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Oxidation of the Molybdenum(III) Aquo Dimer with $Co(C_2O_4)_3{}^{3-}$ and Other Oxidants†

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Oxidation of the green Mo(III) aquo dimer, $Mo(III)_2$, with $Co(C_2O_4)_3{}^{3-}$, $IrCl_6{}^{2-}$, and O_2 in acidic (*p*-toluenesulfonic acid, HPTS) solutions >0.50 M, $I = 2.0$ M (LiPTS), yields the $Mo(V)_2$ aquo dimer, $Mo_2O_4{}^{2+}$. The same product and 1:4 (moles reductant:moles oxidant) stoichiometry is observed with $Mo(III)_2$ in excess. Two stopped-flow kinetic stages have been observed with $Co(C_2O_4)_3{}^{3-}$ as oxidant. With $Mo(III)_2$ in large excess, the first stage monitored at 600 nm gives limiting kinetics consistent with the reaction sequence $Mo(III)_2 + Co(III) \rightleftharpoons Mo(III)_2, Co(III)$ (K), followed by $Mo(III)_2, Co(III) \rightarrow Mo(III,IV)_2 + Co(II)$ (k_{et}). From studies at 5.2–35.0 °C, K(25 °C) = 5090 M^{-1}, $\Delta H° = 2.9$ kcal mol^{-1}, and $\Delta S° = 26.7$ cal K^{-1} mol^{-1}, where K shows little or no dependence on $[H^+]$. The dependence of the rate constant k_{et} on $[H^+]$ can be expressed as $k_{et} = a + b[H^+]$, where at 25 °C $a = 0.54$ s^{-1} and $b = 0.96$ M^{-1} s^{-1}. Both first and second stages can be monitored at 420 nm, and rate constants for the second stage only are obtained at 360 nm. With $Co(C_2O_4)_3{}^{3-}$ in large excess (high background absorbance), rate constants (0.15–0.28 s^{-1}) obtained at all three wavelengths are also consistent with the second stage. A process (or processes) relating to the first-order decay of the $Mo(III,IV)_2$ intermediate is suggested. With $Mo(III)_2$ in excess, all the $Co(C_2O_4)_3{}^{3-}$ is consumed in the first stage, and the second stage results in disproportionation with re-formation of appropriate amounts of $Mo(III)_2$. Two stages are also observed in the oxidation of $Mo(III)_2$ (excess) with O_2. For two runs at 420 nm, the pseudo-first-order rate constant for the first stage (8.1 s^{-1}) is followed by a second stage (0.15 s^{-1}).

Introduction

It was assumed in two earlier studies[1,2] that green Mo(III) aquo ions obtained in solution correspond to mononuclear $Mo(H_2O)_6{}^{3+}$. Bowen and Taube[3] established that the mononuclear Mo(III) aquo ion is pale yellow and therefore that this assignment was incorrect. Ardon and Pernick[4] subsequently identified the green aquo ion as a binuclear 4^+ di-μ-hydroxo or μ-oxo species. An X-ray crystal structure of green $[Mo_2(OH)_2(O_2CCH_3)(edta)]^-$ (edta = ethylenediaminetetraacetate) has been reported,[5] and the existence of such a di-μ-hydroxo molybdenum(III) complex (together with the similarity of spectra;[6] inset to Figure 1) supports a preference for the di-μ-hydroxo structure.[4] The aquo ion can accordingly be formulated as $Mo_2(OH)_2{}^{4+}$, although here we choose to use the abbreviation $Mo(III)_2$. Recent EXAFS studies[7] also support a structure in which bridging O atoms are protonated.

No quantitative studies on the $Mo(III)_2$ aquo ion involving redox or substitution have yet been reported. The aim of the present work is to study the solution behavior with inorganic redox partners so as to enable comparisons with the mononuclear aquo ion, Mo^{3+}. The involvement of Mo(IV) and comparisons with the known behavior of $Mo(IV)_3$, the only Mo(IV) aquo ion which has been characterized,[8] is also of interest. Oxygen-free acidic solutions were used, the anion present being *p*-toluenesulfonate, with ionic strengths adjusted to 2.0 M (LiPTS).

