Whitesides et al.[4] resides in the identity of the primary light-absorbing species present at the onset of irradiation. In an attempt to clarify this point, we performed the following experiment. The suspension that forms upon stirring 70 mg of **1** with 10 mL of pentane[23] was filtered, and the absorption spectrum of the resulting solution was measured. The absorbance in the ultraviolet region was found to (i) possess a maximum at ~246 nm (cf. Figure 1) and (ii) be considerably larger than that expected if CuCl and uncomplexed ccCOD were the only absorbing species present.[24] These observations provide convincing evidence for the presence of a ground-state cuprous chloride–ccCOD complex in solution. Moreover, this complex, rather than free ccCOD, accounts for the major fraction of the total radiation absorbed by the system. It seems likely, therefore, that the mechanism in Scheme II also governs the photochemical behavior of pentane suspensions of **1**.

Concluding Remarks

In a recent survey of the Cu(I)-sensitized photoreactions of olefins, we categorized the mechanisms by which these processes occur into three general classes.[2] These are presented in Scheme III, where the symbol Cu(I) is used in a generic sense to denote some Cu(I) compound. Of the photoreactions surveyed, the CuCl/ccCOD system provided the lone example of a class 2 mechanism. This assignment must now be seriously doubted in view of the compelling evidence that a ground-state complex plays a pivotal role (i.e., class 1 behavior) in the sensitization process. Indeed, we feel that a class 2 mechanism constitutes, at most, a minor pathway in this system.

In a broader context, it is worthwhile to consider the conditions under which a class 2 mechanism might be expected to occur. Inasmuch as this pathway involves the interaction of a photoexcited olefin with a ground-state Cu(I) species, the lifetime of the olefin excited state must be sufficiently long to permit this bimolecular process to compete effectively with other modes of deactivation. Under the assumption that (1) bimolecular sensitization occurs with a diffusion-controlled rate constant of 10^{10} L mol^{-1} s^{-1} (a typical value for diffusion in common organic solvents)[25] and (2) the concentration of Cu(I) is 2×10^{-4} mol L^{-1}, it can be shown that the lifetime of the olefin excited state must be $>1 \times 10^{-7}$ s in order to attain a sensitization quantum yield of 0.2. Generally, the lowest lying singlet and triplet states of olefins which are not constrained to rigid geometries possess lifetimes appreciably shorter than this value since rapid radiationless deactivation may occur via a twisting motion about a C=C bond.[26,27] Since the 1,5-cyclooctadiene framework is reasonably flexible as evidenced by the isolation of three isomeric forms, the unimportance of a class 2 sensitization mechanism in this system is not surprising. The obvious, though unproven corollary of the above argument is that olefins which cannot undergo facile twisting motions should be more prone to this type of mechanism because of longer excited state lifetimes.

(23) These quantities correspond to those used in ref 4.
(24) For example, the absorbance at the 246-nm maximum is 0.24, whereas a value <0.05 should be observed if CuCl and ccCOD were the only absorbing species in solution.
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Properties of New Aquo Ions Obtained on Reduction of the Trinuclear Aquomolybdenum(IV) Ion Mo₃O₄⁴⁺ †

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Reduction of the Mo(IV) aquo ion, $Mo_3O_4^{4+}$, with Zn/Hg or by electrochemical methods at a potential ca. –0.25 V (vs. NHE) in *p*-toluenesulfonic acid (HPTS) and [H$^+$] = 0.5–4.0 M gives a new green aquo ion which titrates for Mo(III). The ion is oxidized by ClO₄$^-$ as well as O₂ and is characterized by a spectrum (λ_{max}, nm (ϵ, M^{-1} cm^{-1} per Mo)) with adsorptions at 420 (sh) (ca. 100), 635 (80), and 825 (45). The ease of chemical and electrochemical reoxidation to Mo^{IV}_3 suggests that the essential trinuclear core structure is retained. The Mo^{III}_3 ion is more strongly held on a cation-exchange column than the 4+ Mo^{IV}_3 ion, consistent with protonation of bridging oxo ligands. Cyclic voltammetry studies suggest minor structural changes prior to formation of Mo^{III}_3. On addition of Mo^{III}_3 to Mo^{IV}_3, electrochemical reduction of Mo^{IV}_3, or (partial) oxidation of Mo^{III}_3, preferably at [H$^+$] ≥ 4.0 M, a mixed-oxidation-state species is obtained which titrates for $Mo^{III}_2Mo^{IV}$ and has absorption maxima at 398 (230), 495 (sh) (ca. 115), and 1050 (100). At lower [H$^+$], the extent of formation decreases, and at [H$^+$] ≤ 0.5 M it is <30%. Consistent with these observations, when the [H$^+$] (<4.0 M) of solutions of $Mo^{III}_2Mo^{IV}$ is decreased, amounts of Mo^{III}_3 and Mo^{IV}_3 are obtained. Reduction potentials determined in 2 M HPTS are –0.10 V for $Mo^{IV}_3 + 2e^- \rightleftharpoons Mo^{III}_2Mo^{IV}$ and –0.18 V from experiments involving oxidation of the Mo^{III}_3 species, $Mo^{III}_2Mo^{IV} + e^- \rightleftharpoons Mo^{III}_3$. No evidence was obtained for a $Mo^{III}Mo^{IV}_2$ ion.

