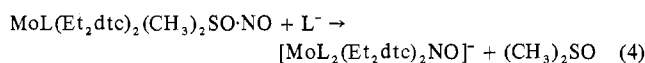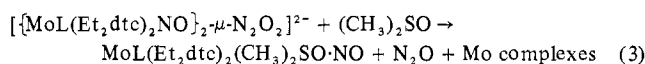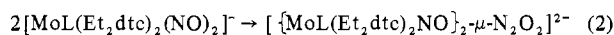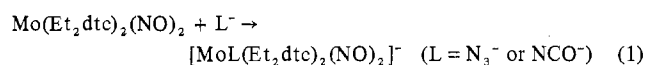steric effects. The dibenzyldithiocarbamate ligand is the least electron donating of the series studied[16] and also the most bulky. These properties would be expected to act in opposition but the increased rates do suggest that the electronic effect is dominant and the metal center has become more positive for the benzyl substituent. Figure 4 indicates a systematic difference between NaN$_3$ and KN$_3$ as reagent. Variations in rate constants were found also for other salts when present in the cis-Mo(Et$_2$dtc)$_2$(NO)$_2$–NaN$_3$ reaction in amounts comparable to the NaN$_3$. The variation is shown in parentheses: CsBr (+40%); Ba(NO$_3$)$_2$ (unchanged); MgF$_2$ (+8%); CaBr$_2$ (−12%). It is likely that different ion clusters are responsible for all these effects in the aprotic solvent employed. In addition, both water and dioxygen affected the rates. For example, if the cis-Mo(Et$_2$dtc)$_2$(NO)$_2$–NaN$_3$ reaction solution in (CH$_3$)$_2$SO was made 0.57 M with respect to water, the rate constant was reduced by 20%. In a dioxygen-saturated solution a 50% retardation was observed. A reduction in rate in the presence of water is understood in terms of increased solvation of the anion but the effect of dioxygen is not clear. The presence of nitrogen oxide similarly leads to a decrease in the reaction rate.

Stoichiometry of the Reactions of cis-Mo(Et$_2$dtc)$_2$(NO)$_2$ with Azide and Cyanate. The mechanistic studies reported here may be combined with the previously described synthesis and characterization of products[7] in the equations

$$Mo(Et_2dtc)_2(NO)_2 + L^- \rightarrow$$
$$[MoL(Et_2dtc)_2(NO)_2]^- \quad (L = N_3^- \text{ or } NCO^-) \quad (1)$$

$$2[MoL(Et_2dtc)_2(NO)_2]^- \rightarrow [\{MoL(Et_2dtc)_2NO\}_2\text{-}\mu\text{-}N_2O_2]^{2-} \quad (2)$$

$$[\{MoL(Et_2dtc)_2NO\}_2\text{-}\mu\text{-}N_2O_2]^{2-} + (CH_3)_2SO \rightarrow$$
$$MoL(Et_2dtc)_2(CH_3)_2SO\cdot NO + N_2O + Mo \text{ complexes} \quad (3)$$

$$MoL(Et_2dtc)_2(CH_3)_2SO\cdot NO + L^- \rightarrow$$
$$[MoL_2(Et_2dtc)_2NO]^- + (CH_3)_2SO \quad (4)$$

Decomposition of the hyponitrito-bridged complex accounts for the formation and yields of N$_2$O (see Experimental Section) as well as the isolation of [Mo(NCO)$_2$(Et$_2$dtc)$_2$NO]$^-$ in about 40% yield as the tetraethylammonium salt. Equation 3 is an attempt to account for the decomposition reaction. When L = N$_3^-$ there is evidence for greater lability in the products. Not only is the yield smaller (about 10%) but also the known Mo(Et$_2$dtc)$_3$NO complex is obtained in moderate amounts. For this reason the preferred synthetic route for MoN$_3$(Et$_2$dtc)$_2$(CH$_3$)$_2$SO·NO is by substitution in the corresponding cyanato complex.[7] Although the oxygen atom left

after the breakdown of the hyponitrito bridge could be transferred to the solvent giving dimethyl sulfone, all attempts to detect this product were unsuccessful. However current work involving thin-layer chromatographic separation of the cyanate reaction product mixture followed by infrared measurements has permitted recognition of molybdenum oxo groups in an otherwise unidentified species.[17]

Similar chemistry to that described for cis-Mo(Et$_2$dtc)$_2$-(NO)$_2$ in this paper is also found with cis-W(Et$_2$dtc)$_2$(NO)$_2$. However, the reactions with azide or cyanate are much too slow but may be accelerated by irradiation with light from a xenon lamp. Complexes of the type (Et$_4$N)[WL$_2$(Et$_2$dtc)$_2$NO] (L = N$_3^-$, NCO$^-$, or NCS$^-$) have been isolated and will be described fully elsewhere. In the reactions involving light, activation of the nitrosyl groups is suggested to take place by charge transfer from metal to the nitrosyl, attended by coordination of the anion to give a hyponitrito-bridged complex analogous to that shown in Figure 6.