Experimental Section

Materials. The Mo(III) aquo dimer was prepared by reduction of Mo(VI) in the form of sodium molybdate (Analar, Hopkin, and Williams) (100 mL, 10^{-2} M) in 1.0 M HPTS on a Zn/Hg column under rigorous O_2-free condition.[4] The Zn/Hg was prepared by stirring zinc shot (Analar, Hopkin, and Williams; 8–30 mesh size) in a 2% solution of mercury(II) chloride (Analar BDH) for ca. 10 min. This was then washed three times with 2 M HCl, and a column (25 cm long, 1-cm diameter) was prepared. Quickfit tapered joints were used to enable the column to be used anaerobically. The column was deoxygenated with water (250 mL) (previously deoxygenated by bubbling N_2 through it) from a separating funnel fitted to the top of the column. The water was run down the column in such a way as to exclude all gas present initially. Product solutions were transferred via narrow gauge plastic PTFE tubing (Jencon) by applying excess N_2 gas pressure. These were diluted to give [HPTS] = ca. 0.5 M, and the solution was then loaded onto an ice-cooled Dowex 50W-X2 cation-exchange column (30 cm long, 1.2-cm diameter). A sharp green band was absorbed onto the resin; a small amount of lighter green complex did not bind. On washing with 100-mL portions of 0.50 M HPTS and then 1.0 M HPTS, a pale yellow-brown solution (probably $Mo_2O_4{}^{2+}$) was eluted. The green band of $Mo(III)_2$ was eluted slowly with 2.0 M HPTS. The concentration of H^+ was determined by exchanging onto an Amberlite IR 120(H) resin and titrating the total H^+. The concentration of $Mo(III)_2$ was determined by addition of excess Fe(III) to oxidize to Mo(VI) and titrating the Fe(II) formed with Ce(IV). The absorption spectrum (Figure 1) gives peak positions (λ/nm (ϵ/M^{-1} cm^{-1})) at 360 (910), 572 (96), and 624 (110) (absorption coefficients per dimer). The preparation was carried out some ten times, and ϵ values were reproducible to ±4%. Details previously reported are 360 (612), 572 (78), and 624 (86).[4]

Potassium tris(oxalato)colbaltate(III), $K_3[Co(C_2O_4)_3]\cdot 3H_2O$, was prepared as previously described, with peak positions (λ/nm (ϵ/M^{-1} cm^{-1})) at 420 (215) and 603 (165).[10,11] The Cr(III) analogue $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ with peaks at 420 (85) and 573 (70) was also prepared.[10] The complex $K_3[Ir(C_2O_4)_3]\cdot 4H_2O$ was obtained as described by Kruszyna et al.,[12] with the use of a modification of Delépine's procedure.[13] Purification was achieved with use of a QAE-Sephadex Q50-120 anion-exchange column (Sigma Chemicals). A yellow band was washed with LiPTS (0.25 M, 50 mL and 0.50 M, 150 mL) and eluted with 2.0 M HPTS (ca. 50 mL). The product (ca. 0.010 M) has a well-defined peak at 286 nm (ϵ 4100 M^{-1} cm^{-1}). Sodium hexachloroiridate(IV), $Na_2[IrCl_6]\cdot 6H_2O$ (Johnson and Matthey), with a peak position at 487 nm (4075 M^{-1} cm^{-1}), and cylinder O_2 were used. Lithium *p*-toluenesulfonate was prepared from *p*-toluenesulfonic acid (Sigma Chemicals) as described elsewhere.[11]

Stability of $Mo(III)_2$ Solutions. Stock solutions of $Mo(III)_2$ (typically ca. 10^{-2} M) were stored at ca. 0 °C in 2.0 M HPTS under strict anaerobic conditions (N_2). Such solutions were stable for up to 2 weeks without serious deterioration (<5%). Solutions at 25 °C

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† No reprints available.

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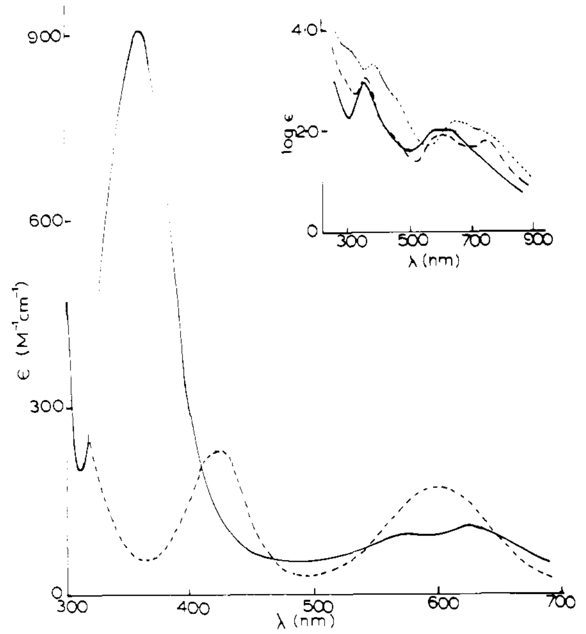

Figure 1. Spectra of Mo(III) aquo dimer $Mo(III)_2$ in 2.0 M HPTS (ε's per dimer) (—) and $Co(C_2O_4)_3^{3-}$(- - -). Inset: a comparison of the spectra $Mo(III)_2$ (—) with complexes $[Mo_2(OH)_2(O_2CCH_3)(EDTA)]^-$ (– –) and $[Mo_2(OH)_2(NCS)_2(EDTA)]^{2-}$ (- - -) both at pH ca. 6.

diluted to ca. 1.6×10^{-3} M $Mo(III)_2$ with $[H^+] = 0.11$–1.00 M and $I = 1.0$ M (LiPTS) gave small absorbance changes with time at λ 360 nm which can be summarized as follows: first stage, 5–7% decrease over 100–200 min: second stage, a further 1–6% decrease over 20 h. Absorbance changes are consistent with a $Mo(III)_2 \rightarrow Mo(V)_2$ conversion and probably arise from the introduction of small amounts of O_2 during the dilution procedure.

