Kinetic Studies on the Oxidation of Hexa-aquamolybdenum(III) with $[IrCl_6]^{2-}$, $[Co(C_2O_4)_3]^{3-}$, and Aquavanadium(IV) †

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Three one-equivalent reagents $[IrCl_6]^{2-}$, $[Co(C_2O_4)_3]^{3-}$, and VO^{2+} oxidise hexa-aquamolybdenum(III), according to equations, for example, $2Mo^{III} + 4Ir^{IV} \longrightarrow Mo^{V}_2 + 4Ir^{III}$, with the aquamolybdenum(V) dimer, $Mo_2O_4^{2+}$, the sole molybdenum product. Rate laws are consistent with a rate-determining first stage, *e.g.* $Mo^{III} + Ir^{IV} \longrightarrow Mo^{IV} + Ir^{III}$, in which Mo^{IV} is formed. No build-up of Mo^{IV} was detected. Reactions were studied with the molybdenum(III) reactant in excess. With $[IrCl_6]^{2-}$ (reduction potential 0.89 V) first-order rate constants, $k_{obs.}$, from the (stopped-flow) decay of $[IrCl_6]^{2-}$ at 489 nm gave a dependence $k_{obs.}/2[Mo^{III}] = k_a + k_b[H^+]^{-1}$, where at 25 °C, $I = 0.2$ M [Li(pts)], $k_a = 3.4 \times 10^4$ M^{-1} s^{-1} and $k_b = 2.9 \times 10^4$ s^{-1}. On replacing *p*-toluenesulphonate (pts^-) by trifluoromethanesulphonate ($tfms^-$) $k_{obs.}$ showed little variation (*ca.* 12%). The oxidant absorbance decay was also monitored in the $[Co(C_2O_4)_3]^{3-}$ (0.58 V) and VO^{2+}(aq) (0.36 V) reactions ($t_{\frac{1}{2}} > 1$ min). At 25 °C, $I = 2.0$ M [Li(pts)] the method of initial rates (R) gave dependences $R_{Co} = 2k_c[Mo^{III}][Co^{III}] + 4k_d[Mo^{III}]^2 + 2k_e[Mo^{III}]$ for $[Co(C_2O_4)_3]^{3-}$ ($k_c = 0.34$ M^{-1} s^{-1}), and $R_V = 2k_f[Mo^{III}][V^{IV}] + 4k_d[Mo^{III}]^2 + 2k_e[Mo^{III}]$ for VO^{2+} ($k_f = 3.3 \times 10^{-3}$ M^{-1} s^{-1}). On replacing pts^- by $tfms^-$ the oxidant-independent terms k_d (1.87×10^{-3} M^{-1} s^{-1}) and k_e (4.9×10^{-5} s^{-1}), which are common to both reactions, make no contribution. It is concluded that pts^- complexes to aquamolybdenum(III). Rate constants for the $[IrCl_6]^{2-}$ reaction are much faster than those obtained for substitution into the molybdenum(III) co-ordination sphere, and an outer-sphere mechanism is strongly implied. The $[Co(C_2O_4)_3]^{3-}$ oxidation (k_c) is independent of $[H^+]$ and exhibits behaviour consistent with an inner-sphere substitution-controlled process.

Although the preparation and characterisation of the pale yellow monomeric aquamolybdenum(III) ion was reported in the early 1970s,[1-5] the only previous redox study is a brief report on the oxidation with nitrate.[6] A comparison of the u.v.-visible spectrum of aquamolybdenum(III) with that of $[MoCl_6]^{3-}$ is the basis for presuming that the ion is hexa-aqua.[3] Substitution reactions ($t_{\frac{1}{2}} > 1$ min) with Cl^-, NCS^-, and $HC_2O_4^-$ as the incoming ligand have been reported.[5,7] The ion is difficult to study because of its reactivity with both O_2 and perchlorate ions. Strongly acidic *p*-toluenesulphonic acid (Hpts) and trifluoromethanesulphonic acid (Htfms) and salts as appropriate were therefore used in this study. Although both are generally regarded as poor donors, the effects noted with pts^- imply that this ion co-ordinates to aquamolybdenum(III), to give significant contributions to reactivity patterns.

