by the one-electron cofactor oxidants (Fe/S or FADH) and may be due to a thermodynamically unstable but kinetically detectable Mo(V) monomer intermediate (current evidence indicates the two Mo centers of xanthine oxidase are some distance apart and probably buried within the protein, precluding a disproportionation reaction). It is perhaps significant that the relative redox potentials used for the two steps in a recently postulated mechanism for the reduction of xanthine oxidase by dithionite, $Mo(VI) + e^- \rightarrow Mo(V)$, −0.060 V, and $Mo(V) + e^- \rightarrow Mo(IV)$, −0.030 V,[18] indicate the Mo(V) monomer state is in fact unstable relative to the Mo(VI) and Mo(IV) states, as with the results for the Mo(V) complexes reported here. It is also interesting when the same mechanism is applied to the reduction of the enzyme by xanthine, the assumed relative potentials for the two reactions must be reversed, which is attributed to complex formation with xanthine, making the Mo(V) monomer a thermodynamically stable state.[18] Work in this laboratory to determine the effects of complexing by xanthine and similar substrates on the reduction potentials of both Mo(VI) and Mo(V) complexes is under way.

Experimental Section

Cyclic voltammetry and coulometry were performed with a three-electrode system, using a PAR Model 174A polarographic analyzer and a PAR Model 173 potentiostat equipped with a digital coulometer. A Beckman platinum inlay electrode was used as working electrode for cyclic voltammetry and a platinum gauze electrode for coulometry. The gauze electrode served as the counterelectrode for cyclic voltammetry. The anode compartment, containing a platinum gauze electrode in 0.10 M TEACl in DMF, was separated from the coulometric cell by a Vycor glass disk. The reference electrode for both coulometry and cyclic voltammetry was a calomel electrode containing 0.10 M TEACl in H_2O as electrolyte. This electrode was immersed in a reference compartment containing 0.10 M TEACl in DMF and separated by a Vycor glass disk from the reference compartment. The reference electrode compartment was separated from the solution by a medium glass frit. The potential of the reference electrode was measured vs. a SCE using a potentiometer and found to be +0.037 ± 0.005 V.

All electrochemical measurements were made in a gastight cell (Metrohm) under prepurified N_2. All solvents were deaerated using prepurified N_2. Solvents containing the electrolyte were preelectrolyzed at a potential corresponding to that to be used for coulometry. In all cases, small offset currents of a few microamperes were used to correct for background.

Samples were withdrawn using a gastight syringe and injected into a stoppered spectrophotometric cell under N_2 to obtain electronic spectra. Spectra were recorded under N_2 using a Varian 635 recording spectrophotometer. For ESR spectra, samples were introduced into a stoppered ESR cell under N_2 for room-temperature work or frozen in ESR tubes in liquid N_2 for low-temperature work. Spin concentrations were estimated by comparison with recorded spectra for the same complex which had been calibrated by double integration vs. $K_3Mo(CN)_8$.

Baker analyzed DMF, reported to contain <0.03% H_2O, was dried over Linde AW-500 molecular sieves for 24 h before use. After opening, DMF was stored over P_2O_5 and used within 48–72 h. Comparisons with DMF dried by distillation in vacuo over P_2O_5 before storing over sieves showed no detectable differences with respect to electrochemical behavior or stability of complexes. TEACl was obtained from Eastman Kodak Co. and recrystallized 3 times from pentane/chloroform mixtures. It was then dried overnight at 110 °C in vacuo and stored over P_2O_5. Cyclic voltammograms of solvent and electrolyte were obtained each day to determine if any detectable decomposition or H_2O adsorption had occurred.

The preparations of all Mo(V) complexes except MoOCl(mee) and MoOCl(mpe) have been described previously.[7]

