where $x = -J/kT$, g is the spectroscopic splitting factor, and $N(\alpha)$ is the temperature-independent, high-field paramagnetic factor. For the second structure (Figure 1b), if it is assumed that the exchange integral between the central and end chromium atoms is the same for either end of the complex and the exchange integral between the end chromiums is zero, the energy states become

$$-J\{S'(S'+1) - S(S+1) - S^*(S^*+1)\}$$

where $S^* = S_1 + S_3 = 3, 2, 1$, and 0, $S' = S_1 + S_2 + S_3 = {}^9/_2, {}^7/_2, {}^5/_2, {}^3/_2$, and ${}^1/_2$, and the central chromium is numbered 2. The magnetic susceptibility is given by eq 2. Independent

$$\chi_A = (g^2N\beta^2/12kT)\{165\exp(-21x) + 84[\exp(-12x) + \exp(-18x)] + 35[\exp(-5x) + \exp(-11x) + \exp(-15x)] + 10[1 + \exp(-6x) + \exp(-10x) + \exp(-12x)] + \exp(-7x) + \exp(-3x)\}/\{5\exp(-21x) + 4[\exp(-12x) + \exp(-18x)] + 3[\exp(-5x) + \exp(-11x) + \exp(-15x)] + 2[1 + \exp(-6x) + \exp(-10x) + \exp(-12x)] + \exp(-7x) + \exp(-3x)]\} + N(\alpha) \quad (2)$$

measurements of the g value (1.942) of the trimer were carried out by ESR (paper 1, Figure 3d), and thus J and $N(\alpha)$ are the only parameters to be fitted. In the fitting $N(\alpha)$ was assumed to be zero because it is generally small for Cr(III)[15] and has a minor effect on the fitting. The experimental $1/\chi_A$ values, plotted in paper 1, Figure 4 as a function of temperature, lie on a good straight line. The slope of this line, however, is appreciably greater than the theoretical line calculated from either the symmetric triangle model or the linear model by about 19% in both cases. The reason for this discrepancy is not apparent. If the theoretical curves are made to pass through about the middle temperature of the data, values of J/k of −16 and −22° are found for the symmetric triangle and the linear models, respectively. The fit does not help to distinguish between the two structures.[23]

Because of the similarity[24] of the spectrum to that of $Cr(H_2O)_6^{3+}$ (paper 1, Figure 1) and the relatively small value of $-J/k$[25] it is likely that the chromiums are not connected by linear oxide bridges but rather by bent oxide or hydroxide bridges.[15] From the empirical formula, acidity considerations, and symmetry of structures, it is likely that only OH^- groups would be present in the two structures of Figure 1. The value of $-J/k$ = 22° for the linear structure seems rather large compared to values of 6–10° in double-hydroxide-bridged dimers (except for the tetramer[20,21]). It is more difficult to predict a $-J/k$ value for the symmetric triangular structure of Figure 2a of paper 1, but the experimental value of 16° would appear possible.

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Registry No. $Cr_3(OH)_4(OH_2)_{10}$, 60938-70-7; $Cr_3(OH)_4(OH_2)_9$, 78939-63-6.

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(23) In ref 9, because of a calculational error, it was erroneously concluded that the linear model was preferred.

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Kinetic Studies on the Oxidation of Trimeric Aquomolybdenum(IV)[†]