Properties of the aqua-ions of Mo have been summarised recently.[8] In addition to the monomer, green dimeric [9] and trimeric [10] aqua-ions of Mo^{III} have been characterised, and their electrochemical properties studied.[11,12] The only stable aqua-ion of Mo^{IV} is a trimeric ion with core structure $Mo_3O_4^{4+}$,[13,14] whereas Mo^{V} exists as a dimer $Mo_2O_4^{2+}$.[15] This mismatch in structures of the aqua-ions results in an exceptionally varied redox chemistry. A communication has appeared on the present work.[16]

Experimental

Materials.—Hexa-aquamolybdenum(III) was obtained by aquation of hexachloromolybdate(III), $K_3[MoCl_6]$, under rigorous anaerobic conditions, using a procedure previously described.[5] Aqueous solutions of white crystalline *p*-toluenesulphonic acid (Sigma Chemicals) were used. A Dowex 50W-X2 cation-exchange column (1 cm diameter, 12 cm long, jacketed with ice-cold water) was used in the purification procedure. Solutions were transferred *via* thin-walled polytetrafluoroethylene tubing (Jencon TWT22), using excess gas pressure to force the solution from one vessel to another, and stored at *ca.* 0 °C. The Mo^{III} was determined by oxidation to Mo^{VI} with an excess of iron(III) sulphate in 1 M H_2SO_4, and titration of the Fe^{II} so formed with Ce^{IV} (ferroin indicator). The absorption spectrum in 1 M Hpts, peak positions λ/nm (ε/M^{-1} cm^{-1}) 310 (23.2) and 380 (14.1), is in good agreement with previous values,[3-5] the 10% smaller absorption coefficients (ε) representing an improvement in techniques. Elution of the Mo^{III} from the Dowex column with 1 M Hpts gave 0.015—0.020 M Mo^{III}, and with 2 M Hpts, 0.04—0.06 M stock solutions. Using a similar procedure with trifluoromethanesulphonic acid (Aldrich) a 310 nm absorbance peak of 22.0 M^{-1} cm^{-1} (in 1 M Htfms) was obtained. The Htfms had to be first purified by distillation under reduced pressure (*ca.* 15 mmHg). Initial stages of such preparations were in Hpts, the final elution involving use of Htfms.

To prepare Li(pts) anhydrous Li_2CO_3 (*ca.* 70 g BDH Reagent Grade) was added slowly with stirring to a solution of Hpts (500 g in 200 cm^3 water) at *ca.* 80 °C, until the pH was around 4.0. The solid was recrystallised from hot (80 °C) water. Solutions were standardised by ion exchange using Dowex 50W-X2 cation resin (H^+ form) and titration of the Hpts acid generated with standard NaOH solution. A solution of Li(tfms) was prepared in a similar manner.

Sodium hexachloroiridate(IV), $Na_2[IrCl_6]\cdot 6H_2O$ (Johnson Matthey), absorption maximum 489 nm ($\varepsilon = 4\,075$ M^{-1} cm^{-1}),[17] was used as supplied. Sodium hexachloroiridate(III), $Na_3[IrCl_6]\cdot 12H_2O$ (Johnson Matthey), had first to be recrystallised from ethanol–water to give absorption peaks at 358 nm (74 M^{-1} cm^{-1}) and 417(87).[17]

A sample of potassium tris(oxalato)cobaltate(III), $K_3[Co(C_2O_4)_3]\cdot 3H_2O$, was obtained as described by Bailar and Jones.[18] Peak positions λ/nm (ε/M^{-1} cm^{-1}) at 420(215) and 603(165) were in good agreement with literature values, 420(220) and 605(170).[19] The solid (and solutions) are photosensitive, and containing vessels were therefore covered with aluminium foil.

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† *Non-S.I. units employed:* M = mol dm^{-3}, mmHg ≈ 134 Pa.

Table 1. First-order rate constants, $k_{obs.}$, for the $[IrCl_6]^{2-}$ oxidation of hexa-aquamolybdenum(III) at 25.2 °C; ionic strength and $[H^+]$ adjusted to 0.02 M with Hpts or Htfms as indicated

$10^4[Mo^{III}]$	$10^5[IrCl_6^{2-}]$		$10^4[Mo^{III}]$	$10^5[IrCl_6^{2-}]$	
M		$10^{-2}k_{obs.}/s^{-1}$	M		$10^{-2}k_{obs.}/s^{-1}$
3.1	6.1	0.59	6.2	6.1	1.06
3.9	6.1	0.68	7.5	6.1	1.34
4.3	6.1	0.72	8.0	12.3	1.47
4.8	6.1	0.89	3.0	6.1	0.63 [b]
4.9	12.3	0.85	4.5	6.1	1.04 [b]
5.0	6.1	0.87 [a]	6.0	6.1	1.33 [b]
5.0	6.1	0.96	7.0	6.1	1.48 [b]

[a] $[IrCl_6^{3-}]$ = 5.0 × 10^{-3} M. [b] Acid used was Htfms.