Applicability of Beer's Law. Absorbances of $(0.025$–$1.20) \times 10^{-3}$ M $Mo(III)_2$ in 2.0 M HPTS, $I = 2.0$ M, at 25 °C were measured at λ 360 nm (Perkin-Elmer 554). Solutions >ca. 4×10^{-4} M obeyed Beer's Law in a perfectly satisfactory manner. However, more dilute solutions (which become difficult to handle quantitatively) appear to give absorbances less than expected, the decrease being ca. 10% (1.5×10^{-4} M) and 50% (2.5×10^{-5} M). Concentrations $<4 \times 10^{-4}$ M were avoided in subsequent studies.

Products and Stoichiometry. First observations implied that the Mo(V) aquo dimer $Mo_2O_4^{2+}$ is the product of the reaction, and under conditions $Mo(III)_2$:4Co(III) a change of green (color of both reactants) to pale yellow (color of $Mo(V)_2$) was observed. The product spectrum with a shoulder at 295 nm is diagnostic of $Mo(V)_2$ (ε 3660 M^{-1} cm^{-1} (per dimer)). The Co(II) aquo ion, with a peak at 505 nm (4.8 M^{-1} cm^{-1}), has an absorption coefficient of 14 M^{-1} cm^{-1} at 295 nm. For a solution of $Mo(III)_2$ (4.0×10^{-4} M) and $Co(C_2O_4)_3^{3-}$ (16.0×10^{-4} M), at 25 °C, [HPTS] = 2.0 M, reaction was complete within 3 min. For a 1:2 mole ratio of $Mo(III)_2$ (1.75×10^{-3} M) to $Co(C_2O_4)_3^{3-}$ (3.5×10^{-3} M), it was concluded from changes at 360 nm, absorbance coefficients (ε/M^{-1} cm^{-1}: $Mo(III)_2$ 900, $Mo(V)_2$ 35); Co(III) 80, and Co(II) <1) that 50% of the $Mo(III)_2$ remains on completion of the reaction. The final spectrum corresponded to $Mo(V)_2$ formation. It was concluded that the stoichiometry could be expressed as in (1), where under acidic conditions the Co(II) product

$$Mo(III)_2 + 4Co(III) \rightarrow Mo(V)_2 + 4Co(II) \qquad (1)$$

rapidly aquates to Co^{2+}. A similar 1:4 stoichiometry with $Mo(V)_2$ as product was observed for the one-electron oxidant $IrCl_6^{2-}$, with relevant details of absorption peaks (λ/nm (ε/M^{-1} cm^{-1})) being for $IrCl_6^{2-}$, 298 (1470), 450 (3050), 487 (4075), and 580 (250), and for $IrCl_6^{3-}$, 358 (74) and 420 (87) (eq 2). With O_2 as oxidant, observations were consistent with the stoichiometry as in (3).

$$Mo(III)_2 + 4Ir(IV) \rightarrow Mo(V)_2 + 4Ir(III) \qquad (2)$$

$$Mo(III)_2 + O_2 \xrightarrow{4H^+} Mo(V)_2 + 2H_2O \qquad (3)$$

Kinetics. Reactions were investigated with the use of a Durrum-Gibson stopped-flow spectrophotometer. Ionic strengths were adjusted to 2.0 M (LiPTS). Rigorous anaerobic conditions were required, and the stopped-flow was flushed with O_2-free 2.0 M HPTS prior to loading. Fresh $Co(C_2O_4)_3^{3-}$ solutions were made up for each run to avoid effects of the slow decomposition.[14] Exploratory experiments with $Co(C_2O_4)_3^{3-}$ as oxidant indicated that the reaction sequence was complex, and reactions were followed at both Co(III) peak positions 420 and 600 nm, as well as the $Mo(III)_2$ peak at 360 nm. A saturated stock solution of O_2 in 2.0 M HPTS was determined with the use of a Beckman 0260 oxygen analyser (0.001 23 M). Rate constants were obtained from the slopes of first-order plots of absorbance (A) changes ln $|A_t - A_\infty|$ against time.

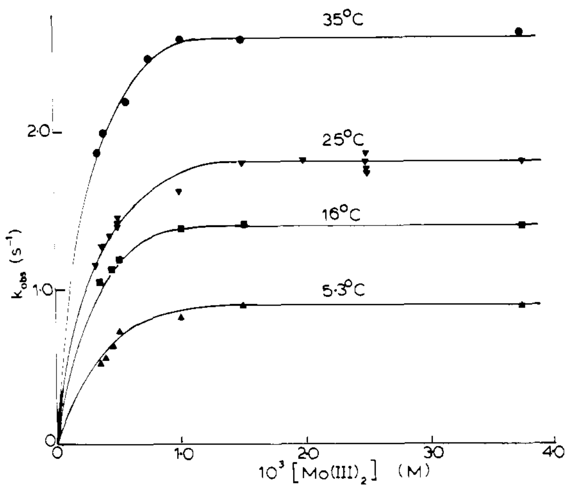

Figure 2. Variation of first-order rate constants k_{obsd} with $[Mo(III)_2]$ for the first stage of the oxidation of $Mo(III)_2$ (in excess) with $Co(C_2O_4)_3^{3-}$ (ca. 10^{-4} M) ($[H^+] = 2.0$ M HPTS, $I = 2.0$ M, λ 600 nm).