References and Notes

(1) J. A. Broomhead, J. Budge, W. Grumley, and T. Norman, *Inorg. Nucl. Chem. Lett.*, **11**, 519 (1975).
(2) M. Gargano, P. Giannoccaro, M. Rossi, A. Sacco, and G. Vasapollo, *Gazz. Chim. Ital.*, **105**, 1279 (1975).
(3) C. D. Meyer and R. Eisenberg, *J. Am. Chem. Soc.*, **98**, 1364 (1976).
(4) B. F. G. Johnson and S. Bhaduri, *J. Chem. Soc., Chem. Commun.*, 650 (1973).
(5) B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 3325 (1974).
(6) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).
(7) J. A. Broomhead, J. R. Budge, W. D. Grumley, T. R. Norman, and M. Sterns, *Aust. J. Chem.*, **29**, 275 (1976).
(8) J. A. Broomhead, J. Budge, and W. Grumley, *Inorg. Synth.*, **16**, 235 (1976).
(9) R. H. Herber, "Inorganic Isotope Syntheses", W. A. Benjamin, New York, N.Y., 1962, p 100.
(10) R. L. Martin and D. Taylor, *Inorg. Chem.*, **15**, 2970 (1976).
(11) R. Davis, M. N. S. Hill, C. E. Holloway, and B. F. G. Johnson, *J. Chem. Soc. A*, 994 (1971).
(12) R. D. Feltham, W. R. Silverthorn, and G. McPherson, *Inorg. Chem.*, **8**, 344 (1969).
(13) S. Bhaduri, B. F. G. Johnson, A. Pickard, P. R. Raithby, G. M. Sheldrick, and C. I. Zuccaro, *J. Chem. Soc., Chem. Commun.*, 354 (1977).
(14) S. Bhaduri, B. F. G. Johnson, C. J. Savory, J. A. Segal, and R. H. Walter, *J. Chem. Soc., Chem. Commun.*, 809 (1974).
(15) B. F. Hoskins, F. D. Williams, D. H. Dale, and D. C. Hodgkin, *Chem. Commun.*, 69 (1969).
(16) A. R. Henrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **13**, 1933 (1974).
(17) J. A. Broomhead and C. Boreham, to be submitted for publication.

Electrochemical Properties of Aquomolybdenum Ions in Noncomplexing Acidic Electrolytes

PURUSH CHALILPOYIL and FRED C. ANSON*

The electrochemistry of molybdenum in oxidation states III–VI in trifluoromethanesulfonic acid is examined. The electrochemical oxidations of both the monomeric and dimeric forms of aquomolybdenum(III) are irreversible and are preceded by rate-limiting chemical reactions. Oxidation of both monomeric and dimeric Mo(III) leads to dimeric Mo(V) but there is evidence of the intermediacy of unstable monomeric Mo(V) during the oxidation of monomeric Mo(III). The reduction of Mo(IV) is quasi-reversible and diffusion controlled. The product of the reduction is a new form of (probably) dimeric Mo(III). The stable, dimeric form of Mo(V) is reduced to the previously described dimeric form of Mo(III). The reduction of Mo(VI) produces differing sets of products depending upon the potentials where the electrolysis is carried out. At −0.2 V vs. SCE, the monomeric form of Mo(V) appears to be formed initially but it dimerizes rapidly.

The aqueous chemistry of molybdenum in oxidation states II,[1,2] III,[1-7] IV[7-15] and V[7,10,16-20] has attracted considerable

recent attention. Both monomeric and dimeric forms of oxidation state III are now well characterized[1-7] and there is

a variety of evidence[20-22] that a monomeric form of Mo(V) exists (at least transiently) along with the now well recognized dimeric form.[16] Most previous electrochemical studies have been confined to hydrochloric and sulfuric acid electrolytes in which mixtures of complexes are often present. In the present study, trifluoromethanesulfonic acid was employed as the supporting electrolyte to allow examination of the electrochemical behavior of aquomolybdenum ions in the absence of complex formation. One objective of the work was to compare the electrochemistry of the simple aquo ions with that exhibited by the first-row congener of molybdenum, chromium. The results show that the contrasts in the electrochemical behavior of the aquo ions of molybdenum and chromium are much more prominent than the similarities.

Experimental Section

Materials. Trifluoromethanesulfonic acid, obtained from Minnesota Mining and Manufacturing Co. (Minneapolis, Minn.), was purified by distillation under reduced pressure. Small quantities of chloride persisted in the acid even after two distillations. The chloride was removed by precipitation with silver trifluoromethanesulfonate (prepared by dissolving Ag_2O in CF_3OH_3H). The silver chloride precipitate was removed by filtration and the filtrate was electrolyzed at -0.08 V (vs. SCE) at a mercury pool electrode to remove the small excess of Ag^+ present.

Reagent grade ammonium molybdate was used without further purification. K_3MoCl_6 was prepared according to a published procedure.[23]

Solutions of monomeric Mo^{3+} were prepared by hydrolysis of K_3MoCl_6 in 2 M CF_3SO_3H as described by Bowen and Taube.[1,2] The chloride ion released was removed from these solutions by column chromatography at 5 °C which also separated the Mo^{3+} ion from the small quantities of other molybdenum species present. In some experiments, where chloride ions did not interfere, the hydrolyzed solutions were used directly without chromatographic purification.

Bio-Rad AG 50W-X4 ion exchange resin was purified by the procedure of Deutsch[24] and was treated with chromous ion to remove any traces of residual oxidant present.[2]

All solutions were deoxygenated by bubbling with argon gas which had been passed through solutions of chromium(II). Water was triply distilled, the second stage from alkaline permanganate.

Instrumentation and Techniques. UV and visible absorption spectra were recorded with a Cary 14 spectrophotometer.

Electrochemical experiments (except controlled-potential electrolysis) were carried out in a conventional compartmentalized cell. The saturated calomel reference electrode (SCE) was isolated from the test solution by means of a glass frit of medium porosity. Polarography and voltammetry were performed with standard dropping mercury electrodes or hanging drop mercury electrodes.

Controlled-potential electrolyses were carried out in a three-compartment cell with both the reference and the counterelectrode individually isolated from the test solutions by glass frits. The main compartment of the cell contained a stirred mercury pool electrode (7 cm² in area).

Polarograms were obtained with a Princeton Applied Research (PAR) Model 174 instrument and an X-Y recorder. The dropping mercury electrode was mechanically controlled to a drop time of 1 s. The mercury flow rate was 1.6 mg s⁻¹. Potential scan rates during the recording of polarograms were typically 5 mV s⁻¹.

Controlled-potential electrolyses were carried out with a PAR Model 173 potentiostat equipped with a Model 179 digital coulometer. The same potentiostat and a Model 175 universal programmer were employed to obtain the cyclic voltammograms and current-reversal chronopotentiograms. Chronocoulometry experiments were carried out with a computer-based digital data acquisition and analysis system described earlier.[25] All potentials are quoted with respect to a SCE.