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Oxidations of the Mo(IV) aquo trimer, $Mo_3O_4^{4+}$, with $IrCl_6^{2-}$ and $Fe(phen)_3^{3+}$ have been studied under the conditions $[H^+] = 0.6$–2.0 M and $I = 2.0$ M ($LiClO_4$). With Mo^{IV}_3 in large excess, the $IrCl_6^{2-}$ reaction can be expressed as $2Mo^{IV}_3 + 6Ir^{IV} \rightarrow 3Mo^{V}_2 + 6Ir^{III}$, and the initial step $Mo^{IV}_3 + IrCl_6^{2-}$ is rate determining. Second-order rate constants k_{Ir} are dependent on $[H^+]$: $k_{Ir} = k_{-1}[H^+]^{-1}$, where at 25 °C $k_{-1} = 1.36\ s^{-1}$, $\Delta H^* = 14.1$ kcal mol^{-1}, and $\Delta S^* = -9.6$ cal K^{-1} mol^{-1}. An alternative stoichiometry $Mo^{IV}_3 + 4Ir^{IV} \rightarrow Mo^{V}_2 + Mo^{VI} + 4Ir^{III}$ cannot be entirely ruled out, and at nearly equivalent amounts of reactants the slower oxidation of Mo^{V}_2 to Mo^{VI} contributes. With $Fe(phen)_3^{3+}$ a different reactivity pattern is observed in that oxidation of Mo^{V}_2 is more rapid than that of Mo^{IV}_3, and the equation $Mo^{IV}_3 + 6Fe(phen)_3^{3+} \rightarrow 3Mo^{VI} + 6Fe(phen)_3^{2+}$ applies. This different behavior is accounted for by the reaction of $Fe(phen)_3^{3+}$ occurring exclusively by an outer-sphere mechanism, whereas $IrCl_6^{2-}$ can react inner sphere. The initial step, $Mo^{IV}_3 + Fe(phen)_3^{3+}$, is again rate determining and at 25 °C k_{-1} for the $[H^+]^{-1}$-dependent path is $0.53\ s^{-1}$, $I = 2.0$ M. No evidence was obtained for stable trimeric mixed-oxidation-state species as product(s) of the oxidation of Mo^{IV}_3. The complex $Co(C_2O_4)_3^{3-}$ does not oxidize Mo^{IV}_3, whereas (as reported elsewhere) oxidation of aquo Mo^{III} and Mo^{III}_2 through to Mo^{V}_2 is rapid. It is concluded that oxidation of monomeric and/or dimeric Mo(IV) occurs more readily than that of the trimer. No oxidation of Mo^{IV}_3 by the two-electron oxidant $PtCl_6^{2-}$ is observed.

Introduction

The aim in this and related studies is a better understanding of the redox solution chemistry of aquomolybdenum ions. Studies on aquo ions are generally regarded as a point of reference indicating the behavior expected of a paticular oxidation state. In the case of molybdenum the aquo ions are not always simple monomeric species, and the versatility observed is quite striking.[1] Known ions include for Mo(III) the monomer, $Mo(H_2O)_6^{3+}$,[2,3] and the aquo dimer, here written as Mo^{III}_2.[4] Recent work by Murmann and Shelton,[5] following earlier crystallographic studies by Cotton and co-workers with

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[†] No reprints available.

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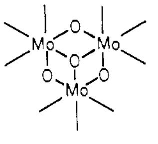
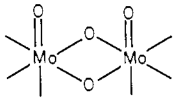
oxalate and edta as ligands,[6] has indicated that the Mo(IV) aquo ion is a trimer with core structure $Mo_3O_4^{4+}$ as in I. Likewise the Mo(V) aquo ion is established as a dimer with an $Mo_2O_4^{2+}$ core as in II.[7] Structures I and II appear to be the simplest stable aquo ions of Mo(IV) and Mo(V), respectively. In strongly acidic solutions, pH <1, Mo(VI) is believed to be present as an equilibrium mixture of monomeric and dimeric forms.[8]



I



II

Other redox studies involving Mo aquo ions are concerned with the oxidation of Mo(III),[9] Mo^{III}_2,[10] and Mo^{V}_2.[11]

Experimental Section

Reactants. Solutions of the Mo(IV) aquo trimer, $Mo_3O_4^{4+}$, in perchlorate were prepared as previously.[12-14] Stock solutions were stored under O_2-free conditions to avoid oxidation (<10% per day in air). Difficulties were experienced in earlier studies due to the instability of Mo^{IV}_3 stock solutions in perchlorate. Thus while solutions in 2.0 M $HClO_4$ were sometimes stable for 1 day, others gave a red to yellow change consistent with the Mo^{IV}_3 to Mo^{V}_2 conversion within 1–2 h. It was found that such solutions could be stabilized by the addition of $IrCl_6^{2-}$. The following modified procedure was therefore adopted under rigorous oxygen-free conditions. To a ca. 0.003 M solution of Mo^{IV}_3 in 2.0 M $HClO_4$, ca. 10% of the 1:1 Mo(IV) to Ir(IV) stoichiometric amount of $Na_2(IrCl_6)\cdot 6H_2O$ was added as solid. The Ir(IV) oxidizes some Mo(IV) and in addition (presumably) also removes trace impurities responsible for the instability of solutions (which was the aim of the procedure). After completion of the reaction the solution was diluted fourfold (to $[H^+] = 0.50$ M) and loaded onto a Dowex 50W-X2 cation-exchange (H^+ form) column ca. 2 cm in length. The column was washed with 0.50 and 1.00 M $HClO_4$ to remove reaction products, and the red Mo^{IV}_3 band was eluted with 2.0 M $HClO_4$. Such solutions gave satisfactory stability certainly over 1-day periods. A solution of Mo^{IV}_3 in 2 M *p*-toluenesulfonic acid, HPTS (colorless crystalline samples from Aldrich or Sigma), was prepared by a similar procedure but without the addition of $IrCl_6^{2-}$. Solutions of Mo^{IV}_3 were standardized spectrophotometrically at λ_{max} 505 (ϵ 63 M^{-1} cm^{-1}) and 303 nm (ϵ 265 M^{-1} cm^{-1}) (both ϵ's calculated per Mo) and stored at 0 °C.