Addition of $Cr(C_2O_4)_3^{3-}$ and $Ir(C_2O_4)_3^{3-}$ to $Mo(III)_2$. The effect of two redox-inactive complexes on the UV–visible spectrum of $Mo(III)_2$ was investigated in order to comment on whether association of $Mo(III)_2$ with $Co(C_2O_4)_3^{3-}$ is likely to be inner or outer sphere. Outer-sphere association is expected to have a smaller perturbation on the spectra (mainly through charge-transfer bands) than inner-sphere association. A solution of $Mo(III)_2$ (10^{-3} M) and $Cr(C_2O_4)_3^{3-}$ (10^{-3} M) at 25 °C in 2.0 M HPTS was scanned over the range 250–900 nm. The resultant spectrum was to within experimental error the sum of the component parts and remained constant for >20 min. Similarly, a solution of $Mo(III)_2$ (10^{-3} M) and $Ir(C_2O_4)_3^{3-}$ (5×10^{-3} M) at 25 °C in 2.0 M HPTS was examined. The $Ir(C_2O_4)_3^{3-}$ complex has no absorption at >500 nm, and the spectrum of $Mo(III)_2$ with characteristic peaks at 572 and 624 nm was identified. It was concluded that extensive inner-sphere complexing does not occur with either of the tris(oxalato) complexes.

Complexing of Oxalate to $Mo(III)_2$. Oxalic acid (18.5×10^{-3} M) was added to $Mo(III)_2$ (1.85×10^{-3} M) in 2.0 M HPTS, and spectra (300–700 nm) were recorded at 25 °C. An increase in absorbance at 360 nm with formation of a shoulder at 420 nm was observed over ca. 4 h. A plot of ln $(A_\infty - A_t)$ against time was linear for 1 half-life only (possible due to complexing of more than one oxalate). A rate constant of 1.6×10^{-4} s^{-1} was obtained.

Treatment of Data. A nonlinear least-squares program[15] (weighting factor $1/y^2$) was used.

Results

$Co(C_2O_4)_3^{3-}$ as Oxidant. The kinetics monitored by stopped flow with $Mo(III)_2$ in large excess will be considered first. Two stages are observed at 420 nm. The first stage (exclusively) can be followed at 600 nm and the second stage (exclusively) at 360 nm.

At 600 nm, first-order plots were linear to 85% completion. The dependence of rate constants k_{obsd} (Table I)[16] on [Mo-

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Table II. Oxidation of $Mo(III)_2$ (in Excess) with $Co(C_2O_4)_3^{3-}$ (λ 600 nm, I = 2.0 M (LiPTS)). First Stage of the Reaction[a]

temp, °C	K, M^{-1}	k_{et}, s^{-1}
5.2	3800	0.90
16.0	4700	1.41
25.0[b]	5100	1.80
25.0[c]	4700	1.40[d]
35.0	6400	2.59

[a] Values of association constants (K) and electron-transfer rate constants (k_{et}) are as defined in (5) and (6). [b] $[H^+]$ = 2.0 M (HPTS). [c] $[H^+]$ = 1.0 M (HPTS). [d] Excluded for ln (k_{et}/T) plot.

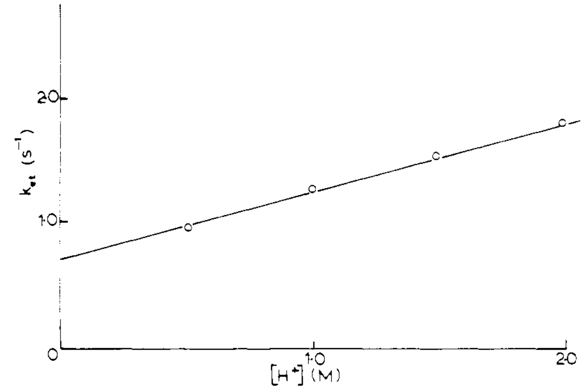

Figure 3. Dependence of the first-order limiting rate constant (k_{et}) on $[H^+]$ for the oxidation of $Mo(III)_2$ (2.5 × 10^{-3} M) with $Co(C_2O_4)_3^{3-}$ (10^{-4} M) at 25 °C (I = 2.0 M (LiPTS), λ 600 nm).

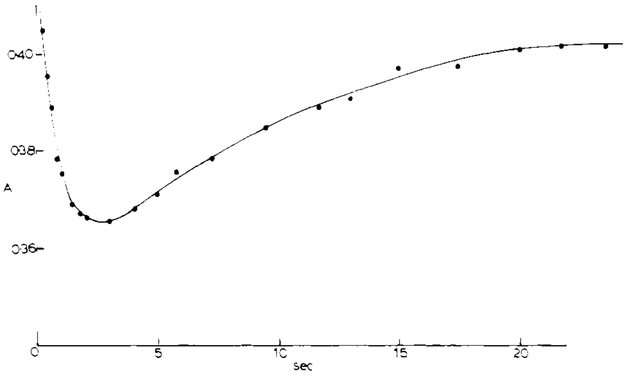

Figure 4. Graph of absorbance (A) with time (per 1-cm path length) for the $Mo(III)_2$ (5.0 × 10^{-4} M) oxidation with $Co(C_2O_4)_3^{3-}$ (10^{-4} M) at 25 °C ($[H^+]$ = 2.0 M HPTS, I = 2.0 M, λ 420 nm).