Purified solutions of monomeric Mo^{3+} were stored in 1.5 M CF_3SO_3H under positive argon pressure at 5 °C. Aliquots from these solutions were transfered into the electrolytic cell by means of a stainless steel needle and syringe. Experiments were conducted with solutions at the laboratory temperature (22 ± 2 °C).

The net oxidation state of molybdenum in reduced solutions was determined by adding a sample to an excess of a deoxygenated solution of Ce^{4+} in 2 M sulfuric acid. Excess of a standard ferrous sulfate solution was added, and the unreacted Fe^{2+} was determined by
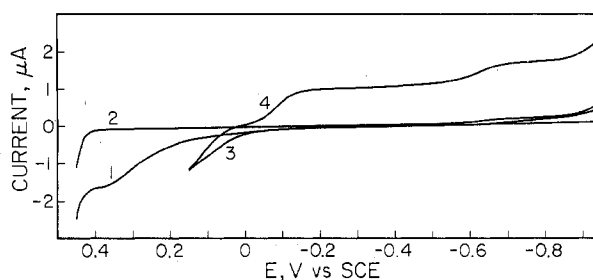

Figure 1. Sampled dc polarograms of (1) 10 mM Mo^{3+} in 1.5 M CF_3SO_3H, (2) 1.5 M CF_3SO_3H alone, and (3) 1.0 mM Mo^{3+} in 2 M CF_3SO_3H also containing 6 mM chloride. Curve 4 shows a normal-pulse polarogram of the same solution as in (3). The initial potential was $+0.15$ V. The behavior is unchanged in chloride-free supporting electrolyte.

back-titration with a standard solution of Ce^{4+}.

Results

Molybdenum(III) Monomer. Monomeric molybdenum(III), Mo^{3+}, prepared and purified as described in the Experimental Section gave an absorption spectrum in 1.5 M CF_3SO_3H quite similar to that reported by Bowen and Taube.[2]

No previous electrochemical measurements on the Mo^{3+} ion have been published. Figure 1 shows a sampled dc polarogram of a 10 mM solution of Mo^{3+}. No reduction wave is obtained and the single oxidation wave is poorly developed, extending over several hundred millivolts. The ill-defined limiting current between 0.35 and 0.40 V corresponds to about 10% of that expected for a diffusion-controlled one-electron oxidation reaction. Chronocoulometric experiments[26] performed with the same solution (the potential was stepped from -0.25 to $+0.40$ V) also indicated that the oxidation rate was far below the diffusion-controlled limit.

Controlled-potential oxidation of a 10 mM solution of Mo^{3+} at $+0.35$ V at a stirred mercury pool electrode proceeded very slowly but after several hours of electrolysis, 2 faradays were consumed/mol of molybdenum. The resulting solution gave a spectrum[16] and polarogram[27] corresponding to dimeric molybdenum(V), Mo^V_2.

Normal-pulse polarograms of solutions of Mo^{3+} with the initial potential maintained at values where Mo^{3+} is being oxidized prior to the application of the cathodic pulse show a reduction wave with $E_{1/2}$ at -0.09 V (Figure 1, curve 4), which is not present in the dc polarogram of the original solution (Figure 1, curve 1) nor in the solution resulting from its controlled-potential oxidation at $+0.4$ V (Figure 8). Cyclic voltammograms of Mo^{3+} solutions also contain a cathodic wave near -0.09 V as do current-reversal chronopotentiograms[28] obtained with Mo^{3+} solutions. As will be shown later, neither Mo^{IV}_2 nor Mo^V_2 have reduction waves in this region.

Solutions of Mo^{3+} stored under argon for several weeks decompose to yield a mixture of Mo^{IV}_2 and Mo^V_2 with reduction waves at $E_{1/2} = -0.35$ and -0.60 V, respectively. Heating on a water bath at 85 °C accelerates this process.

Molybdenum(III) Dimer, Mo^{III}_2. When molybdenum(III) is prepared from molybdenum(VI) by reduction with zinc amalgam or by electrolysis, a dimeric product results.[7] Previous reports[29] have invoked a variety of species depending on the identity and concentrations of acid employed. Ardon and Pernick[5] recently reported the absorption spectrum of a chromatographically purified molybdenum(III) dimer in noncomplexing acidic electrolytes.

If a Mo(VI) solution in 2 M CF_3SO_3H is reduced at -0.75 V, 3 faradays of charge/mol of Mo(VI) are consumed, and a green solution is obtained. Titration of this solution with a standard solution of Ce(IV) requires 3 equiv of oxidant/mol of molybdenum present. The UV–visible absorption spectrum
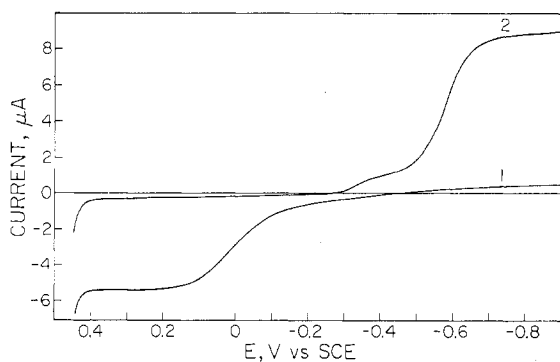
Figure 2. Sampled dc polarograms of (1) 1.25 mM Mo^{III}_2 produced by reduction of Mo(VI) at -0.75 V in 2 M CF_3SO_3H and (2) after oxidation at 0.3 V.