A stock solution of penta-aquavanadium(IV) in Hpts (or Htfms), ε 17.2 M^{-1} cm^{-1} at 760 nm peak, was prepared from vanadyl sulphate, $VO(SO_4)\cdot 6H_2O$ (BDH, Analar), by loading onto an ion-exchange column (Dowex 50W-X2) and elution with the appropriate 2 M acid. The column procedure was repeated to ensure that no free sulphate was present. A solution of hexa-aquavanadium(III), ε 8.35 M^{-1} cm^{-1} at 400 nm peak, was prepared by electrolytic reduction of VO^{2+} to V^{2+}, and mixing equal amounts of V^{2+} and VO^{2+}. Solutions of the di-μ-oxo-bis[triaquaoxomolybdenum(V)] ion $[Mo_2O_4(H_2O)_6]^{2+}$, hereafter $Mo_2O_4^{2+}$, in Hpts were prepared by adopting earlier procedures.[20] The spectrum was as reported previously.[21]

Products and Stoicheiometries.—A 1 : 2 stoicheiometry was indicated for the molybdenum(III) reduction of $[IrCl_6]^{2-}$, equation (1), by monitoring the absorbance decay of $[IrCl_6]^{2-}$

$$2Mo^{III} + 4[IrCl_6]^{2-} \longrightarrow Mo^{V}_2 + 4[IrCl_6]^{3-} \qquad (1)$$

at 489 nm, and formation of aquamolybdenum(V) dimer, $Mo_2O_4^{2+}$, at 295 nm (ε 3 550 M^{-1} cm^{-1} per dimer). Further oxidation of $Mo_2O_4^{2+}$ by $[IrCl_6]^{2-}$ is on a much slower timescale,[22] and with the molybdenum(III) reactant in excess can be assumed not to contribute.

With $[Co(C_2O_4)_3]^{3-}$ as oxidant $Mo_2O_4^{2+}$ was also identified as product. Evidence for aquation and redox decomposition processes (2) and (3), where $[Co(C_2O_4)_2(C_2O_4)(H_2O)]^{3-}$ has

$$[Co(C_2O_4)_3]^{3-} + H_2O \rightleftharpoons [Co(C_2O_4)_2(C_2O_4)(H_2O)]^{3-} \qquad (2)$$

$$[Co(C_2O_4)_3]^{3-} + [Co(C_2O_4)_2(C_2O_4)(H_2O)]^{3-} \longrightarrow 2Co^{2+} + 2CO_2 + 5C_2O_4^{2-} \qquad (3)$$

one oxalate monodentate has been obtained.[23,24] At 25 °C, with 9.0 × 10^{-3} M $[Co(C_2O_4)_3]^{3-}$ in 2.00 M Hpts, I = 2.0 M, first-order plots of absorbance change at 420 nm were linear for 2.5 h (about one half-life) and gave a rate constant of 7.7 × 10^{-5} s^{-1} as compared to a value 12.6 × 10^{-5} s^{-1} in 2.0 M $HClO_4$. Final spectra for the oxidation of Mo^{III} could be quantified in terms of equation (4), assuming 10% de-

$$2Mo^{III} + 4[Co(C_2O_4)_3]^{3-} \longrightarrow Mo^{V}_2 + 4Co^{II} + 12C_2O_4^{2-} \qquad (4)$$

composition of $[Co(C_2O_4)_3]^{3-}$, and *ca.* 2% oxalate complexing to $Mo_2O_4^{2+}$ to give $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ (peak at 305 nm, ε 7 040 M^{-1} cm^{-1}).[25] The complexing of free oxalate to Mo^{III} [equation (5)] has been studied and is a slower process,[7] which

$$Mo^{III} + HC_2O_4^- \rightleftharpoons MoC_2O_4^+ + H^+ \qquad (5)$$

has little influence. Even when there is prior equilibration of Mo^{III} (1.0 × 10^{-3} M) with $H_2C_2O_4$ (1.0 × 10^{-2} M) followed by oxidation with $[Co(C_2O_4)_3]^{3-}$ (2.0 × 10^{-4} M) in 2.0 M Hpts (I = 2.0 M), the rate constant 1.63 × 10^{-2} s^{-1} (λ 420 nm) is only some 30% larger than in the absence of equilibrated oxalic acid. No contribution to initial rates is to be expected therefore.

The only observable products from the molybdenum(III) reduction of VO^{2+} are $Mo_2O_4^{2+}$ and V^{III}, consistent with equation (6). A well defined isosbestic point is observed at 598 nm (see Figure 6).

$$2Mo^{III} + 4V^{IV} \longrightarrow Mo^{V}_2 + 4V^{III} \qquad (6)$$

Kinetic Studies.—The oxidation with $[IrCl_6]^{2-}$ was monitored by stopped-flow spectrophotometry at the 489 nm oxidant peak. Conventional spectrophotometry was used to follow the slower $[Co(C_2O_4)_3]^{3-}$ and VO^{2+} oxidations at 420 and 760 nm respectively. The incidence of side reactions in the case of the $[Co(C_2O_4)_3]^{3-}$ oxidation suggested the initial slope method which was also appropriate in view of the complex rate law and contribution from terms zero order in oxidant concentration. Similarly, contributions from rate-law terms zero order in oxidant concentration were apparent with VO^{2+}, and the same procedure was adopted. Initial slopes of absorbance (converted into concentration units) against time were determined by a graphical method.