Introduction

It has now been established that the Mo(IV) aquo ion is a triangulo trinuclear species having an $Mo_3O_4^{4+}$ core structure, with three water molecules coordinated to each molybdenum.[1]

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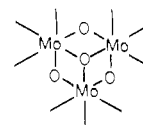
† No reprints available.

Thus, X-ray crystal structures of $M_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]$, $M = Cs^+$, NH_4^+,[2] and $(Me_4N)_4[Mo_3O_4(NCS)_8(H_2O)]$,[3] together with studies using oxygen-18 labeled solvent water,[1] have served to demonstrate that the Mo_3O_4 unit present in crystals is retained in solution.

Over the past 10 years the structure of this aquo ion has been the subject of considerable debate. Ardon and colleagues[4] have favored a dimeric structure of charge 4+ from their ion-exchange and cryoscopic studies. Earlier kinetic work from this group on the substitution reaction of NCS^- with aquo Mo(IV) appeared to favor a mononuclear structure.[5] Recent extended X-ray absorption fine structure (EXAFS) measurements on the ion in 4 MHCl have shown the existence of Mo–Mo interactions within the first coordination sphere.[6] Although the results were interpreted in terms of dimeric Mo(IV), the trimer Mo^{IV}_3 (as Mo_3O_4) also gives a satisfactory fit to EXAFS data. The case for the Mo^{IV}_3 aquo ion is now compelling.[7] It has also been demonstrated that monomeric and/or dimeric Mo(IV) species, generated in the oxidation of Mo^{III} and Mo^{III}_2 aquo ions, are readily oxidized through to Mo^V_2 and are much more redox active than Mo^{IV}_3.[8] A summary of properties of the aquo ions of Mo has recently appeared.[9]

Earlier unpublished work[10] has shown that the Mo(IV) aquo ion, when passed down an O_2-free Zn/Hg Jones reductor column, is quantitatively converted to green Mo(III). The present study is concerned with the identity and properties of this product which is not the green Mo^{III}_2 aquo dimer[11] and bears no resemblance to the pale yellow monomer $Mo(H_2O)_6^{3+}$.[12] A mixed-oxidation-state Mo(III)/Mo(IV) aquo ion detected in previous studies,[13,14] but not correctly characterized, is also considered.

A preliminary account of this work has appeared.[15]

Experimental Section

Materials. A sample of aquo Mo(IV) trimer (ca. 0.1 M) in 2–3 M HPTS (*p*-toluenesulfonic acid; Aldrich) was prepared by the procedure previously described.[16,17] The concentration of aquo Mo(IV) was determined spectrophotometrically at 505 nm ($\epsilon = 63$ M^{-1} cm^{-1} per Mo).[16] Solutions were also standardized by addition of excess Fe(III) to oxidize the Mo(IV) to Mo(VI) and by titrating the Fe(II) formed with Ce(IV) with ferroin as indicator. Solutions of Mo^{IV}_3 were stored under N_2, and an O_2-free atmosphere was maintained although air oxidation is slow (<10% per day). Zinc shot (Hopkin and Williams, 8–30 mesh) was amalgamated by treating it with mercury(II) chloride (2% solution) for ca. 10 min. and then washing.