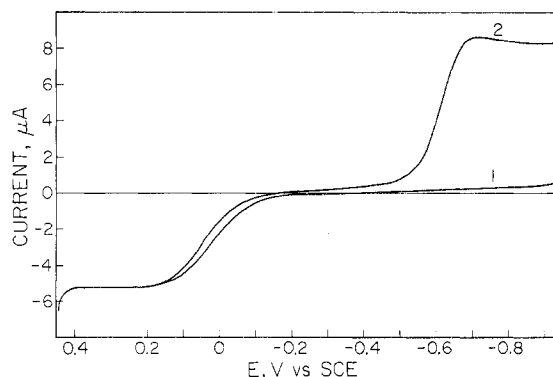**Figure 3.** (1) Sampled dc polarogram of 1.25 mM Mo^{III}_2 produced by two-stage reduction of Mo(VI) in 2 M HTFMS (see text). (2) Normal-pulse polarogram of the same solution. The initial potential was 0.3 V.
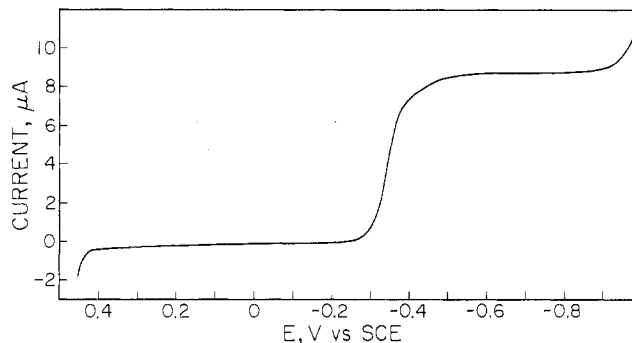

Figure 4. Sampled dc polarogram of 1.25 mM Mo^{IV}_2 in 2 M CF_3SO_3H.

of the reduced solution resembles that reported for Mo^{III}_2 by Ardon and Pernick but is quantitatively different. For example, the molar extinction coefficient at 360 nm is about twice the reported value.[5]

A sampled dc polarogram of a solution of Mo^{III}_2 prepared by electrolytic reduction of Mo(VI) is shown in Figure 2, curve 1. The oxidation wave with $E_{1/2}$ at 0.015 V is somewhat better developed than the corresponding wave for monomeric Mo^{3+} (Figure 1), and the ratio of the limiting current to the concentration of Mo(III) is considerably larger. However, the current is still only about half as large as that expected for a two-electron oxidation to Mo(V). It was established that the wave is not a diffusion-limited one-electron oxidation by chronocoulometric measurements[26] which were consistent with the presence of a rate-limiting chemical step preceding the electron-transfer reaction.

Controlled-potential oxidation of the reduced solution at $+0.3$ V consumes 1.4 to 1.6 faradays/mol of molybdenum present and produces a solution which gives polarogram 2 in Figure 2. The same two reduction waves, with $E_{1/2}$ values near -0.35 and -0.60 V, are also present in cyclic voltammograms and in normal-pulse polarograms recorded with the original reduced solution of Mo(III) with the initial potential positioned on the limiting-current plateau of the oxidation wave (e.g., $+0.3$ V). Polarogram 2 in Figure 2 shows that the species responsible for the two waves are stable under the conditions of the controlled-potential electrolysis.

If, instead of reducing Mo(VI) in a single electrolysis at -0.75 V, it is reduced in two stages, first at -0.2 V and subsequently at -0.75 V, a solution is obtained which gives a spectrum that matches the one reported by Ardon and Pernick[5] for Mo^{III}_2. The reduction at -0.2 V proceeds smoothly to give Mo^{V}_2. The subsequent reduction at -0.75 V consumes an additional 2 faradays/mol of molybdenum and produces a bluish green solution with an absorption spectrum in 2 M CF_3SO_3H quite close to that reported for Mo^{III}_2 in 1 M *p*-toluenesulfonic acid.[5]

Figure 3 shows sampled dc and normal-pulse polarograms of a solution prepared by such a two-stage reduction. The position and magnitude of the oxidation wave with $E_{1/2}$ near 0.015 V are quite similar to that in Figure 2 except for the absence of the small currents at potentials between -0.3 and -0.1 V. The limiting anodic current for this wave is also smaller than the diffusion-limited value and was shown to be governed by a slow chemical step preceding the electrode reaction.

Controlled-potential oxidation at $+0.3$ V of solutions of Mo^{III}_2 proceeds slowly but smoothly to Mo^{V}_2, with 2 faradays/mol of molybdenum being consumed. Both the spectra and the dc polarogram of the resulting solution are identical with those for solutions prepared by reducing Mo(VI) at -0.2 V or oxidizing monomeric Mo^{3+} at $+0.4$ V.

Note that the normal-pulse polarogram recorded with Mo^{III}_2 obtained by the two-stage reduction (Figure 3, curve 2: the initial potential was maintained on the plateau of the oxidation wave) shows only the single reduction wave that is also present in the solution resulting from exhaustive electrolysis at $+0.3$ V. There is no evidence of the wave at -0.09 V obtained with monomeric Mo^{3+} nor of the wave at -0.35 V that results when the Mo(III) is prepared by a one-stage reduction at -0.75 V (Figure 2).

Molybdenum(IV). A sample of Mo(IV) was prepared in 2 M CF_3SO_3H by adaptation of a procedure described by Souchay et al.[10] A 17-mM solution of Mo(VI) in 2 M CF_3SO_3H was converted to Mo^{III}_2 by two-stage reduction, at -0.2 and -0.75 V. Upon addition of half of an equimolar quantity of Mo(VI), reaction 1 appeared to proceed rapidly

$$Mo(III) + Mo(VI) \rightarrow Mo(IV) + Mo(V) \qquad (1)$$

to produce a solution containing equimolar quantities of Mo(III), Mo(IV), and Mo(V). Maintaining the resulting solution on a water bath at 85 °C for 1 h under argon caused the initially dark mixture to lighten and become brownish red. A dc polarogram obtained with an aliquot of the cooled solution contained only the single-reduction wave shown in Figure 4. No anodic wave appeared before oxidation of the mercury electrode commenced. The Mo(IV) species present is apparently not readily oxidized to Mo(V). The reduction wave with $E_{1/2} = -0.35$ V matches the small wave observed in polarogram 2 in Figure 2. The absorption spectrum of this solution shows a band at 550 nm (ϵ 68), which agrees with that reported recently by Ardon and Pernick and attributed to dimeric molybdenum(IV), Mo^{IV}_2.[7,11,12]