Sodium hexachloroiridate(IV), $Na_2[IrCl_6]\cdot 6H_2O$ (Johnson and Matthey) was used without further purification. The spectrum obtained gave a maximum at 487 nm (ϵ 4075 M^{-1} cm^{-1}) to minimum 460 nm (ϵ 2070 M^{-1} cm^{-1}) ratio in accordance with literature values.[15] Solutions of $IrCl_6^{2-}$ in $HClO_4$ (0.10–1.00 M) were stable to aquation over 24 h when stored in the dark at 25 °C. Teflon needles were used in transference and deoxygenation procedures.

Sodium hexachloroiridate(III) (Johnson and Matthey) was purified by a procedure previously described.[16] Stock solutions of $IrCl_6^{3-}$ in 0.10 M $HClO_4$ gave a spectrum peak position 358 nm (ϵ 76 M^{-1} cm^{-1}), based on a molecular formula $Na_3[IrCl_6]\cdot 12H_2O$, in satisfactory agreement with that in the literature (λ_{max} 358 nm, ϵ 74 M^{-1} cm^{-1}).[15]

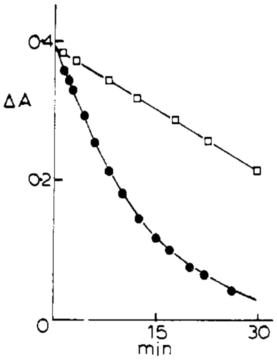


Figure 1. Plot of absorbance ΔA changes at 487 nm (1-cm path length optical cell) for the $IrCl_6^{2-}$ (1.0×10^{-4} M) oxidation of Mo^{IV}_3 (3.7×10^{-4} M) (●) and Mo^{V}_2 (5.9×10^{-4} M) (□) at 25 °C, $[H^+] = 1.00$ M, and $I = 2.00$ M ($LiClO_4$).

Tris(1,10-phenanthroline)iron(III) perchlorate, $[Fe(phen)_3](ClO_4)_3$, was prepared by a procedure described elsewhere.[17] A solution in 5.0 M $HClO_4$ gave a spectrum with λ_{max} 340 nm (ϵ 5700 M^{-1} cm^{-1}) and λ 510 nm (ϵ ~300 M^{-1} cm^{-1}), in satisfactory agreement with literature values.[11] Solutions in 5 M $HClO_4$ were stored at 0 °C and used within 5 h of preparation.

The Fe(II) complex $Fe(phen)_3^{2+}$ is known to have a peak at 510 nm (ϵ 10 900 M^{-1} cm^{-1}).[16]

A sample of potassium tris(oxalato)cobaltate(III), $K_3[Co(C_2O_4)_3]\cdot 3H_2O$, peak positions at 420 (ϵ 215 M^{-1} cm^{-1}) and 603 nm (ϵ 165 M^{-1} cm^{-1}), was prepared as described previously.[18]

Ammonium hexachloroplatinate(IV), $(NH_4)_2[PtCl_6]$ (Johnson and Matthey), was used without further purification.