Electrochemistry. The cell used was of a standard three-electrode design with a saturated calomel electrode and hanging-Hg-drop electrode in the outer test solution and an inner anode compartment
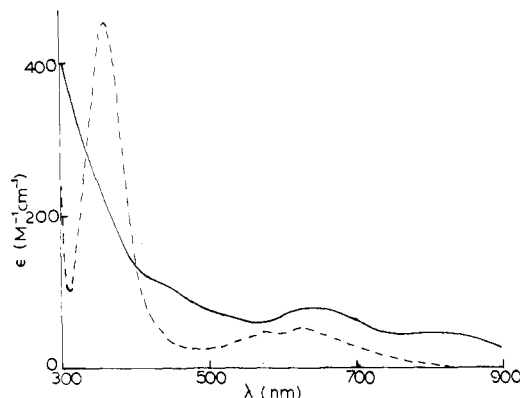
of 14-mm diameter glass tubing, closed at the lower end with a No. 3 sinter and containing a Pt wire electrode. For the electrolytic reduction, the Hg pool and Pt counterelectrode were connected to the terminals of a Farnell stabilized power supply Model E 3011. For the cyclic voltammetry measurements, the hanging-Hg-drop (Metrohm E140), Pt counter, and calomel reference electrodes (Radiometer K401) were connected to the required terminals of a Chemical Electronnics Model DD50SU potentiostat. The output potential to the working electrode was monitored with an Advanced Instruments DMM2 digital multimeter. The voltammograms were recorded on a Lloyd Model PL51 X-Y recorder. The cell temperature was monitored with a Comark Model 3007 digital thermometer using a NiCr/NiAl thermocouple connected to the outside of the cell.

Spectrophotometry. Spectra were recorded with a Perkin-Elmer 550 and 554 scan UV–visible spectrophotometers. Near-IR spectra were obtained on a Unicam SP700 instrument. All absorption coefficients (ϵ) reported are per Mo atom.

Chromatography. Ion-exchange experiments were conducted using Dowex 50W-X2 (Sigma Chemical) cation-exchange resins previously treated with 2 M HPTS and deoxygenated water (N_2 gas stream). The resins were always flushed on the column with a N_2 stream (entering at the bottom of the column) for at least 4 h and were then treated with two bed volumes of O_2-free HPTS of appropriate concentration prior to loading of the sample. The jacketed column (typically 12 cm long by 1-cm diameter) was cooled by circulating ice-cold water.

Conditions. Molybdenum(III) ions react rapidly with O_2, so rigorous O_2-free (N_2) procedures (Atlas nylon syringes, stainless-steel or Teflon needles, rubber serum caps) were required. Perchlorate ions also react with Mo(III) and HPTS; a strong acid with PTS^-, having weak donor properties, was therefore used. Ionic strengths were adjusted to $I = 2.0$ M with sodium *p*-toluenesulfonate, except when [HPTS] in excess of 2.0 M was required. The NaPTS used was prepared by addition of NaOH to HPTS and recrystallization.

Results

Spectrophotometry. Under rigorous O_2-free conditions, aquo Mo^{IV}_3 in HPTS is reduced to a green Mo(III) ion by both amalgamated zinc (here used as a small batch and not as a column) and by electrochemical methods at a Hg-pool cathode. The same spectrum (λ_{max}, nm (ϵ, M^{-1} cm^{-1} per Mo) 420 (sh) (ca. 100), 635 (80), 825 (45)) is obtained for all HPTS concentrations employed (0.5–4.0 M) (Figure 1). A potential of ca. -0.25 V (vs. NHE) is typically required to form the green Mo(III) species. Its oxidation state (3.0 ± 0.05) was verified by titration with Ce(IV). The spectrum is different from that of the previously prepared Mo(III) dimer (360 (450), 572 (48), and 624 (55); Figure 1). Reoxidation to Mo^{IV}_3 of a 5 mM solution (3 mL), with $[H^+] = 2.0$ M, occurs readily (<10 min) on intermittent bubbling of O_2 through a solution, which suggests that the trimeric structure Mo^{III}_3 is retained.

Careful monitoring of spectra during the electrochemical change has indicated that certainly at [HPTS] ≥ 1.0 M an intermediate is formed. At [HPTS] ≥ 4.0 M, concentrations

Figure 1. Comparision of spectra of the Mo(III) aquo dimer (---) and aquo trimer (—) in 2 M HPTS solution.