Cyclic voltammograms of solutions of Mo^{IV}_2 in 0.2 M HCl exhibit a reversible wave at low scan rates (up to 500 mV/s), with a peak separation of about 30 mV (Figure 5, curve 1).
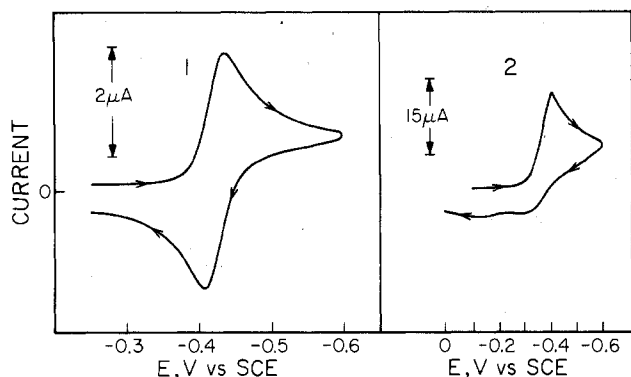
Figure 5. Cyclic voltammograms obtained with a hanging mercury drop electrode (0.032 cm^2) of (1) 0.25 mM Mo$^{IV}_2$ in 0.2 M HCl (scan rate 0.1 V/s) and of (2) 1.25 mM Mo$^{IV}_2$ in 2 M CF$_3$SO$_3$H (scan rate 1.0 V/s).

Figure 7. Cyclic voltammogram of a 2.5 mM solution of the new Mo(III) species produced by reduction of Mo$^{IV}_2$ in 2 M CF$_3$SO$_3$H; scan rate 0.1 V/s, hanging mercury drop electrode (0.032 cm^2).

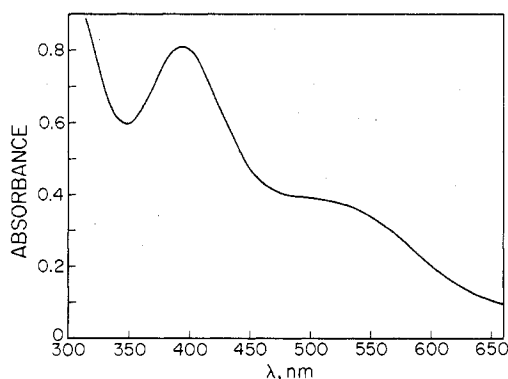**Figure 6.** Absorption spectrum of the Mo(III) species produced by reduction of Mo$^{IV}_2$ in 2 M CH$_3$SO$_3$H. The total molybdenum concentration was 2.5 mM and the optical path length was 1 cm.

Figure 8. Sampled dc polarograms of 2.5 mM Mo(VI) in 2 M CF$_3$SO$_3$H during the course of its reduction at −0.2 V. The number of faradays consumed per mole of Mo(VI) were (1) 0, (2) 0.25, (3) 0.5, (4) 0.75, and (5) 1.0.

Such behavior was first reported by Lamache and Souchay.[31] In 2 M CF$_3$SO$_3$H, the anodic portion of the voltammogram is much less well developed and appears to split into two waves (Figure 5, curve 2).

Controlled-potential reduction of Mo$^{IV}_2$ solutions at −0.45 to −0.50 V consumes 1 faraday/mol of molybdenum and produces a solution of Mo(III) with the spectrum shown in Figure 6. This spectrum differs from those of both monomeric Mo^{3+} and the dimeric ion, Mo$^{III}_2$, characterized by Ardon and Pernick.[5] The cyclic voltammogram of this new form of Mo(III), shown in Figure 7, appears to contain two closely spaced anodic peaks. However, controlled-potential oxidation of the solution at 0.1 V consumes 1 faraday/mol of molybdenum to yield a solution of Mo$^{IV}_2$ with a spectrum matching that of the original solution. The conversion of the new form of Mo(III) to Mo$^{IV}_2$ can also be effected by heating the solution for a few minutes to 85 °C.

Molybdenum(V) and Molybdenum(VI). The polarography of molybdenum(V) and -(VI) have received extensive study in a variety of media.[8,30,31] The behavior is quite sensitive to both the nature of the supporting electrolyte and the concentration of molybdenum employed. Since no previous studies have been reported in CF$_3$SO$_3$H, the behavior we observed in this medium is recorded here to allow a comparison with the electrochemistry of the lower oxidation states.