All runs were carried out under rigorous air-free conditions using rubber seals, syringes, needles, and N_2-gas streams. Plastic and not stainless-steel needles had to be used with $[IrCl_6]^{2-}$, and with this oxidant it was also necessary to decrease the ionic strength of 0.20 M to avoid side reactions possibly involving Hpts.

Treatment of Data.—Rate constants $k_{obs.}$ for the $[IrCl_6]^{2-}$ reaction have been halved to account for the stoicheiometry (1), it being assumed that each Mo^{III} is involved in the rate-determining step. Individual rate-law terms (and not listed rates R_{Co} and R_v) were corrected for the stoicheiometry of the $[Co(C_2O_4)_3]^{3-}$ and VO^{2+} reactions.* Unweighted standard least-squares fits of data were carried out.

Results

$[IrCl_6]^{2-}$ *as Oxidant.*—First-order rate constants $k_{obs.}$ (Table 1) obtained with Mo^{III} in large excess of the stoicheiometric amount, [Hpts] = 0.2 M, give a linear dependence on $[Mo^{III}]$ as shown in Figure 1. The second-order rate constant

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* Stoicheiometry factors for rate constants k_c, k_d, k_e, and k_f were not included in ref. 16.

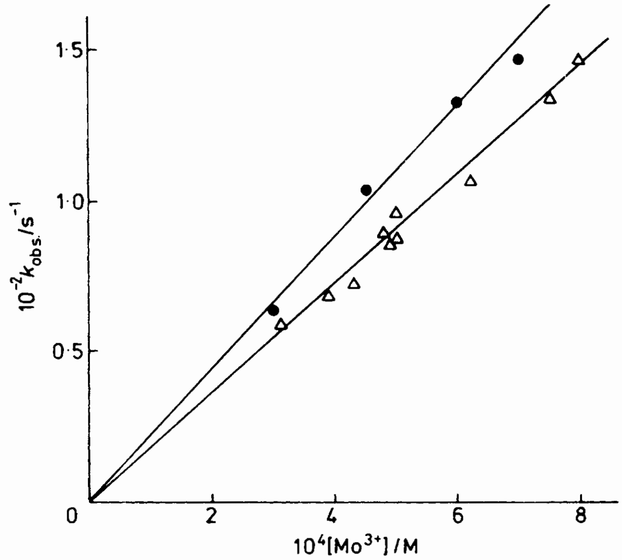

Figure 1. The dependence of first-order rate constants k_{obs} (25.2 °C), for the hexa-aquamolybdenum(III) reduction of $[IrCl_6]^{2-}$ (6.1×10^{-5} M), on the concentration of Mo^{III} in 0.20 M Hpts (△) and 0.20 M Htfms (●), I = 0.20 M

Table 2. The variation of second-order rate constants, k_{Ir}, for the $[IrCl_6]^{2-}$ (6.1×10^{-5} M) oxidation of hexa-aquamolybdenum(III) [(3—8) $\times 10^{-4}$ M] with [H$^+$] at 25.2 °C, I = 0.20 M (Li$^+$). Anions present, pts$^-$ or tfms$^-$, are as indicated

$[H^+]$/M [a]	0.10	0.12	0.15	0.20
$10^{-5}k_{Ir}$/M^{-1} s^{-1}	3.28	2.75	2.37	1.81
$[H^+]$/M [b]	0.067	0.10	0.20	
$10^{-5}k_{Ir}$/M^{-1} s^{-1}	4.2	3.2	2.09	

[a] pts$^-$. [b] tfms$^-$.