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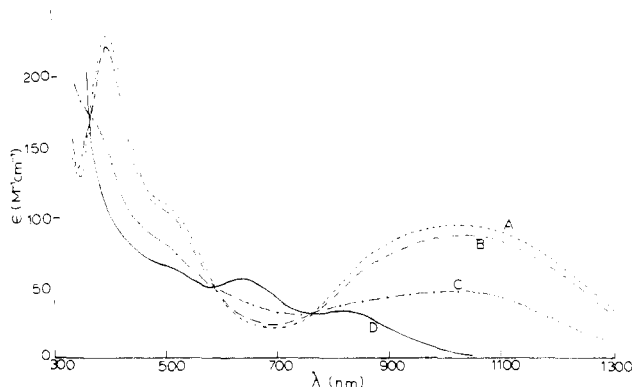(17) Arden, M.; Pernick, M. *J. Am. Chem. Soc.* **1973**, *95*, 6871.

Figure 2. Extent of formation of $Mo^{III}_2Mo^{IV}$ (peak at 1050 nm) when 2:1 amounts of Mo^{III}_3 and Mo^{IV}_3 are mixed in 4.0 (A), 2.00 (B), and 0.50 M HPTS (C). Spectrum D is obtained by addition of Mo^{III}_3 and Mo^{IV}_3 spectra, with the assumption of no reaction.
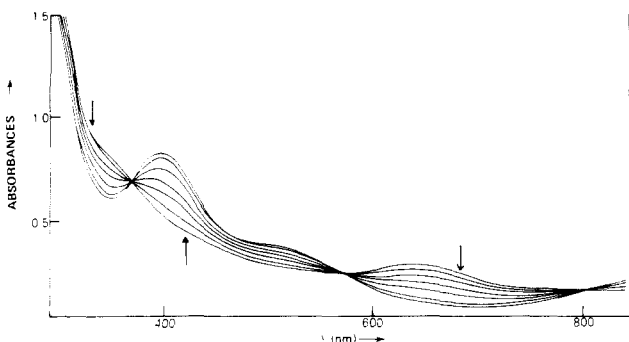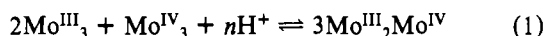

Figure 3. Changes in spectra (at ∼1-min intervals) observed on O_2 oxidation of Mo^{III}_3 to $Mo^{III}_2Mo^{IV}$ with [HPTS] > 2.0 M.

Figure 4. Cyclic voltammograms for the reduction of aquo Mo^{IV}_3 with [H$^+$] of 0.50 (A), 1.0 (B), and 2.0 M (C). Scan rate was 100 mV s^{-1}.

of the orange-pink intermediate maximize. The intermediate is characterized by a spectrum with absorptions of (λ_{max}, nm (ϵ, M^{-1} cm^{-1})) 398 (230), 495 (sh) (ca. 115), and 1050 (100). When amounts of Mo^{III}_3 and Mo^{IV}_3 are mixed with HPTS in the range 0.5–4.0 M, the same intermediate is formed, the proportion increasing with increasing [H$^+$] (Figure 2). Retention of crossover points in these spectra suggest that the same 2:1 ratio of Mo^{III}_3 to Mo^{IV}_3 is retained at all times and that there is only one other colored component, namely, the intermediate. Titration of the intermediate with Ce(IV) gives a formal oxidation state of 3.33 ± 0.05, corresponding to a mixed-oxidation-state ion which can be represented as $Mo^{III}_2Mo^{IV}$.

Attempts were made to estimate the [H$^+$] involvement in (1). With the assumption that over the [H$^+$] range 0.5–2.0

$$2Mo^{III}_3 + Mo^{IV}_3 + nH^+ \rightleftharpoons 3Mo^{III}_2Mo^{IV} \qquad (1)$$