$(III)_2]$ is shown in Figure 2. A plot of k_{obsd}^{-1} against $[Mo(III)_2]^{-1}$ is linear consistent with the dependence shown in (4),

$$k_{obsd} = \frac{Kk_{et}[Mo(III)_2]}{1 + K[Mo(III)_2]} \qquad (4)$$

where association (K) of the reactants $Mo_2(OH)_2^{4+}$ and $Co(C_2O_4)_3^{3-}$ is proposed prior to electron transfer (k_{et}) (eq 5 and 6). From the temperature dependence in 2.0 M HPTS (I = 2.0 M), K(25 °C) = 5090 ± 560 M^{-1}, $\Delta H°$ = 2.9 ± 1.9 kcal mol^{-1}, $\Delta S°$ = 26.7 ± 6.1 cal K^{-1} mol^{-1}, and k_{et}(25 °C), which is a composite term (see below), 1.8 s^{-1}, $\Delta H_{et}^{\ddagger}$ = 5.2 ± 0.5 kcal mol^{-1}, $\Delta S_{et}^{\ddagger}$ = −39.8 ± 1.9 cal K^{-1} mol^{-1}. A listing of K and k_{et} values is given in Table II.

$$Mo(III)_2 + Co(III) \overset{K}{\rightleftharpoons} Mo(III)_2,Co(III) \qquad (5)$$

$$Mo(III)_2,Co(III) \xrightarrow{k_{et}} \text{products} \qquad (6)$$

The $[H^+]$ dependence of the limiting plateau rate constant (k_{et}) was investigated (Table I[16]) with $[Mo(III)_2]$ = 2.5 × 10^{-3} M, which lies well within the plateau region. The dependence of k_{et} on $[H^+]$ (Figure 3) is summarised by (7) where, at 25 °C, a = 0.54 s^{-1} and b = 0.96 M^{-1} s^{-1}.

$$k_{et} = a + b[H^+] \qquad (7)$$

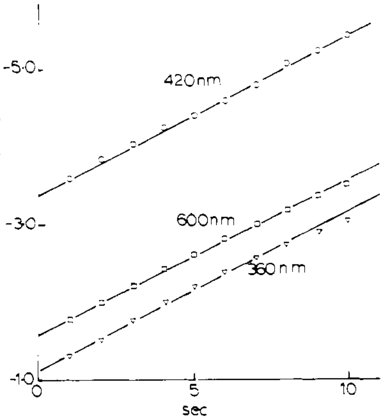

Figure 5. First-order plots of absorbance changes ln ($A_t - A_\infty$) against time for the oxidation of $Mo(III)_2$ (5.0 × 10^{-4} M) with $Co(C_2O_4)_3^{3-}$ (10^{-2} M) at 25 °C ($[H^+]$ = 2.0 M HPTS, I = 2.0 M).

Table III. First-Order Rate Constants (25 °C) for the Oxidation of $Mo(III)_2$ (in Excess) with $Co(C_2O_4)_3^{3-}$ ($[H^+]$ = 2.0 M (HPTS), I = 2.0 M, λ 420 nm)

10^4 × $[Mo(III)_2]$, M	10^4 × $[Co(C_2O_4)_3^{3-}]$, M	k_{obsd}',[a] s^{-1}	k_{obsd}'',[b] s^{-1}
5.0	1.0	1.15	0.16
5.0	1.0	1.17	0.20
5.0	1.0		0.18
5.0	1.0		0.21
10.0	1.0		0.28
10.0	1.0		0.19
20.0	1.0		0.27
20.0	3.5		0.28

[a] First stage. [b] Second stage.

Table IV. First-Order Rate Constants[a] (25 °C) for the Oxidation of $Mo(III)_2$ (in Excess) with $Co(C_2O_4)_3^{3-}$ (10^{-4} M) ($[H^+]$ = 2.0 M (HPTS), I = 2.0 M, and λ 360 nm)

10^4 × $[Mo(III)_2]$, M	k_{obsd}'', s^{-1}	10^4 × $[Mo(III)_2]$, M	k_{obsd}'', s^{-1}
5.0	0.21	5.0	0.20
5.0	0.26	10.0	0.28

[a] Rate constants are for the second stage, k_{obsd}'', as defined in Table III.

At 420 nm with $Mo(III)_2$ again in excess, two distinct stages are observed (Figure 4). With the use of an estimated A_∞^E for the first stage first-order plots of ln ($A_t - A_\infty^E$) against time were linear for 2 half-lives, with k_{obsd}' = ca. 1.16 s^{-1}, which is similar to k_{obsd} determined at 600 nm. Rate constants k_{obsd}'' for the second stage were also obtained (Table III).