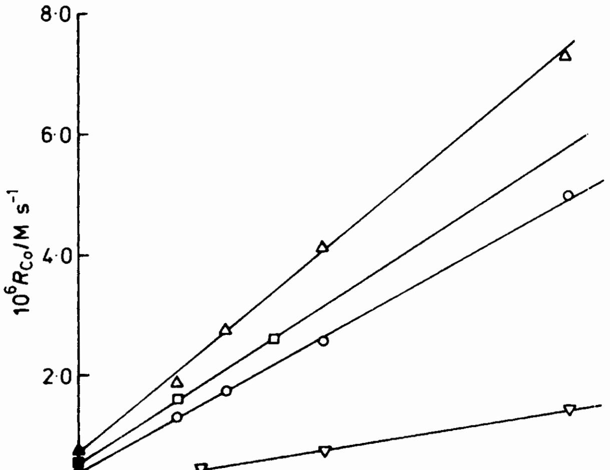

Figure 2. The dependence of initial rates R_{Co} (25 °C) for the hexa-aquamolybdenum(III) reduction of $[Co(C_2O_4)_3]^{3-}$ on concentration of $[Co(C_2O_4)_3]^{3-}$ with $10^3[Mo^{III}]$ = 1.0 (▽), 3.0 (○), 4.0 (□), 5.0 M (△); I = 2.0 M (Hpts). Points at $[Co(C_2O_4)_3{}^{3-}]$ = 0 are for the oxidant-independent terms in the corresponding study with VO^{2+} as oxidant

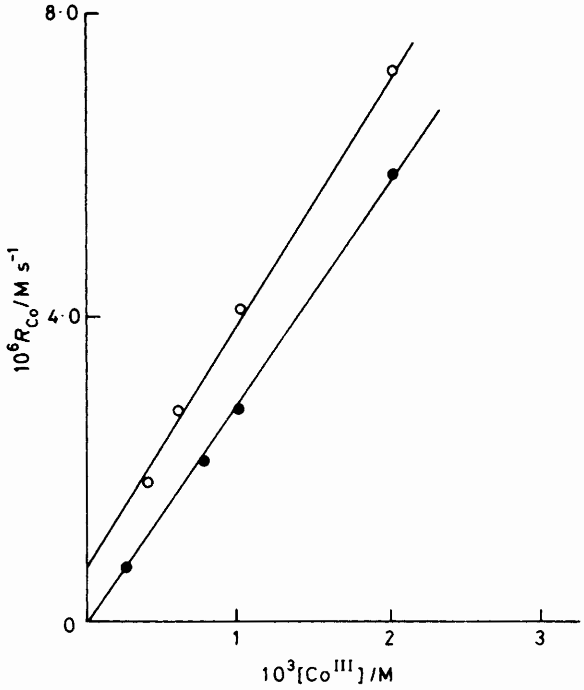

Figure 3. The dependence of initial rates R_{Co} (25 °C) for the hexa-aquamolybdenum(III) (5×10^{-3} M) reduction of $[Co(C_2O_4)_3]^{3-}$ on the concentration of $[Co(C_2O_4)_3]^{3-}$ in 2.0 M Hpts (○) and 2.0 M Htfms (●)

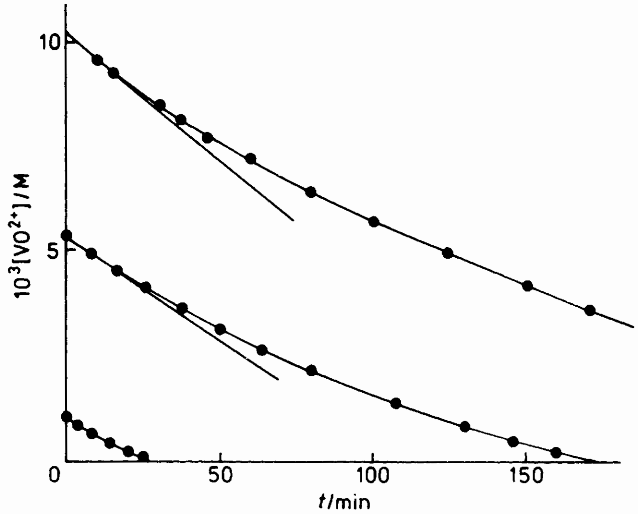

Figure 4. The decrease in concentration of VO^{2+} with time for the VO^{2+} oxidation of hexa-aquamolybdenum(III) (5.0×10^{-3} M) in 2.0 M Hpts monitored at 760 nm. Initial concentrations of VO^{2+} in the three runs (25 °C) were 10.1×10^{-3}, 5.3×10^{-3}, and 0.92×10^{-3} M

$k_{Ir} = (1.8 \pm 0.1) \times 10^5$ M^{-1} s^{-1}. No curvature is observed and it can be concluded that K for outer-sphere association of the 3+ and 2− reactants is <100 M^{-1} at 25 °C, I = 0.20 M pts). On replacing Hpts by Hftms, rate constants increased by some 12% (Figure 1). The [H$^+$] dependence was investigated (Table 2), [H$^+$] = 0.07—0.20 M, and rate constants obtained give a good fit to equation (7). At 25 °C,

$$k_{Ir} = k_a + k_b[H^+]^{-1} \qquad (7)$$

Table 3. Initial rates, R_{Co} (25 °C), for the $[Co(C_2O_4)_3]^{3-}$ oxidation of hexa-aquamolybdenum(III) from slopes of $[Co(C_2O_4)_3]^{3-}$ absorbance changes at 420 nm; ionic strength and $[H^+]$ = 2.0 M made up with Hpts and Htfms (last seven entries)