M, with I = 2.0 M, only single Mo^{III}_3 and Mo^{IV}_3 species are present and the reactants do not change their states of protonation, (2) and (3) may be defined, where K_{app} is the ap-

$$K = [Mo^{III}_2Mo^{IV}]^3/[Mo^{III}_3]^2[Mo^{IV}_3][H^+]^n \qquad (2)$$

$$K = K_{app}/[H^+]^n \qquad (3)$$

parent equilibrium constant at each [H$^+$]. A graph of log K_{app} against log [H$^+$] gives a value of n between 3 and 4. When O_2 is admitted to a Mo^{III}_3 solution with HPTS ≥ 2.0 M, isosbestic points are observed at 366, 571, and 804 nm (Figure 3) for the first stage of reaction. These correspond to the $Mo^{III}_3 \rightarrow Mo^{III}_2Mo^{IV}$ conversion. When $Mo^{III}_2Mo^{IV}$ is allowed to react with O_2, with [HPTS] ≥ 2.0 M, other isosbestics are obtained. Investigations of 2:1 mixtures of Mo^{IV}_3 to Mo^{III}_3 have failed to reveal any evidence for formation of a Mo^{III}-Mo^{IV}_2 ion at HPTS concentrations of 0.5–4.0 M. Significantly, careful analysis of the resulting spectra indicates an
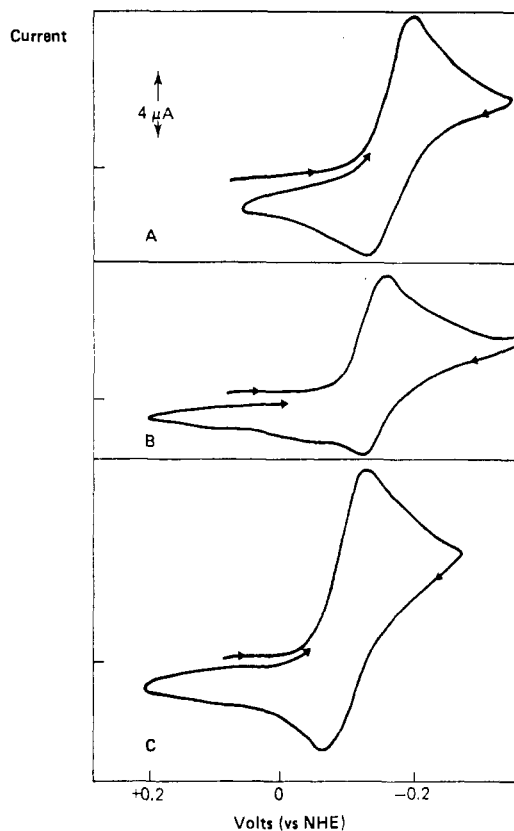
almost quantitative mixture of $Mo^{III}_2Mo^{IV}$ and Mo^{IV}_3 in 4.0 M HPTS, with increasing amounts of Mo^{III}_3 at lower HPTS.

Ion-Exchange Chromatography. Trimeric Mo(IV), $Mo_3O_4^{4+}$, is only eluted from a Dowex50 W X2 cation-exchange column with [HPTS] ≥ 2.0 M. Under similar conditions, the new Mo^{III}_3 aquo ion is more strongly held and is only slowly eluted with [HPTS] = 3.0 M. This suggests that the charge is probably ≥4+ per Mo(III) trimer.

It has also been demonstrated that 2:1 mixtures of Mo^{III}_3 and Mo^{IV}_3 elute essentially as one band, the $Mo^{III}_2Mo^{IV}$ complex at high [HPTS] (3.0 M). When a low (0.5 M) HPTS concentration is used, the single-state Mo^{III}_3 and Mo^{IV}_3 ions are observed as separate bands. Moreover 1:2 mixtures of Mo^{III}_3 and Mo^{IV}_3 give two dominant bands corresponding to $Mo^{III}_2Mo^{IV}$ and Mo^{IV}_3 in 3 M HPTS and separate as unreacted Mo^{III}_3 and Mo^{IV}_3 in 0.5 M HPTS. These experiments also demonstrated that $Mo^{III}_2Mo^{IV}$ is eluted at a faster rate than Mo^{IV}_3 in 2–3 M HPTS.

Electrochemistry. Further confirmation of the formation of an intermediate in the Mo^{IV}_3 reduction at high [HPTS] has been gained from cyclic voltammetry. With the use of a hanging-Hg-drop electrode, cyclic voltammograms for aquo Mo^{IV}_3 (Figure 4) and the new aquo Mo^{III}_3 (Figure 5) in various HPTS concentrations are readily obtained under O_2-free conditions. Reduction potentials have been estimated from response curves at different HPTS concentrations and are as listed in Table I.