Product Analysis and Stoichiometry. Reactions were studied under O_2-free conditions (syringes, Teflon needles, rubber serum caps, N_2 gas). Preliminary experiments (all at 25 °C, $[H^+] = 1.0$ M, $I = 2.0$ M $LiClO_4$) indicated that the $IrCl_6^{2-}$ oxidation of Mo^{IV}_3, (1), and

$$2Mo^{IV}_3 + 6Ir^{IV} \rightarrow 3Mo^{V}_2 + 6Ir^{III} \qquad (1)$$

$IrCl_6^{2-}$ oxidation of Mo^{V}_2, (2), proceed at comparable rates (Figure

$$Mo^{V}_2 + 2Ir^{IV} \rightarrow 2Mo^{VI} + 2Ir^{III} \qquad (2)$$

1). Absorbance changes were also monitored for runs with, for example, $3[Mo^{IV}_3] = [IrCl_6^{2-}] = 1.80 \times 10^{-4}$ M and $^3/_5[Mo^{IV}_3] = [IrCl_6^{2-}] = 1.8 \times 10^{-4}$ M. At 300 nm absorbance coefficients in M^{-1} cm^{-1} (per monomer unit) are as follows: Mo(IV), 265; Ir(IV), 1190; Mo(V), 1770; Ir(III), 10; Mo(VI), 300 (for a 10^{-4} M solution of sodium molybdate in 1 M H^+). A continuous change in absorbance at 300 nm was observed in both instances with final spectra giving ca. 40 and 10% decreases, respectively. Had no Mo(VI) been produced, small increases in absorbance would have been expected. For a run with $3[Mo^{IV}_3] = [Ir^{IV}] = 2.2 \times 10^{-3}$ M, some Mo^{IV}_3 (peak at 505 nm) remained on completion of the reaction. It was preferable to carry out kinetic runs with Mo^{IV}_3 in large excess of $IrCl_6^{2-}$, thereby favoring (1) over (2). A stoichiometry consistent with (1) was assumed to apply. Under these conditions, however, the stoichiometry could not be fixed experimentally with sufficient precision to rule out contributions from a route involving generation of monomeric Mo^{V} as in (3), which is then oxidized to Mo(VI) in competition with

$$Mo^{IV}_3 - 3e^- \rightarrow Mo^{V}_2 + Mo^{V} \qquad (3)$$

dimerization to Mo^{V}_2. With use of techniques previously reported,[15] it was demonstrated that >90% of the Ir^{III} product is present as $IrCl_6^{3-}$.

The $Fe(phen)_3^{3+}$ oxidation of Mo^{V}_2 is more rapid than the reaction with Mo^{IV}_3, and since a single rate-determining step is observed, a stoichiometry as in (4) is assumed. Reactions (either redox or

$$Mo^{IV}_3 + 6Fe^{III} \rightarrow 3Mo^{VI} + 6Fe^{II} \qquad (4)$$

nonredox) between Mo^{IV}_3 and Mo^{VI} were tested for and found to be small. Thus when Mo^{VI} and Mo^{IV}_3 were mixed at 25 °C on a Durrum-Gibson stopped-flow spectrophotometer at concentrations $(2.7\text{–}4.5) \times 10^{-4}$ and 1.5×10^{-4} M, respectively, $[H^+] = 1.0$ M, small

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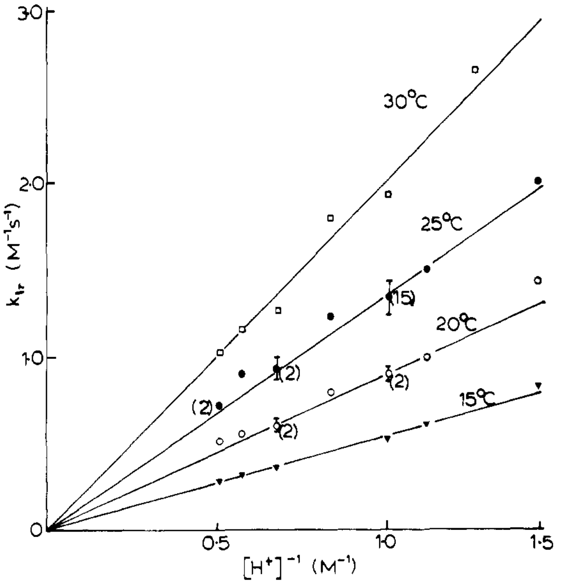

Figure 2. Dependence of second-order rate constants k_{Ir} on [H$^+$] for the $IrCl_6^{2-}$ oxidation of Mo^{IV}_3 at I = 2.00 M ($LiClO_4$). Numbers of runs averaged are indicated in parentheses.