$10^3[Mo^{III}]$	$10^3[Co(C_2O_4)_3^{3-}]$		$10^3[Mo^{III}]$	$10^3[Co(C_2O_4)_3^{3-}]$	
M		$10^6R_{Co}/M\ s^{-1}$	M		$10^6R_{Co}/M\ s^{-1}$
1.0	0.20	0.24	5.0	0.40	1.86
	0.50	0.46		0.60	2.76
	1.00	0.70		1.00	4.1
	2.00	1.42		2.00	7.3
3.0	0.40	1.32	1.0	1.00	0.52
	0.60	1.72	3.0	1.00	1.68
	1.00	2.55	4.0	1.00	2.29
	2.00	4.9	5.0	0.25	0.73
4.0	0.40	1.55		0.75	2.12
	0.80	2.60		1.00	2.78
				2.00	5.9

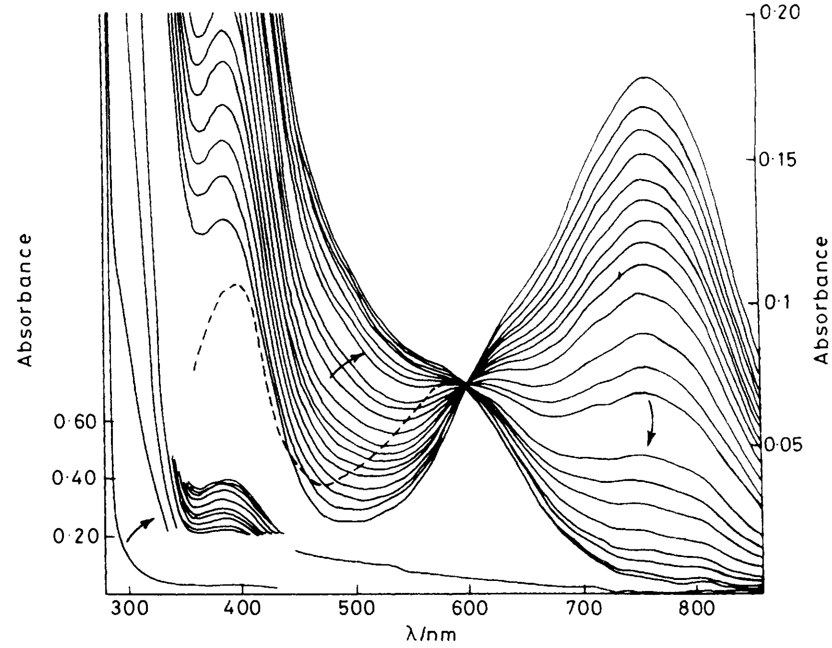

Figure 5. Absorbance spectra at *ca.* 20 min intervals for hexa-aquamolybdenum(III) (5 × 10^{-3} M) reduction of VO^{2+} (0.010 M) in 2.0 M Hpts at 25 °C, I = 2.0 M. Different scales apply to changes recorded at the left- and right-hand sides of the figure. The broken line is for the absorbance of a 0.010 M solution of aquavanadium(III)

$k_a = (3.4 \pm 1.1) \times 10^4\ M^{-1}\ s^{-1}$, $k_b = (2.9 \pm 0.2) \times 10^4\ s^{-1}$ at I = 0.20 M [Li(pts)]. Addition of the product $[IrCl_6]^{3-}$ (5.0 × 10^{-3} M) had no effect on rate constants, Table 1.

$[Co(C_2O_4)_3]^{3-}$ *as Oxidant.*—Initial slopes (λ 420 nm) are listed in Table 3. At a fixed $[Mo^{III}]$ and in 2.0 M Hpts a linear dependence on $[Co(C_2O_4)_3^{3-}]$ is observed, Figure 2. The intercepts, corresponding to oxidant-independent contributions, are the same as those observed (and explored more fully) for the VO^{2+} oxidation of Mo^{III} (see below). Furthermore, the slopes in Figure 2 give a linear dependence on $[Mo^{III}]$. The rate law is accordingly as in equation (8), with

$$R_{Co} = 2k_c[Mo^{III}][Co(C_2O_4)_3^{3-}] + 4k_d[Mo^{III}]^2 + 2k_e[Mo^{III}] \quad (8)$$