Cyclic voltammograms for Mo^{IV}_3 (Figure 4) show a quasi-reversible reduction process, the midpoint potential of which shifts in the positive direction with increasing [H$^+$] (0.5–4.0 M) (Table I). This is explained by formation of the mixed-valence $Mo^{III}_2Mo^{IV}$ intermediate at the higher [H$^+$]. It has previously been shown[14] that reduction of Mo^{IV}_3 at a Hg-pool electrode (−0.150 V vs. NHE), in 2 M trifluoromethanesulfonic acid, gives a spectrum identical with that now reported
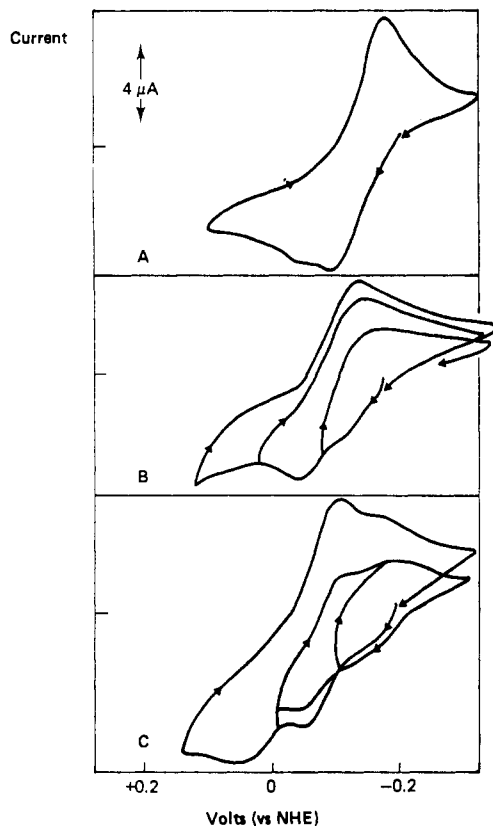
Figure 5. Cyclic voltammograms for the oxidation of aquo Mo^{III}_3 with [H$^+$] of 0.50 (A), 1.0 (B), and 2.0 M (C). Scan rate was 100 mV s^{-1}.

Table I. Reduction Potentials (vs. NHE) from Cyclic Voltammograms (Estimated Errors ±0.002 V)^a

[H$^+$], M	$Mo^{IV}_3/$ $^*Mo^{III}_2Mo^{IV}$, V	$Mo^{IV}_3/$ $Mo^{III}_2Mo^{IV}$,^{b} V	$Mo^{III}_2Mo^{IV}/$ Mo^{III}_3,^{b} V
0.5	−0.156	−0.137	(−0.165)^c
1.0	−0.137	−0.113	(−0.173)^c
1.7	−0.114	−0.078	−0.175
2.0	−0.100	−0.066	−0.175
4.0	−0.090	−0.045	−0.190

^{a} Ionic strengths adjusted to 2.0 M (NaPTS) except for the [H$^+$] = 4.0 M experiment. The reduced form obtained initially on reduction of Mo^{IV}_3 is referred to as $^*Mo^{III}_2Mo^{IV}$. ^{b} From studies on reduced solutions. ^{c} Not obtainable from voltammograms owing to low formation of $Mo^{III}_2Mo^{IV}$. Values estimated by extrapolation of data at higher [H$^+$] values.

for the $Mo^{III}_2Mo^{IV}$ ion. Examination of cyclic voltammograms for solutions of Mo^{III}_3 at varying [H$^+$] values (Figure 5) provides an explanation. At the higher [H$^+$] values (ca. 2.0 M), two distinct oxidation processes are observed, the first giving $Mo^{III}_2Mo^{IV}$ and the second, Mo^{IV}_3. Electrolyses at potentials more negative than ca. −0.2 V vs. NHE (cf. −0.76 V vs. NHE for Zn/Hg) are required to generate Mo^{III}_3 over the [H$^+$] range employed (0.5–4.0 M). Two reduction processes are presumably not seen in the cyclic voltammograms of Mo^{IV}_3 at the higher [H$^+$] levels because a rate-limiting structural rearrangement of $Mo^{III}_2Mo^{IV}$ is required at the Hg drop before reduction to Mo^{III}_3 can occur. Thus there are two structurally similar forms of $Mo^{III}_2Mo^{IV}$, one of which can be rapidly reduced to Mo^{III}_3 and the other which we refer to as $^*Mo^{III}_2Mo^{IV}$ can be rapidly reoxidized to Mo^{IV}_3. Both these processes are reversible on the cyclic time scale (3–100 mV s^{-1}).