MoOCl(mee) and MoOCl(mpe) were prepared by suspending 0.001 mol of the ligand dihydrochloride and 0.004 mol of $NaOCH_3$ in 90 mL of dry 1:1 C_2H_5OH/CH_3CN. A solution of 0.001 mol of $(NH_4)_2MoOCl_5$ in dry ethanol, which had been filtered to remove NH_4Cl, was then added, and the mixture refluxed for 2 h for MoOCl(mee) and 45 min for MoOCl(mpe). After cooling to room temperature, the solution was filtered, and ~75% of the solvent was removed in vacuo. After the mixture was cooled in an ice bath, the solid was filtered off and dried under vacuum over P_2O_5. All operations were performed under N_2, and extreme care was exercised to keep the solutions free of H_2O. Anal. Calcd for $MoOCl(C_8H_{18}N_2S_2)$: C, 27.16; H, 5.13; N, 7.91; S, 18.13; Cl, 10.02. Found: C, 26.14; H, 5.12; N, 7.91; S, 17.04; Cl, 11.50. Calcd for $MoOCl(C_{10}H_{22}N_2S_2)$: C, 31.44; H, 5.81; N, 7.33; S, 16.80; Cl, 9.29. Found: C, 30.61; H, 5.98; N, 7.05; S, 16.26; Cl, 11.03.

$MoO_2(ox)_2$ was prepared by the method of Fleck and Ward.[19]

$MoO_2(tox)_2$ was prepared by the same procedure as that used for $MoO_2(ox)_2$.[19] Anal. Calcd for $MoO_2(C_{18}H_{12}N_2S_2)$: C, 48.22; H, 2.70; N, 6.25; S, 14.30. Found: C, 49.31; H, 2.82; N, 6.44; S, 13.79.

MoO_2(mee) and MoO_2(mpe) were prepared by addition of 0.003 mol of the ligand dihydrochloride to 10 mL of H_2O, followed by addition of 0.003 mol of $Na_4MoO_4{\cdot}2H_2O$ in 10 mL of H_2O. The yellow precipitate was filtered off, washed with H_2O and C_2H_5OH, recrystallized from hot C_2H_5OH, and dried under vacuum over P_2O_5. Anal. Calcd for $MoO_2(C_8H_{18}N_2S_2)$: C, 28.74; H, 5.43; N, 8.37; S, 19.17. Found: C, 28.71; H, 5.51; N, 8.45; S, 19.10. Calcd for $MoO_2(C_{10}H_{22}N_2S_2)$: C, 33.15; H, 6.12; N, 7.73; S, 17.70. Found: C, 31.92; H, 6.07; N, 7.88; S, 16.90.

MoO_2(sap) was prepared by dissolving 0.003 mol of ligand in 60 mL of 2 M NaOH, followed by addition of 0.003 mol of $Na_2MoO_4{\cdot}2H_2O$ in 20 mL of H_2O. After filtration, concentrated HCl was added slowly until a yellow-brown precipitate formed. The solution was allowed to stand 30 min, after which it was filtered, and the precipitate was washed with H_2O and dried under vacuum over P_2O_5. Anal. Calcd for $MoO_2(C_{13}H_9NO_2)$: C, 46.04; H, 2.67; N, 4.13. Found: C, 46.78; H, 2.97; N, 4.46.

$(NH_4)_2MoOCl_5$ was prepared as previously reported.[7]

N,N'-Dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine was synthesized according to the procedure of Karlin and Lippard.[20] *N,N'*-Bis(2-mercapto-2-methylpropyl)ethylenediamine was a gift from Dr. Peter Kroneck, Fachbereich Biologie, University of Konstanz, and was synthesized by the procedure of Corbin and Work.[21]

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Registry No. *cis*-$MoOCl_3$(bpy), 35408-53-8; *trans*-$MoOCl_3$(bpy), 35408-54-9; *cis*-$MoOCl_3$(phen), 38237-92-2; *trans*-$MoOCl(ox)_2$, 67650-70-8; *trans*-$MoOCl(tox)_2$, 67650-71-9; *cis*-MoOCl(salphen), 64085-34-3; *trans*-MoOCl(mee), 67598-30-5; *trans*-MoOCl(mpe), 67598-31-6; *trans*-$(C_2H_5)_4HMoOCl_2$(sap), 67598-33-8; $MoO_2(ox)_2$, 17856-49-4; $MoO_2(tox)_2$, 17926-52-2; MoO_2(mee), 67598-34-9; MoO_2(mpe), 67598-35-0; MoO_2(sap), 67598-36-1; MoO_2Cl_2, 13637-68-8; phen, 66-71-7; bpy, 366-18-7; $(NH_4)_2MoOCl_5$, 17927-44-5.