Rate constants for the single stage observed at 360 nm, with $Mo(III)_2$ in excess (Table IV), are in the same range as k_{obsd}'' in Table III. Slight departure from first-order kinetics was observed in the early stage, consistent with a previous reaction step. Runs with $Co(C_2O_4)_3^{3-}$ in excess were also monitored at 360 nm and (one run in each case) at 420 and 600 nm. A high background absorbance impairs accuracy. First-order plots were linear to 2.5 half-lives. Rate constants, k_{Co} (Table V), suggest that the second stage k_{obsd}'' is being followed.

$IrCl_6^{2-}$ as Oxidant. Attempts were made to follow the reaction at 25 °C in 2.0 M HPTS at the $IrCl_6^{2-}$ peak at 487 nm, with $Mo(III)_2$ (10^{-3} M) in tenfold excess. A lower limit for the first-order rate constant is 100 s^{-1}.

Table V. First-Order Rate Constants (25 °C) for the Oxidation of $Mo(III)_2$ (5.0×10^{-4} M) with $Co(C_2O_4)_3^{3-}$ (in Excess) ($I = 2.0$ M (LiPTS), λ 360 nm, Except As Stated)

$[H^+]$, M	$[Co(C_2O_4)_3^{3-}]$, M	k_{Co}, s^{-1}
2.0	0.010	0.21
	0.010	0.15
	0.0080	0.26
	0.016	0.26
	0.024	0.27
	0.010	0.28
2.0[a]	0.010	0.21
2.0[b]	0.010	0.21
1.7	0.010	0.15
1.3	0.010	0.15
1.0	0.010	0.16
0.5	0.010	0.21

[a] λ 420 nm. [b] λ 600 nm.

Table VI. First-Order Rate Constants (25 °C) for the Oxidation of $Mo(III)_2$ with O_2 ($[H^+] = 2.0$ M (HPTS), $I = 2.0$ M)

$10^4 \times$ $[Mo(III)_2]$, M	$10^5 \times$ $[O_2]$, M	k_a, s^{-1}	k_b, s^{-1}
5.0[a]	5.0	8.0	0.16
5.0[a]	5.0	8.2	0.13
4.5[b]	5.0		0.20[c]

[a] λ 420 nm. [b] λ 360 nm. [c] Only stage observed.

O_2 as Oxidant. The kinetics were studied briefly at 360 and 420 nm. At 420 nm two stages were observed (Table VI). A fast decrease in absorbance followed by a slower partial recovery. For the first stage, a rate constant of 8.1 s^{-1} (k_a) was obtained at 25 °C in 2.0 M HPTS. The second stage gave a rate constant (k_b) of 0.16 s^{-1}. Linearity of first-order plots was satisfactory in both cases (5 and 2.5 half-lives, respectively). At 360 nm a single-stage absorbance decrease giving a first-order rate constant of 0.20 s^{-1} (linearity, 3.5 half-lives) was obtained, again at 25 °C in 2.00 M HPTS.

Discussion

All three oxidants, $Co(C_2O_4)_3^{3-}$, $IrCl_6^{2-}$, and O_2, oxidize $Mo(III)_2$ to the Mo(V) dimer, $Mo_2O_4^{2+}$. The oxidation with $IrCl_6^{2-}$ is fast and outside the stopped-flow range and was not studied further. Since there is no reaction of the Mo(IV) aquo trimer with $Co(C_2O_4)_3^{3-}$ and little or no reaction with O_2, and since the $IrCl_6^{2-}$ oxidation of $Mo(IV)_3$ can be studied by conventional spectrophotometry, clearly $Mo(IV)_3$ is not formed as an intermediate in any of these reactions.

The oxidation of $Mo(III)_2$ with $Co(C_2O_4)_3^{3-}$ and O_2 involves at least two stages. Thus at 420 nm with $Mo(III)_2$ in excess, a fast absorbance decrease is followed by a slower absorbance increase. With $Co(C_2O_4)_3^{3-}$ as oxidant, the first stage can be monitored more accurately as the only change at 600 nm (decrease of the $Co(C_2O_4)_3^{3-}$ absorbance), and details of this process will be considered first.

The limiting kinetics observed, (4), can be explained by the reaction sequence (5) and (6) in which rapid association (K) occurs prior to electron transfer (k_{et}). At 25 °C, $I = 2.0$ M (LiPTS), the association constant $K = 4730 \pm 700$ M^{-1} in 1.0 M HPTS is not significantly different from that in 2.0 M HPTS, $K = 5090 \pm 570$ M^{-1}. There is no spectroscopic evidence for inner-sphere complexing of $Mo(III)_2$ with redox-inactive $Cr(C_2O_4)_3^{3-}$ and $Ir(C_2O_4)_3^{3-}$ at concentrations which, assuming similar behavior to that observed for $Co(C_2O_4)_3^{3-}$, would be expected to give >60% association. Complexing with oxalate in 2.0 M HPTS is moreover slow (ca. 4 h). It is therefore concluded that K corresponds to outer-sphere ion-pair formation between the (4+) $Mo(III)_2$ and (3−) $Co(C_2O_4)_3^{3-}$ reactants. Thermodynamic parameters for K are $\Delta H° = 2.9$ kcal mol^{-1} and $\Delta S° = 26.7$ cal K^{-1} mol^{-1}, which compare to values observed for $Fe(CN)_6^{4-}$ association with $Co(NH_3)_5py^{3+}$, $\Delta H° = 0$ kcal mol^{-1} and $\Delta S° = 15$ cal K^{-1} mol^{-1}, with $K = 2400$ M^{-1} at 25 °C, $I = 0.10$ M.[17] An association governed primarily by electrostatics with some H bonding between coordinated H_2O and oxalate ligands seems likely. The positive $\Delta S°$ values are consistent with desolvation resulting from the charge neutralization which occurs when association takes place.