(2%) changes in transmission were observed at ca. 300 nm ($t_{1/2}$ = 0.15 s). When the mixture is heated or when Mo^{VI} is added in excess, Mo blue formation is observed and varying degrees of Mo^{IV}_3 interaction with Mo^{VI} are apparent. The resultant spectrophotometric changes did not correspond to formation of Mo^{V}_2. Interactions between Mo^{V}_2 and Mo^{VI} to give Mo blue have also been observed. The low solubility of the $Fe(phen)_3^{3+}$ complex did not permit a study with oxidant in excess except at high [H$^+$]. The slowness of the Mo^{IV}_3 oxidation by $Fe(phen)_3^{3+}$ (runs requiring >20 min) resulted in some aquation of the product $Fe(phen)_3^{2+}$ to Fe^{2+}, with subsequent Fe^{2+} reduction of $Fe(phen)_3^{3+}$ contributing.[19]

Kinetics. Absorbance (A) changes were monitored on SP500 and SP8000 Unicam spectrophotometers at 487 (decay of $IrCl_6^{2-}$) and 510 nm (formation of $Fe(phen)_3^{2+}$). Decrease of $Co(C_2O_4)_3^{3-}$ was monitored at both 420 and 603 nm. For the $Fe(phen)_3^{3+}$ oxidation calculated A_∞ values were used because of the incidence of $Fe(phen)_3^{2+}$ aquation. Rate constants with Mo^{IV}_3 in large excess were obtained from the slope of plots of ln ($A_t - A_\infty$) against time. Ionic strengths were adjusted to I = 2.0 M ($LiClO_4$), and [H$^+$] was kept at >0.60 M, thereby avoiding a range of [H$^+$] values for which small (as yet unassigned) reversible spectrophotometric changes have been observed.[14] The $Co(C_2O_4)_3^{3-}$ runs were in HPTS (2.0 M) instead of $HClO_4$ because of the longer times involved and greater risk of instability of Mo^{IV}_3.

Runs carried out under argon instead of N_2 gave identical results.

Treatment of Data. A nonlinear least-squares program[20] with weighting $(k_{obsd})^{-2}$ was used to analyze the [H$^+$] dependence and determine the activation parameters for the $IrCl_6^{2-}$ oxidation.

Table I. Second-Order Rate Constants for the Oxidation of Mo^{IV}_3 with $IrCl_6^{2-}$ [I = 2.00 M ($LiClO_4$)]

temp, °C	[H$^+$], M	10^5 × [Mo^{IV}_3], M	10^5 × [Ir^{IV}], M	k_{Ir}, M^{-1} s^{-1}
15.0	0.60	37.0	2.00	1.08
	0.70	37.0	2.00	0.84
	0.90	37.0	2.00	0.60
	1.00	37.0	2.00	0.52
	1.50	37.0	2.00	0.36
	1.75	37.0	2.00	0.32
	2.00	37.0	2.00	0.28
20.0	0.60	42.6	2.13	1.76
	0.70	42.6	2.13	1.44
	0.90	42.6	2.13	1.00
	1.00	37.0	2.00	0.94
	1.00	42.6	2.13	0.84
	1.20	37.0	2.00	0.80
	1.50	37.0	2.00	0.62
	1.50	42.6	2.13	0.58
	1.75	37.0	2.00	0.58
	2.00	37.0	2.00	0.52
25.0	0.60	39.3	2.00	2.60
	0.70	39.3	2.00	2.16
	0.90	39.3	2.00	1.50
	1.00	8.7	1.00	1.26
	1.00	18.0	1.00	1.38
	1.00	26.3	18.0	1.34
	1.00	26.7	1.00	1.38
	1.00	50.0	18.0	1.36
	1.00	30.0	18.0	1.38^a
	1.00	33.7	18.0	1.44
	1.00	37.0	2.00	1.32^b
	1.00	37.0	2.00	1.34^c
	1.00	39.3	2.00	1.34
	1.00	39.3	4.00	1.30
	1.00	39.3	6.00	1.24
	1.00	39.3	8.00	1.24
	1.00	39.3	10.00	1.24
	1.00	45.0	1.00	1.42
	1.20	37.0	2.00	1.24
	1.50	37.0	2.00	1.00
	1.50	39.3	2.00	0.86
	1.75	37.0	2.00	0.90
	2.00	37.0	1.00	0.74
	2.00	39.3	2.00	0.72^d
30.0	0.60	29.3	2.00	3.8
	0.80	29.3	2.00	2.7
	1.00	31.7	2.00	1.94
	1.20	37.0	2.00	1.80
	1.50	29.3	2.00	1.26
	1.75	37.0	2.00	1.16
	2.00	37.0	2.00	1.02