Controlled-potential reduction of Mo(VI) in 2 M CF$_3$SO$_3$H at potentials between −0.2 and −0.4 V proceeds smoothly with the consumption of 1 faraday/mol of molybdenum to yield a solution of Mo(V). Figure 8 contains a set of sampled dc polarograms of a Mo(VI) solution after various stages of reduction to Mo(V). Polarogram 5 corresponds to an almost fully reduced solution. The absorption spectrum of this so-
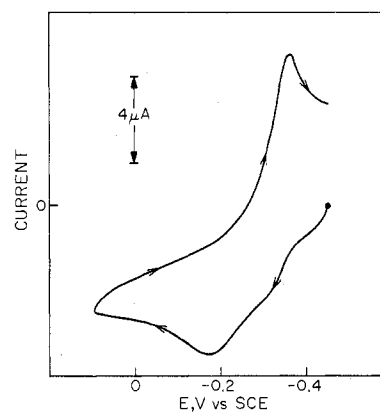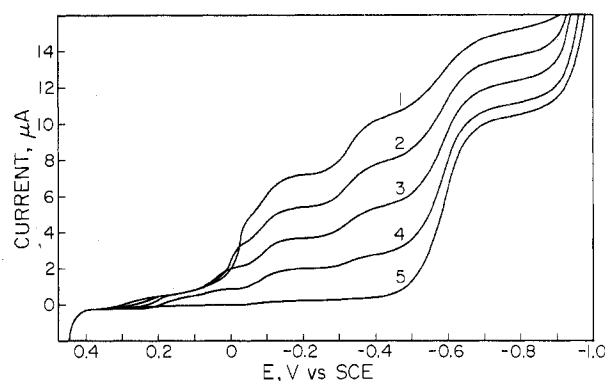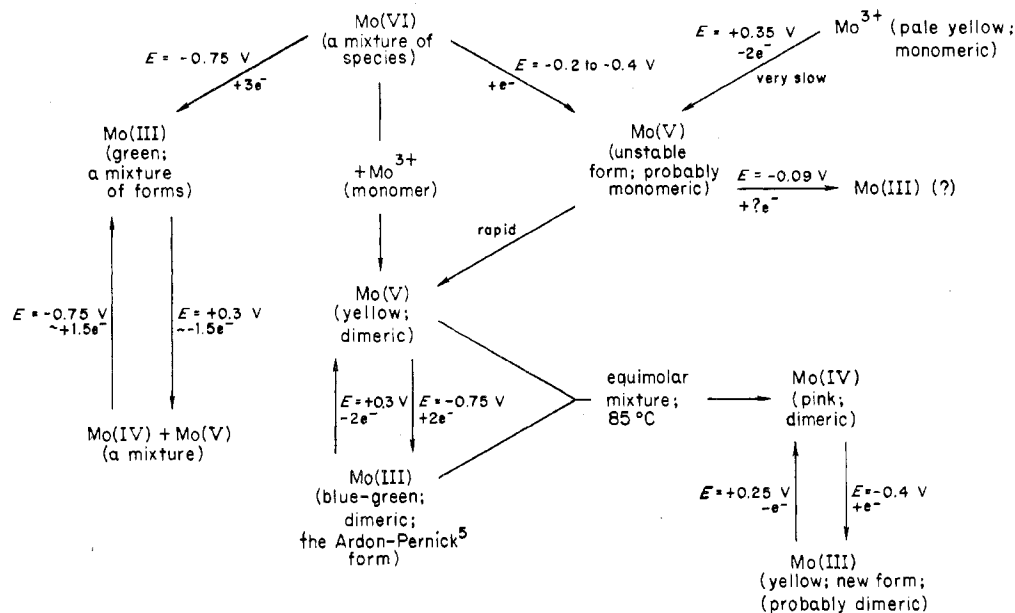
lution matched that of dimeric Mo(V), Mo$^V_2$.[16] As described above, Mo$^V_2$ is converted quantitatively to Mo$^{III}_2$ when subjected to controlled-potential reduction at −0.75 V. Thus, the wave with $E_{1/2}$ near −0.6 V in Figure 8 is assignable to the reduction of Mo$^V_2$(V) to Mo$^{III}_2$(III). (The half-wave potential of this wave becomes more positive as the acidity is increased. For example, in 6 M CF$_3$SO$_3$H $E_{1/2}$ is −0.34 V.) The other two prominent waves in polarograms 1–4 in Figure 8 are quite similar to those observed in 0.2 M HCl by Lamache and Souchay[31] and attributed to the reduction of Mo(VI) to a form of Mo(V) which is more easily reduced to Mo$^{III}_2$ than is the dimeric ion, Mo$^V_2$. Monomeric Mo(V) could be this more easily reduced species because, if it were reduced to monomeric Mo(III), the latter would react with Mo(VI) in the bulk of the solution to yield dimeric Mo$^V_2$. This reaction sequence would account for our observation that controlled-potential electrolyses at all potentials between −0.2 and −0.4 V lead ultimately to a solution containing only Mo$^V_2$.

The wave with $E_{1/2}$ near −0.08 V resembles the cathodic wave observed with normal-pulse polarograms of Mo^{3+}. Apparently the species responsible for this wave may also be generated via the reduction of Mo(VI) and has a lifetime great enough to be detected with dc polarography (at least with 1-s drop times).

Molybdenum Blue. When Mo(VI) solutions at concentrations of 10 mM or more are reduced at −0.75 V at a mercury pool electrode in 2 M in CF$_3$SO$_3$H, the initially colorless solution acquires a dark blue color almost at once. Similar observations have been reported by Souchay and co-workers.[17,30] The species reponsible for the color is doubtless the mixed-oxidation state "molybdenum blue".[32] Its formation

Scheme I. Electrochemical Behavior of Aquomolybdenum Ions (0.5 to 10 mM) in 2 M CF$_3$SO$_3$H[a]

Mo(VI) (a mixture of species)

$E = -0.75$ V, $+3e^-$ → Mo(III) (green; a mixture of forms)

$E = -0.2$ to -0.4 V, $+e^-$ → Mo(V) (unstable form; probably monomeric)

$E = +0.35$ V, $-2e^-$, very slow → Mo^{3+} (pale yellow; monomeric)

Mo(V) (unstable form; probably monomeric) $E = -0.09$ V, $+?e^-$ → Mo(III) (?)

+Mo^{3+} (monomer)

rapid → Mo(V) (yellow; dimeric)

Mo(III) (green): $E = -0.75$ V, ~$+1.5e^-$; $E = +0.3$ V, ~$-1.5e^-$ → Mo(IV) + Mo(V) (a mixture)

Mo(V) (yellow; dimeric): $E = +0.3$ V, $-2e^-$; $E = -0.75$ V, $+2e^-$ → Mo(III) (blue-green; dimeric; the Ardon–Pernick[5] form)

equimolar mixture; 85 °C → Mo(IV) (pink; dimeric)

Mo(IV) (pink; dimeric): $E = +0.25$ V, $-e^-$; $E = -0.4$ V, $+e^-$ → Mo(III) (yellow; new form; (probably dimeric)

[a] Potentials are those employed for electrolyses—not half-wave or standard potentials.

does not appear to have a permanent effect since continued electrolysis removes the blue color and eventually 3 faradays of charge/mol of molybdenum is consumed and the resulting solution contains only Mo^{III}$_2$. The appearance of molybdenum blue becomes briefer as the molybdenum concentration is decreased. We rarely encountered it at concentrations below ca. 0.5 mM.

Discussion

Scheme I gives a summary of the overall electrochemical behavior of the various forms and oxidation states of molybdenum examined in this study. The evidence supporting the details of the scheme will be discussed in what follows.