The rate constant k_{et} is dependent on $[H^+]$ (eq 7). This suggests that the reaction observed is more favorable on addition of a proton. Protonation of a μ-hydroxo (or alternatively μ-oxo) bridge of the $Mo(III)_2$ reactant is possible. Such an effect is of considerable interest since (if anything) oxidation of a metal ion generally demands an increase in hydrolysis as a preliminary to oxidation. If the effect is real, and it seems too big to be attributed to a medium effect resulting from the exchange of Li^+ for H^+, then protonation of a bridge, possible as a first step leading to bridge cleavage, is envisaged. This may be an indication as to the nature of the second stage of the reaction and some incompatibility of Mo(III) and Mo(IV) in a binuclear unit. Alternatively protonation of $Co(C_2O_4)_3^{3-}$ may be occurring although such a step does not contribute to the $Co(C_2O_4)_3^{3-}$ oxidation of $Mo(H_2O)_6^{3+}$ (range of $[H^+]$ values 0.5–2.0 M).[11]

Attention will now be switched to the second stage(s) in the oxidation of $Mo(III)_2$ by $Co(C_2O_4)_3^{3-}$. The first stage, monitored at 600 nm with $Mo(III)_2$ in excess, results in complete consumption of $Co(C_2O_4)_3^{3-}$. At 420 nm the absorbance first decreases and then (second stage) increases. The second stage must therefore by independent of $Co(C_2O_4)_3^{3-}$.

With $Co(C_2O_4)_3^{3-}$ in excess, concentrations were such that only the slower stage could be monitored, and rate constants (k_{Co}) at the three wavelengths 360, 420, and 600 nm were in agreement. However, in general, values of k_{Co} are subject to a large amount of scatter: 0.15–0.28 s^{-1}. Values of k_{obsd}'' for the second stage with $Mo(III)_2$ in excess also fall in this range, 0.16–0.28 s^{-1} at 420 nm and 0.20–0.28 s^{-1} at 360 nm, and it seems likely that the same process is being followed.

As far as detailed interpretation of the second stage is concerned, the absorbance increase at 420 nm most likely corresponds to $Mo(III)_2$ re-formation. The products $Mo(V)_2$ and Co(II) do not absorb appreciably at 420 nm, and the magnitude of absorbance changes is certainly consistent with this explanation. At 360 nm the decrease in absorbance then corresponds to decay of the intermediate. It is also noted that with $Mo(III)_2$ in excess the final spectrum is as expected for $Mo(III)_2$ along with $Mo(V)_2$ and Co(II), and no other absorbance was detected. The manner in which such a disproportionation is achieved is of interest, however. As far a can be ascertained, the kinetics observed are first order, and an unacceptable fit to a second-order rate law is obtained. Therefore the overall net disproportionation of an intermediate is achieved by some rate-determining process as in (8) or (9),

$$Mo(III,IV)_2 \rightarrow Mo(III) + Mo(IV) \qquad (8)$$

$$Mo(III,IV)_2 \rightarrow {}^*Mo(III,IV)_2 \qquad (9)$$

where in (9) $^*Mo(III,IV)_2$ represents an activated species (possibly formed by cleavage of one or two bridges). With $Co(C_2O_4)_3^{3-}$ in excess, it is possible that (8) or (9) should be effective as a rate-controlling second stage prior to further involvement of $Co(C_2O_4)_3^{3-}$.

At this stage it should be recalled that the N_3^- oxidation of the $Mo(III)_2$ complex $[Mo_2(OH)_2(O_2CCH_3)(EDTA)]^-$ yields a cyclic $Mo(III,III,IV,IV)_4$ mixed oxidation state tetramer,[18] as well as the $Mo(V)_2$ complex $[Mo_2O_4(EDTA)]^{2-}$.

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The dimer to tetramer step appears to be required to stabilize the Mo(III,IV) unit which has the benefit of being held together by the EDTA ligand in a "basketlike" configuration. It is also of interest that Mo(III) and Mo(V) species are known to combine to give the Mo(IV) aquo trimer, but only at elevated temperatures (90 °C for ca. 1 h).[19]

Two stages were also observed in the O_2 oxidation of $Mo(III)_2$. Rate constants for the second stage (0.13–0.20 s^{-1}) overlap with the range of values obtained in the second stage with $Co(C_2O_4)_3^{3-}$ as oxidant and could well correspond to the same process. Overall, however, a more complicated reaction sequence is likely with O_2, and unlike the O_2 oxidation of Mo^{3+}[11] we are unable to comment further as to the detailed mechanism.