[a] Argon used instead of N_2. [b] 1.2 × 10^{-3} M $IrCl_6^{3-}$ added. [c] 2.4 × 10^{-3} M $IrCl_6^{3-}$ added. [d] Run at 420 nm.

Results

Reaction with $IrCl_6^{2-}$. Plots of ln ($A_t - A_\infty$) against time with Mo^{IV}_3 in large excess were linear to ca. 80% completion, consistent with the rate law (5). The factor of 3 follows from

$$-\frac{d[Ir^{IV}]}{3dt} = k_{obsd}[Ir^{IV}] \tag{5}$$

the assumption that after initial one-electron oxidation of Mo^{IV}_3 there are two rapid steps. First-order rate constants k_{obsd} gave a linear dependence on [Mo^{IV}_3] (6). For a run at

$$-\frac{d[Ir^{IV}]}{3dt} = k_{Ir}[Mo^{IV}_3][Ir^{IV}] \tag{6}$$

25 °C using stoichiometric amounts of the reactants, [Mo^{IV}_3] = 0.60 × 10^{-4} M, [$IrCl_6^{2-}$] = 1.8 × 10^{-4} M, and [H$^+$] = 1.0 M, a plot of $1/\Delta A$ gives a linear plot to 40% completion and a rate constant of 1.33 M^{-1} s^{-1} in accordance with data in Table I. A dependence on [H$^+$] as in Figure 2 was observed, (7),

$$k_{Ir} = k_{-1}[H^+]^{-1} \tag{7}$$

where at 25 °C, k_{-1} = 1.36 ± 0.016 s^{-1}. A more detailed dependence, $k_1 = k_0 + k_{-1}[H^+]^{-1} + k_{-2}[H^+]^{-2}$, was also considered. At 25 °C this gives k_0 = 0.44 ± 0.16 M^{-1} s^{-1}, k_{-1} = 0.36 ± 0.40 s^{-1}, and k_{-2} = 0.56 ± 0.24 M s^{-1}. However such an analysis of data at other temperatures did not give an acceptable (unidirectional) trend in k_0, k_{-1}, or k_{-2} values, and since analyses in terms of k_0 and k_{-1}, or alternatively k_{-1} and k_{-2}, exhibited similar features, (7) was regarded as a better description. From the temperature dependence, activation parameters for k_{-1} in (3) are $\Delta H^\ddagger$ = 14.1 ± 0.4 kcal mol^{-1} and $\Delta S^\ddagger$ = −9.6 ± 1.5 cal K^{-1} mol^{-1}. No effect was observed when the product $IrCl_6^{3-}$ was present initially (Table I).

Reaction with $Fe(phen)_3^{3+}$. First-order plots with Mo^{IV}_3 in large excess were linear to >75% at [H$^+$] ≥ 1.5 M, but to only

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Table II. Second-Order Rate Constants (25 °C) for the Oxidation of Mo^{IV}_3 with $Fe(phen)_3^{3+}$ [I = 2.00 M ($LiClO_4$)]

$[H^+]$, M	$10^4 \times [Mo^{IV}_3]$, M	$10^4 \times [Fe(phen)_3^{3+}]$, M	k_{Fe}, $M^{-1}\ s^{-1}$
0.7	13.6	0.42	0.71
1.0	13.6	0.42	0.47
1.3	13.6	0.42	0.40
1.5	13.6	0.42	0.35
1.7	13.3	0.42	0.25
1.9	13.3	0.42	0.21
1.9	0.22	9.14	0.27
2.0	0.27	4.50	0.22

50–75% completion for the slower runs at $[H^+] > 1.5$ M (when side reactions are effective[19]). Rate constants k_{Fe} defined by the rate law (8) are listed in Table II. Good agreement in

$$\frac{d[Fe^{II}]}{6dt} = k_{Fe}[Mo^{IV}_3][Fe^{III}] \qquad (8)$$

k_{Fe} is obtained when the oxidant $Fe(phen)_3^{3+}$ is in excess. The $[H^+]$ dependence of k_{Fe} is of the same form as (7) with $k_{-1} = 0.52 \pm 0.04\ s^{-1}$ at 25 °C.