Both monomeric Mo^{3+} and the dimeric ion characterized by Ardon and Pernick,[5] Mo^{III}$_2$, undergo two-electron oxidations to give the dimeric Mo^V$_2$ ion. The rates of oxidation of both forms of Mo(III) are limited by chemical reactions that precede the electrode reaction. The rate is particularly low in the case of Mo^{3+} for which the overall electrode process results in the conversion of a monomeric to a dimeric species. The transient species which gives a pulse polarographic wave at −0.09 V (Figure 1) may well be an unstable form of Mo(V) that is produced initially when Mo^{3+} is oxidized. This species must convert spontaneously into Mo^V$_2$ during exhaustive controlled-potential oxidation of Mo^{3+} because the wave at −0.09 V is not present in polarograms of oxidized solutions. A likely candidate for this transient species is monomeric Mo(V) which persists in solutions of much higher acidity[21] or in the presence of stabilizing ligands.[22] Added evidence for the transient existence of a form of molybdenum(V) different from the stable dimeric ion is the presence of a wave near −0.09 V in the polarograms for the reduction of Mo(VI) (Figure 8) and the fact that catalytic reduction of perchlorate ensues[31] when Mo(VI) is reduced at potentials, e.g., −0.25 V, where Mo^V$_2$ is the sole stable product formed in the absence of perchlorate. Since perchlorate is not reduced by Mo^V$_2$, the active reductant appears to be another species formed during the one-electron reduction of Mo(VI) which is largely monomeric at millimolar concentrations in 2 M acid.[33,34] Either monomeric Mo(V) or the product of its further reduction are leading candidates for this reactive intermediate. Lamache and Souchay[31] argued that a transient, more reactive form of

Mo(III) is the species responsible for the reduction of perchlorate. This interpretation seems sound inasmuch as Mo^V$_2$ does not react with perchloric acid even at concentrations where some monomerization of Mo(V) might be expected.[21] The reactive form of Mo(III) cannot be the dimer of Ardon and Pernick[5] because its rate of reaction with perchlorate is not great enough to account for the current enhancements observed by Lamache and Souchay.[31] In fact, these authors report that the addition of perchlorate is without effect on the magnitude of the polarographic current corresponding to the reduction of Mo^V$_2$ to Mo^{III}$_2$. One obvious possibility is that the transient, reactive form of Mo(III) is the monomeric Mo^{3+} ion prepared by Bowen and Taube.[1,2] However, Lamache and Souchay[31] report a well-developed, anodic wave in a cyclic voltammetric study of the reactive form of Mo(III), and Mo^{3+} exhibits no such wave.

The most familiar form of aquomolybdenum(III), Mo^{III}$_2$, is dimeric to begin with, but its structure may nevertheless differ enough from that of Mo^V$_2$ (e.g., a single oxo or hydroxy bridge in Mo^{III}$_2$ compared with the double oxo bridge in Mo$_2$O$_2$$^{2+}$ [16]) that some chemical rearrangements are required before electron transfer can occur. Since no transient oxidation product is present in the normal-pulse polarogram of Mo^{III}$_2$ (Figure 3), the initial reaction product can apparently convert rapidly to the stable Mo^V$_2$ ion.

The third form of Mo(III) listed in Scheme I could only be obtained via Mo(IV). Solutions of the latter were readily prepared by reacting equal amounts of Mo^V$_2$ with Mo^{III}$_2$. The resulting pink solution could be repeatedly cycled between Mo(IV) and the new, yellow form of Mo(III) by controlled-potential reduction at −0.4 V followed by oxidation at +0.25 V. The Mo(IV)/Mo(III) couple also exhibits a quasi-reversible cyclic voltammogram in 2 M CF$_3$SO$_3$H (Figure 7) and fully reversible behavior in the presence of 0.2 M chloride (Figure 5). The value of $E_p - E_{p/2}$ for the voltammograms (33 mV) and the slope of plots of log $(i/(i_d - i))$ vs. E for polarograms obtained in either supporting electrolyte (42 mV) are too small to correspond to a one-electron process. They are indicative of a two-electron process which is not completely Nernstian.[35,36] These data constitute one reason for believing that both the Mo(IV) and Mo(III) species involved are dimeric.

The new, yellow form of Mo(III) might be presumed to have a structure quite similar to Mo^{IV}_2[11] in view of their facile interconvertability. The same line of reasoning would suggest that the structure of Mo^{IV}_2 differs substantially from that of Mo^V_2 since it proved impossible to electrooxidize Mo^{IV}_2 to Mo^V_2 under conditions where the electrochemical conversion of both Mo^{3+} and Mo^{III}_2 to Mo^V_2 is slow but complete. There has been some disagreement as to whether Mo(IV) is a monomeric or dimeric ion.[7,11,13] The electrochemical data, while far from definitive, favor the dimeric assignment which is also supported by recent cryoscopic measurements.[12]

A mixture of the two forms of dimeric Mo(III) is obtained if Mo(VI) is reduced in one stage at –0.75 V. This result can be understood by recognizing that reaction 1 can proceed in the bulk of the stirred solution where the electrogenerated Mo^{III}_2 will encounter Mo(VI) during the first third of the electrolysis. Mo^V_2 and Mo^{IV}_2 are thereby introduced into the solution. The Mo^V_2 is reduced further at –0.75 V to Mo^{III}_2 but the Mo^{IV}_2 is reduced to the new, yellow form of Mo(III). Thus, by the time the electrolysis is complete, 3 faradays/mol of Mo(VI) is consumed and a mixture of the two forms of Mo(III) is obtained. Reoxidation of the mixture at +0.3 V consumes only 1.4–1.6 faradays/mol and yields a solution with the spectrum and polarographic response (Figure 2) expected for a mixture of Mo^{IV}_2 and Mo^V_2. Titration of the Mo(III) mixture with Fe^{3+} also requires 1.4–1.6 equiv and produces the same mixture of Mo^{IV}_2 and Mo^V_2. The precise ratio of the two oxidation states obtained depends upon stirring conditions and the rate of reaction 1, but the fact that 1.4–1.6 faradays/mol were typically required during the reoxidation step indicates that Mo^{IV}_2 and Mo^V_2 are formed in approximately equal amounts.