In conclusion, at least two stages are evident in the oxidation of $Mo(III)_2$ with both $Co(C_2O_4)_3^{3-}$ and O_2. With $Co(C_2O_4)_3^{3-}$ the first stage involving precursor ion-pair adduct formation followed by electron transfer is fairly well understood. Mechanistic assignments for the second observed stage are not as clearcut. Tentative suggestions include formation of a $Mo(III,IV)_2$ intermediate which decays in a first-order process giving a net disproportionation when $Mo(III)_2$ is in excess. This process is oxidant independent.

One general feature to note is the relative ease of oxidation of $Mo(III)_2$ as compared to Mo^{3+}, with rate constants some 10^2 times faster for the dimer. This can be attributed to the ease of formation of the primary $Mo(III,IV)_2$ product as opposed to monomeric Mo(IV). The greater degree of hydrolysis of Mo(III) in the dimer may also favor reaction. It is unlikely that reduction potentials for the monomer and dimer are identical.[9]

As far as substitution properties of Mo^{3+} and $Mo(III)_2$ are concerned, rate constants (25 °C) for the complexing of the aquo ions (2×10^{-3} M) with oxalate (2×10^{-2} M) in 2.0 M HPTS can be compared. Values obtained are for Mo^{3+} (1.4×10^{-3} s^{-1}) and for $Mo(III)_2$ (1.6×10^{-4} s^{-1}). From this limited information, it appears that $Mo(III)_2$ is more inert than Mo^{3+}. Kinetic studies on the 1:1 complexing of NCS^- and Cl^- with Mo^{3+} have been reported previously.[20]

Bino[21] has recently reported a study in which a new Mo(III) dimer, present in 1 M HCl as aquo $Mo_2Cl_4^{2+}$, was identified. This ion (λ_{max} 430 nm) is believed to have an Mo–Mo triple bond and no bridging ligands. On addition of $[Cl^-]$ to the green aquo dimer in the present study, $[Mo(III)_2] = 5 \times 10^{-4}$ M, [HPTS] = 1.0 M, and [NaCl] = 1.0 M; no change in spectrum (Figure 1) was observed over 15 h at 25 °C. The separate existence of dimeric Mo(III) species with multiple Mo–Mo bonds on the one hand, and hydroxo bridging ligands on the other is interesting. No interconversion appears to take place for conditions so far examined.

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Registry No. Mo(III), 51567-86-3; $Co(C_2O_4)_3^{3-}$, 15053-34-6; $IrCl_6^{2-}$, 16918-91-5; O_2, 7782-44-7; $Mo_2O_4^{2+}$, 52757-71-8.

Supplementary Material Available: Table I listing rate constants (2 pages). Ordering information is given on any current masthead page.

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Electrochemical Generation of Monomeric Aquamolybdenum(V) by Reduction of Molybdenum(VI) at High Dilution in Trifluoromethanesulfonic Acid

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The electrochemistry of Mo(VI) in noncomplexing aqueous electrolytes is usually severely complicated by the oligomerization and subsequent adsorption of the reactant. This problem can be circumvented by employing dilute ($\leq 10^{-4}$ M) solutions of Mo(VI) in 1–2 M trifluoromethanesulfonic acid. Under these conditions staircase voltammograms and pulse polarograms exhibit single, reversible waves that are consistent with the one-electron reduction of an unadsorbed, monomeric Mo(VI) species. The pH dependence of the reduction potentials suggests that two protons are consumed in the reduction of each Mo(VI). The monomeric Mo(V) reduction product undergoes spontaneous dimerization with a rate constant estimated as 10^3 M^{-1} s^{-1}. It also reduces perchlorate anions at a significant rate.

The electrochemical reduction of aquamolybdenum(VI) has been studied in a variety of supporting electrolytes.[1-5] An early polarographic study[1] suggested the initial production of a chemically unstable Mo(IV) species while later work by Souchay and co-workers[2,3] proposed that several forms (monomeric, tetrameric, etc.) of Mo(V) were produced and subsequently reduced to Mo(III). A report by Hull[4] indicated that Mo(VI) is reduced in sulfuric acid to produce a Mo(V) species that adsorbs on the electrode, but no structures of possible Mo(V) products were proposed. In all of the previous work the voltammetric responses were highly sensitive to the concentration of Mo(VI). Adsorption on the mercury electrodes was often invoked to account for complex voltammetric behavior although oligomerization of the variety of molybdenum(VI) oxo species present in homogeneous solutions has also been suggested.

The objective of the present work was to establish the nature of the initial product of the reduction of Mo(VI) at concentrations low enough to eliminate both adsorption and oligomerization in trifluoromethanesulfonic acid solutions.

Experimental Section

Materials. Trifluoromethanesulfonic acid (Minnesota Mining and Manufacturing Co.) was purified as previously described.[6] The

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