stoicheiometry factors as indicated. At 25 °C in 2.0 M Hpts, $k_c = 0.34 \pm 0.03\ M^{-1}\ s^{-1}$, and a good fit to equation (8) was obtained with $k_d = 1.87 \times 10^{-3}\ M^{-1}\ s^{-1}$, $k_e = 4.9 \times 10^{-5}\ s^{-1}$ as determined in the VO^{2+} study. No oxidant-independent terms were obtained (k_d and k_e zero) on replacing pts^- with $tfms^-$, Figure 3, when $k_c = 0.29 \pm 0.01\ M^{-1}\ s^{-1}$. Under these conditions it was demonstrated from runs at $[H^+]$ = 0.33, 1.0, and 2.0 M, I = 2.0 M [Li(tmfs)], that k_c (0.29, 0.30, and 0.29 $M^{-1}\ s^{-1}$ respectively) is independent of $[H^+]$. The linear dependence of k_c on $[Co(C_2O_4)_3^{3-}]$ suggests that K for prior association of the reactants is $<100\ M^{-1}$.

VO^{2+} *as Oxidant.*—With Mo^{III} in large excess, the kinetics approach zero-order behaviour, Figure 4, indicating the predominance of oxidant-independent terms in the rate law. A well defined isosbestic point at 598 nm is retained throughout the run, Figure 5. The method of initial slopes (R_v) was again used, where slopes obtained are listed in Table 4. At constant $[Mo^{III}]$ (5.0 × 10^{-3} M), a linear dependence on $[VO^{2+}]$ is observed, Figure 6. We note that contributions from the $[VO^{2+}]$-dependent term are small and can be neglected at $[VO^{2+}] \leq 1.0 \times 10^{-3}$ M. For this condition, plots of

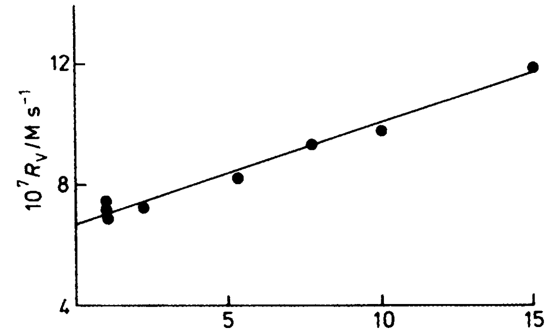

Figure 6. The dependence of initial rates R_V (25 °C) for the VO^{2+} oxidation of hexa-aquamolybdenum(III) (5.0 × 10^{-3} M) on [VO^{2+}] in 2 M Hpts

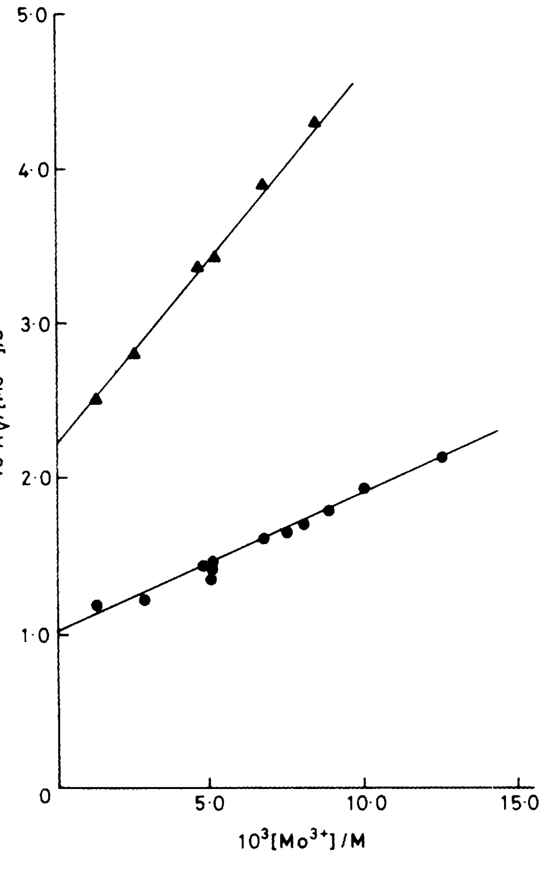

Figure 7. The dependence of R_V/[Mo^{III}] on [Mo^{III}] for the VO^{2+} oxidation of hexa-aquamolybdenum(III) at 25 °C in 1.0 M Hpts (▲) and 2.0 M Hpts (●), I = 2.0 M [Li(pts)]. The concentration of VO^{2+} was ⩽1.0 × 10^{-3} M so that the k_f term makes negligible contribution (see Figure 6)