Reduction potentials for Mo^{IV}_3 (Table I) are seen to shift to more positive values with increasing [H$^+$], implying also that protonation accompanies reduction. The oxidation po-

Table II. Variation of log K_{app} with [H$^+$] for the Formation of $Mo^{III}_2Mo^{IV}$ from Spectroscopy (spec) (λ = 1050 nm) and Electrochemical (elect) Measurements (eq 6)^a

[H$^+$], M	log K_{app} (spec)	log K_{app} (elect)	[H$^+$], M	log K_{app} (spec)	log K_{app} (elect)
0.5	0.60	0.63	1.7		2.62
1.0	1.95	1.63	2.0	3.01	3.27
			4.0	3.86	4.15

^{a} Ionic strengths adjusted to 2.0 M (NaPTS) except for [H$^+$] = 4.0 M experiment.

tential for Mo^{III}_3 shifts slightly negative with increasing [H$^+$], and the combined effect is to increase the difference in reduction potentials for the Mo^{IV}_3 and Mo^{III}_3 ions (ΔE_1). This has the effect[18] of increasing the extent of formation of the mixed-oxidation-state ions as [H$^+$] increases, (4), where K_1

$$\log K_1 = \Delta E_1/0.059 \qquad (4)$$

is the comproportionation equilibrium constant at 25 °C. The question then is why only the $Mo^{III}_2Mo^{IV}$ ion is observed with very little (if any) $Mo^{III}Mo^{IV}_2$. This is explained by considering the second comproportionation equilibrium (eq 5), for which

$$Mo^{III}_2Mo^{IV} + Mo^{IV}_3 \underset{}{\overset{K_2}{\rightleftharpoons}} 2Mo^{III}Mo^{IV}_2 \qquad (5)$$
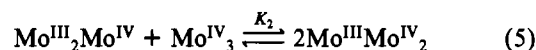
ΔE_2 can be defined. Here the reductant $Mo^{III}_2Mo^{IV}$ has a greater redox potential (Table I) as compared to Mo^{IV}_3, such that ΔE_2 is negative. Hence the value of log K_2 is negative, favoring disproportionation of $Mo^{III}Mo^{IV}_2$ to give $Mo^{III}_2Mo^{IV}$. The value of log K_{app} for the formation of $Mo^{III}_2Mo^{IV}$ is related to log K_1 and log K_2 by (6). Values of log K_{app} calculated

$$\log K_{app} = 2 \log K_1 - \log K_2 \qquad (6)$$

by monitoring the $Mo^{III}_2Mo^{IV}$ concentration at 1050 nm at different [H$^+$] show satisfactory agreement with those calculated by using (6) (Table II).

Discussion

The trimeric Mo^{IV}_3 aquo ion in HPTS solutions is reduced by Zn/Hg or electrochemically at a Hg-pool cathode to a new Mo(III) ion. The ready reversibility of the process is consistent with a trimeric structure and its representation as Mo^{III}_3. An intermediate mixed-oxidation-state ($Mo^{III}_2Mo^{IV}$) ion has also been identified. This ion is obtained on mixing Mo^{III}_3 and Mo^{IV}_3 with [HPTS] ≥ 4.0 M. Its formation is less extensive however at lower [HPTS] and is <30% at [H$^+$] ≤ 0.5 M. No evidence was obtained for the mixed-oxidation-state ion $Mo^{III}Mo^{IV}_2$, which can be explained by its instability with respect to disproportionation to give $Mo^{III}_2Mo^{IV}$ and Mo^{IV}_3 at high [HPTS] and Mo^{III}_3 and Mo^{IV}_3 at low [HPTS].