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(12) Abbreviations used for ligands: phen = *o*-phenanthroline; bpy = α,α'-bipyridyl; ox = 8-hydroxyquinoline; tox = 8-mercaptoquinoline; salphen = disalicylaldehyde *o*-phenylenediimine; mee = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine; mpe = *N,N'*-bis(2-mercapto-2-methylpropyl)ethylenedamine; sap = salicylaldehyde *o*-hydroxyanil.
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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Mass Spectrometric Observation and Bond Dissociation Energy of Dimolybdenum, Mo_2(g)

S. K. GUPTA, R. M. ATKINS, and K. A. GINGERICH*

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The diatomic molecule Mo_2 has been identified, and its thermodynamic properties have been studied in a high-temperature mass spectrometric experiment. From the partial pressures of Mo and Mo_2 measured as a function of temperature in the 2600–3000 K range, the dissociation energy of Mo_2(g) was determined as $D^\circ_{298} = 406 \pm 20$ kJ mol^{-1} or 97 ± 5 kcal mol^{-1}, and $D^\circ_0 = 404 \pm 20$ kJ mol^{-1} or 96.5 ± 5 kcal mol^{-1}. The results are consistent with the trends predicted for the bond energies of diatomic molecules of group 5B and 6B elements in the first and second transition series by theoretical calculations.

Introduction

Currently, there is a great deal of interest in multiple metal–metal bonding in transition metals. An increasing number of theoretical as well as experimental studies of diatomic transition-metal molecules are appearing in the literature. This activity was initiated by the recent realization that a knowledge of the chemical and electronic properties of small transition- and noble-metal clusters is of fundamental importance to the understanding of the catalytic properties of transition metals. Diatomic molecules, or dimers, of a large number of transition metals have been characterized by Knudsen-cell effusion mass spectrometry[1,2] and other techniques such as matrix synthesis and isolation.[3] However, experimental studies of dimers of refractory metals, Nb, Mo, W, Pt, etc., either are lacking entirely or have been unsuccessful. This is presumably because severe experimental difficulties are encountered at the extremely high temperatures at which measurable pressures of the dimers would be obtained.

Very recently, the diatomic species Nb_2 and Mo_2 have been identified by quantitative UV–visible spectroscopy in matrix-condensation experiments by Ozin and co-workers.[3] Nevertheless, the need remains to determine their bond energies in order to establish trans-group and trans-transition series correlations of bonding characteristics of the homonuclear diatomics. The molecule Mo_2 is of particular interest. It is predicted to have the highest dissociation energy among the second transition series diatomic species. A bond order as high as 6 is indicated for Mo_2 from the results of extended Hückel molecular orbital[3] and SCF-Xα-SW[4] calculations. The present study was aimed at the detection and the measurement of the dissociation energy of gaseous Mo_2 under thermal equilibrium conditions.

Experimental Section

A single-focusing, 90° magnetic sector mass spectrometer (Nuclide, Model 12-90-HT) equipped with a Knudsen cell assembly was employed in this investigation. The instrument and the experimental procedures have been described previously[5,6] and only the details specific to this study will be discussed here.

The success of the experiment depended upon a right choice of the material for the Knudsen cell container. Since temperatures up to 3000 K were anticipated, the Knudsen-cell material had to meet two requirements: those of mechanical stability and nonreactivity with molybdenum metal so as not to lower its activity excessively. A tantalum Knudsen cell lined with a graphite cell, both with knife-edge orifices of 0.040-in. diameter, was charged with about 180 mg of niobium powder and heated to about 3000 K in the mass spectrometer. The purpose of this treatment was twofold: one, to coat the inside of the cell with a layer of highly refractory niobium carbides and two, to attempt observation of Nb_2.[7] A dramatic decrease in the ion currents due to carbon species (in fact, C_3 could no longer be detected) at about 2900 K indicated that all of the carbon of the inner cell had reacted with niobium and/or with the tantalum cell itself. The cell was then charged with fine cuttings of molybdenum foil (190 mg) along with a small amount of gold for pressure calibration purposes.

A 21-eV electron beam at a total emission of 0.3 mA was employed to ionize the Knudsen cell effusate. The ions were accelerated through a potential of 4.5 kV and were detected through a 20-stage π-type electron multiplier with Be–Cu dynodes. The potential at the multiplier shield was maintained at approximately −2000 V. Ion currents of Mo^+ (m/z 98) and Mo_2^+ (m/z 192) were measured as a function of temperature in the 2600–3000 K range. Ions were identified by