Reaction with $Co(C_2O_4)_3^{3-}$. The reaction was studied in 2.0 M HPTS instead of $HClO_4$, which sometimes gives irreproducible effects. Reactant concentrations were Mo^{IV}_3 (1.33×10^{-3} M) and $Co(C_2O_4)_3^{3-}$ (8×10^{-3} M). First-order disappearance of $Co(C_2O_4)_3^{3-}$ was monitored at the 420- and 600-nm peak positions (over 3 h) (rate constant $7.2 \times 10^{-5}\ s^{-1}$ at 25 °C). Final spectra indicated no reaction of Mo^{IV}_3 and no formation of Co^{2+}.[21] From separate experiments the rate constant for the decomposition of $Co(C_2O_4)_3^{3-}$ under identical conditions is $7.7 \times 10^{-5}\ s^{-1}$. It is concluded that $Co(C_2O_4)_3^{3-}$ does not oxidize Mo^{IV}_3.

Reactions with $PtCl_6^{2-}$. No $PtCl_6^{2-}$ oxidation of Mo^{IV}_3 was observed over >2 h at 25 °C, with use of reactant concentrations similar to those employed for the $Fe(phen)_3^{3+}$ oxidation.

Discussion

The ease of oxidation of aquomolybdenum(IV) is very much dependent on the structure and whether this is a monomer, dimer, or trimer. Thus $Co(C_2O_4)_3^{3-}$ (0.57 V)[21] does not oxidize the trimer, Mo^{IV}_3, but readily oxidizes both Mo^{III} and Mo^{III}_2 aquo ions through to Mo^{V}_2.[9,10] The implication is that oxidation of monomeric and/or dimeric Mo(IV) species is rapid. Consistent with this observation Chalilpoyil and Anson[22] have reported that it is not possible to electrooxidize Mo^{IV}_3 (at the time believed to be a dimer) to Mo^{V}_2, under conditions when electrochemical conversion of both Mo^{III} and Mo^{III}_2 to Mo^{V}_2 is slow but complete. Once formed, the Mo(IV) trimer, prepared by heating solutions of Mo^{III} with Mo^{V}_2 or Mo^{VI} at 90 °C for 2–3 h, is relatively difficult to oxidize.

This paper reports details of kinetic studies on the oxidation of aquo Mo^{IV}_3 by $IrCl_6^{2-}$ (0.89 V)[23] and $Fe(phen)_3^{3+}$ (1.06 V).[24] Product analyses of the $IrCl_6^{2-}$ reaction by UV–visible spectrophotometry have indicated some oxidation through to Mo(VI). Oxidation of equimolar solutions of Mo^{IV}_3 and Mo^{V}_2 with $IrCl_6^{2-}$ proceed at comparable rates (Figure 1). Kinetic plots with Mo^{IV}_3 in large excess were linear to >80% completion with Mo^{V}_2 the dominant product (eq 1). An alternative possibility, which unfortunately cannot be excluded, involves formation of monomeric Mo(V) from the decay of the primary product $Mo^{IV}_2Mo^{V}$, which is then oxidized through to Mo^{VI}.[11] If this stoichiometry (9) applies, then listed rate constants will be less by a factor of $^3/_4$.