None of the yellow form of Mo(III) is formed during the two-stage reduction of Mo(VI) because complete conversion to Mo(V) is effected during the first stage and the Mo^{III}_2 produced during the second stage encounters only Mo^V_2 in the bulk of the solution. Since these two ions do not react at appreciable rates at room temperature, no Mo(IV) is formed and, therefore, no route is available for the formation of the yellow form of Mo(III). This also accounts for the absence of the wave corresponding to Mo(IV) in the normal-pulse polarogram in Figure 3. Both Mo^{3+} and the new, yellow form of Mo(III) decompose slowly in 2 M CF_3SO_3H to form Mo^{IV}_2. However, if Mo(VI) is added to solutions of Mo^{3+}, the only product is Mo^V_2 while Mo(VI) reacts with Mo^{III}_2 to form both Mo^{IV}_2 and Mo^V_2.

It should be noted that both the spectral and electrochemical properties of the new Mo(III) species differ significantly from those of the monomeric Mo^{3+} ion of Bowen and Taube.[1,2] The two species can easily be distinguished from each other even in mixtures.

The data in hand do not provide much basis for speculations about the structural differences between the blue-green dimeric Mo^{III}_2 ion of Ardon and Pernick and the yellow form obtained by reducing Mo^{IV}_2. However, the sluggishness of the thermodynamically favorable reaction between Mo^{III}_2 and Mo^V_2

to produce Mo^{IV}_2 might well be taken as a signal that considerable structural changes accompany the double-electron transfer despite the fact that very similar oxo- or hydroxy-bridged structures have been proposed for all three of these dimeric ions.[7] One possible implication of the observed behavior is that the Mo^{III}_2 and Mo^V_2 ions share more common structural features than does either of these two ions with Mo^{IV}_2.

References and Notes

(1) A. R. Bowen and H. Taube, *J. Am. Chem. Soc.*, **93**, 3287 (1971).
(2) A. R. Bowen and H. Taube, *Inorg. Chem.*, **13**, 2245 (1974).
(3) K. Kustin and D. Toppen, *Inorg. Chem.*, **11**, 2851 (1972).
(4) Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 767 (1973); *J. Chem. Soc., Dalton Trans.*, 1048 (1975).
(5) M. Ardon and A. Pernick, *Inorg. Chem.*, **13**, 2275 (1974).
(6) Y. Sasaki and A. G. Sykes, Proceedings of 1st International Conference on Chemistry and Uses of Molybdenum, Climax Molybdenum Co., London, 1974, p 64.
(7) M. Ardon and A. Pernick, *J. Less-Common Met.*, **54**, 233 (1977).
(8) P. Souchay, M. Cadiot, and M. Duhameaux, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **262**, 1524 (1966).
(9) M. Lamache and M. Duhameaux, *Rev. Chim. Miner.* **5**, 459 (1968).
(10) P. Souchay, M. Cadiot, and B. Biossat, *Bull. Soc. Chim. Fr.*, 892 (1970).
(11) M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, **95**, 6871 (1973).
(12) M. Ardon, A. Bino, and G. Yahav, *J. Am. Chem. Soc.*, **98**, 2338 (1976).
(13) Th. Ramasami, R. S. Taylor, and A. G. Sykes, *J. Am. Chem. Soc.*, **97**, 5918 (1975).
(14) P. Souchay, *J. Inorg. Nucl. Chem.*, **37**, 1307 (1975).
(15) M. Lamache, *J. Less-Common Met.*, **39**, 179 (1975).
(16) M. Ardon and A. Pernick, *Inorg. Chem.*, **12**, 2484 (1973).
(17) J. P. Simon and P. Souchay, *Bull. Soc. Chim. Fr.*, 1402 (1966).
(18) B. Viossat and M. Lamache, *Bull. Soc. Chim. Fr.*, 1570 (1975).
(19) Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 396 (1975).
(20) G. R. Cayley, R. S. Taylor, R. K. Wharton, and A. G. Sykes, *Inorg. Chem.*, **16**, 1377 (1977).
(21) L. Sacconi and R. Cini, *J. Am. Chem. Soc.*, **76**, 4239 (1954).
(22) J. T. Spence and M. Heydanek, *Inorg. Chem.*, **6**, 1489 (1967).
(23) K. H. Lohmann and R. C. Young, *Inorg. Synth.*, **4**, 97 (1953).
(24) E. A. Deutsch, Ph.D. Thesis, Stanford University, 1967.
(25) G. Lauer, R. Abel, and F. C. Anson, *Anal. Chem.*, **39**, 765 (1967).
(26) D. D. MacDonald, "Transient Techniques in Electrochemistry", Plenum Press, New York, N.Y., 1977, Chapter 4.
(27) L. Guibé and P. Souchay, *J. Chim. Phys.*, **54**, 684 (1957).
(28) Reference 26, Chapter 5.
(29) F. Forster and E. Fricke, *Angew. Chem.*, **36**, 458 (1923); H. Hartmann and H. J. Schmidt, *Z. Phys. Chem.*, **11**, 234 (1957).
(30) M. Lamache-Duhameaux, M. Cadiot, and P. Souchay, *J. Chim. Phys.*, **65**, 1921 (1968).
(31) M. Lamache and P. Souchay, *J. Chim. Phys.*, **2**, 384 (1973).
(32) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Interscience, New York, N.Y., 1972, p 947.
(33) L. Krumenacker and R. J. Bye, *Bull. Soc. Chim. Fr.*, 3099, 3103 (1968).
(34) J. F. Ojo, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 500 (1975).
(35) A "Nernstian" electrode reaction is one for which the potential of the electrode and the concentrations of reactants and product at its surface adhere to the Nernst equation as the electrode reaction procedes. Nernstian reactions are necessarily reversible but the converse need not be true.
(36) Lamache and Souchay[31] report that cyclic voltammograms for Mo(IV) in 0.2 M HCl correspond to a one-electron reversible process because anodic and cathodic peak potentials are separated by ca. 60 mV. However, the peak potential separation in the voltammogram shown in ref 31 is nearer 50 mV which is compatible with a quasi-Nernstian, two-electron reduction of a dimeric reactant.