Behavior on an ion-exchange column relative to the Mo^{IV}_3 aquo ion can be used as a means of estimating the charge on the new aquo ions. It is concluded that the $Mo^{IV}_3 \rightarrow Mo^{III}_3$ conversion does not correspond to conversion of $Mo_3O_4^{4+}$ to $Mo_3O_4^+$, with retention of an identical core structure. The results suggest protonation to give a charge of at least 4+. Possible structures are I and II, with protonation of the apical

I   II
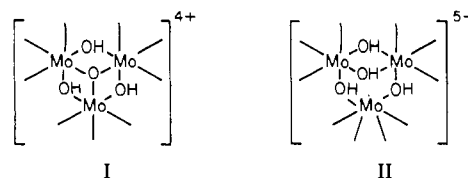
oxo group resulting in cleavage of one Mo–O bond. With use of a similar approach based on ion-exchange behavior, the

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faster elution of $Mo^{III}_2Mo^{IV}$ than Mo^{IV}_3 suggests a charge of <4. However, this is a puzzling result apparently in conflict with the value $n = 3$–4 obtained for (1), which implies a charge on $Mo^{III}_2Mo^{IV}$ of 5+. A possible rationale is that $Mo^{III}_2Mo^{IV}$ does in fact have a charge of 5+ and structure as in III. The
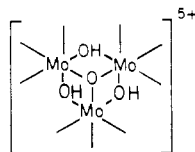
III

sensitivity of $Mo^{III}_2Mo^{IV}$ to $[H^+]$ in the range 0.5–4.0 M suggests deprotonation at the lower $[H^+]$ values which results in disproportionation. This situation could give rise to proton equilibria on the ion-exchange column and results in the elution characteristics displayed. More definitive comments as to structure must await crystallographic information. As yet, no crystalline samples have been isolated.

A feature of the spectrum of the $Mo^{III}_2Mo^{IV}$ ion is the band ca. 1050 nm in the near-IR range of the spectrum (Figure 2). The intensity and broadness of the band is comparable to those observed for other mixed-valence complexes.[19] and an intervalence transition resulting from the $Mo^{III}_2Mo^{IV}$ composition seems appropriate.

It is now possible to modify one aspect of Chalilpoyil and Anson's electrochemical experiments[13] on the reduction of Mo^{IV}_3. The electrolyzing potential of –0.15 V vs. NHE which they used was insufficiently cathodic to give the green Mo^{III}_3 ion, and a solution reported to be a new "yellow" Mo^{III}_2 species was obtained in a non-Nernstian 2e process. It is now clear that this new ion is the $Mo^{III}_2Mo^{IV}$ species. The spectrum reported (Figure 6 of ref 13) is identical with that obtained in the present study (Figure 2). We feel that orange-pink

rather than yellow is a more accurate description of the color of this new ion.

It has previously been reported that when the Mo(IV) aquo ion is reduced polarographically in 2–6 M HCl (and H_2SO_4), uptake of two-thirds and then one-third of an electron per Mo is observed. Anionic complexes are found at the higher acid concentrations, but the Mo(III) product could not in these studies be reoxidized. Surprisingly this significant work did not lead to the conclusion that trimers were present.[14]

Electron-transfer reactions involving Mo^{III}_3, $Mo^{III}_2Mo^{IV}$, and Mo^{IV}_3 interconversions occur readily, making for interesting further studies in this area similar to those recently reported by Meyer and colleagues for trinuclear intervalence Ru complexes.[20]

Finally a mixed-oxidation-state $Mo^{III}_2Mo^{IV}_2$ tetramer has been reported previously.[21] The preparation involves oxidation of the Mo(III) dimer[22] $[Mo_2(CH)_2(O_2OCH_3)(EDTA)]^-$ (EDTA = ethylenediaminetetraacetate) with azide. The EDTA ligand, coordinated in a basket-like fashion to the binuclear structure, is retained in the tetramer. Features of the tetramer established by crystallography[23] are its symmetrical structure with all Mo's identical and both μ-hydroxo and μ-oxo bridging ligands. A closely related Mo^{IV}_4 complex is obtained by controlled O_2 oxidation. Spectra of both species have much bigger absorption coefficients than those for the complexes in the present study. Interestingly, two other complexes previously referred to as polymeric Mo(IV) species[21] may well be complexes having Mo_3O_4 core structures.

Registry No. $Mo_3O_4(H_2O)_9^{4+}$, 74353-85-8; $Mo_3(OH)_4(H_2O)_{10}^{5+}$, 79681-73-5; $Mo_3O(OH)_3(OH_2)_9^{5+}$, 79916-86-2.

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