Table III. Summary of Rate Constants (25 °C) for the $IrCl_6^{2-}$ and $Fe(phen)_3^{3+}$ Oxidation of Mo^{IV}_3 and Mo^{V}_2 Aquo Ions and the $Mo_2O_4(edta)^{2-}$ Complex

reactant	$[H^+]$ dep	k for $IrCl_6^{2-}$	k for $Fe(phen)_3^{3+}$	ratio
$Mo_3O_4^{4+}$ [a]	−1	$1.36\ s^{-1}$	$0.53\ s^{-1}$	0.39
$Mo_2O_4^{2+}$ [b]	0	$0.11\ M^{-1}\ s^{-1}$	$31.0\ M^{-1}\ s^{-1}$	280
$Mo_2O_4^{2+}$ [b]	−1	$0.052\ s^{-1}$	$6.0\ s^{-1}$	120
$Mo_2O_4(edta)^{2-}$ [c]	0	$6.6\ M^{-1}\ s^{-1}$	$1.9 \times 10^3\ M^{-1}\ s^{-1}$	290

[a] This work. [b] Reference 11. [c] Reference 16.

$$Mo^{IV}_3 + 4Ir^{IV} \rightarrow Mo^{V}_2 + Mo^{VI} + 4Ir^{III} \qquad (9)$$

The observation that a twofold excess of $IrCl_6^{3-}$ over $IrCl_6^{2-}$ does not slow down or affect in any way the oxidation of Mo^{IV}_3 supports a reaction scheme involving rapid decay of a primary product $Mo^{IV}_2Mo^{V}$. Thus if the latter were at all long-lived, $IrCl_6^{3-}$ might have been influential in (10). No species with

$$Mo^{IV}_3 + Ir^{IV} \rightleftharpoons Mo^{IV}_2Mo^{V} + Ir^{III} \qquad (10)$$

an average oxidation state between IV and V has yet been identified spectrophotometrically. It was further observed that the two-electron oxidant $PtCl_6^{2-}$ (0.68 V in 1 M HCl)[24] does not oxidize Mo^{IV}_3.

The dominant $[H^+]^{-1}$ dependence observed for both the $IrCl_6^{2-}$ and the $Fe(phen)_3^{3+}$ oxidation is of considerable interest. With $Fe(phen)_3^{3+}$ as oxidant an inner-sphere bridged activated complex is not possible, and an initial acid dissociation of aquo Mo^{IV}_3 followed by outer-sphere electron transfer is proposed. It is now accepted that $[H^+]^{-1}$ pathways do not necessarily implicate OH^- bridging but reflect an increase in hydrolysis as a preliminary to an oxidation process yielding a more extensively hydrolyzed product. A previous example is the rapid outer-sphere $IrCl_6^{2-}$ oxidation of V^{III}, in which VOH^{2+} is the redox-active species.[25] The Mo^{V}_2 product, as $Mo_2O_4^{2+}$, is in a more hydrolyzed state (per Mo) than Mo^{IV}_3, $Mo_3O_4^{3+}$. With $IrCl_6^{2-}$ as oxidant an inner-sphere pathway is not ruled out and gains support from the similarity of $\Delta H^\ddagger$ (14.1 kcal mol^{-1}) and $\Delta S^\ddagger$ (−9.6 cal $K^{-1}\ mol^{-1}$) parameters to those observed for the NCS^- substitution on Mo^{IV}_3, $\Delta H^\ddagger$ (14.9 kcal mol^{-1}) and $\Delta S^\ddagger$ (−8.1 cal $K^{-1}\ mol^{-1}$),[14,26] which also correspond to a dominant $[H^+]^{-1}$ pathway. The suggestion is therefore that the $IrCl_6^{2-}$ oxidation of Mo^{IV}_3 may well be inner sphere and substitution controlled. Additional support for an inner-sphere mechanism comes from the rate constant pattern observed for the $IrCl_6^{2-}$ and $Fe(phen)_3^{3+}$ oxidations of aquo Mo^{IV}_3 and Mo^{V}_2 and the necessarily outer-sphere oxidations of the Mo^{V}_2–edta complex (Table III). The ca. 300 times larger rate constants for $Fe(phen)_3^{3+}$ as compared to $IrCl_6^{2-}$ oxidations of both Mo^{V}_2 reactants are consistent with $Fe(phen)_3^{3+}$ being the stronger oxidant in terms of $E°$ values. The same ratio does not apply however to the Mo^{IV}_3 reactions. For the latter the rate constant for the $IrCl_6^{2-}$ oxidation is considerably enhanced, consistent with the gain that might be expected to result from utilization of a favorable inner-sphere pathway.

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Registry No. Mo^{IV}_3, 74353-85-8; $IrCl_6^{2-}$, 16918-91-5; $Fe(phen)_3^{3+}$, 13479-49-7.

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