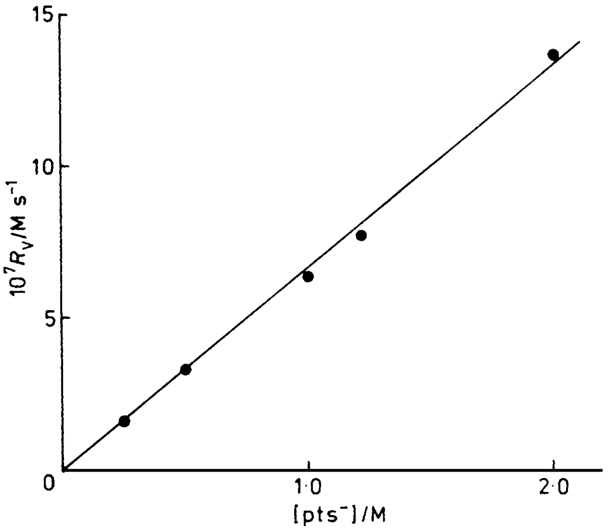

Figure 8. The dependence of R_V on pts$^-$ for the VO^{2+} oxidation of hexa-aquamolybdenum(III) (8.0 × 10^{-3} M) at 25 °C, [H$^+$] = 2.0 M. The ionic strength was maintained constant at 2.0 M by replacing Hpts with Htfms

Table 4. Initial rates, R_V (25 °C), for the VO^{2+} oxidation of hexa-aquamolybdenum(III) from slopes of the VO^{2+} absorbance change at 760 nm, I = 2.0 M [Li(pts)]

[H$^+$]	10^3[Mo^{III}]	10^3[VO^{2+}]	10^7R_V/M s^{-1}	
	M	M	Obs.	Calc.
2.0	1.20	0.24	1.32	1.35
	1.20	0.92	1.42	1.58
	2.50	0.48	3.2	3.1
	2.79	0.92	3.3	3.6
	4.5	0.76	6.4	6.2
	4.8	0.92	6.9	6.7
	5.0	0.92	7.4 [a]	7.1
	5.0	0.92	7.1 [b]	7.1
	5.0	2.15	7.4	7.5
	5.0	5.3	8.2	8.5
	5.0	7.7	9.3	9.3
	5.0	10.1	9.7	10.0
	5.0	15.0	11.8	11.7
	6.7	0.92	10.7	10.2
	7.5	0.92	12.4	11.9
	8.0	0.92	13.6	12.9
	8.8	0.92	15.8	14.7
	10.0	0.92	19.4	17.6
	12.5	0.92	26.7	24.2
1.5	4.50	0.76	10.2	
1.0	1.25	0.25	3.2	
	2.40	0.60	6.8	
	4.5	0.76	15.1	
	5.0	0.92	19.0	
	6.7	0.92	26.2	
	8.0	0.92	36	
0.67	4.5	0.76	21.7	

[a] 5.0 × 10^{-3} M V^{III} added. [b] 5.0 × 10^{-3} M Mo$_2$O$_4{}^{2+}$ added.

R_V/[Mo^{III}] against [Mo^{III}] are linear, Figure 7. Hence a rate law (9) applies. From a fit of data at 2.0 M Hpts, k_f =

$$R_V = 2k_f[\mathrm{Mo^{III}}][\mathrm{VO^{2+}}] + 4k_d[\mathrm{Mo^{III}}]^2 + 2k_e[\mathrm{Mo^{III}}] \qquad (9)$$

(3.3 ± 0.35) × 10^{-3} M^{-1} s^{-1}, k_d = (1.87 ± 0.08) × 10^{-3} M^{-1} s^{-1}, and k_e = (4.9 ± 0.42) × 10^{-5} s^{-1}. Only 33% of the reaction illustrated in Figure 5 proceeds *via* the k_f term. Runs in 1.0 M Hpts are also illustrated in Figure 7 from which it can be concluded that both k_d and k_e are [H$^+$]$^{-1}$ dependent. Assuming exclusive dependences $k_f = k_f'[\mathrm{H^+}]^{-1}$ and $k_e = k_e'[\mathrm{H^+}]^{-1}$, then k_f' = (1.21 ± 0.31) × 10^{-2} s^{-1} and k_e' = (1.06 ± 0.20) × 10^{-4} M s^{-1}. Additions of V^{III} (5.0 × 10^{-3} M) had no effect on the kinetics (Table 4). On replacing pts$^-$ by tfms$^-$, Table 5, k_d and k_e make no contribution, and k_f was considerably decreased (factor of *ca.* 20) to a value *ca.* 1.5 ×

Table 5. Initial rates, R_V (25 °C), for the VO^{2+} (0.92×10^{-3} M) oxidation of hexa-aquamolybdenum(III) from slopes of the VO^{2+} absorbance change at 760 nm, and the effect of replacing pts^- by $tfms^-$, $[H^+] = 2.0$ M, $I = 2.0$ M

$[tfms^-]$	$10^3[Mo^{III}]$	
M		10^7R_V/M s^{-1}
0	8.0	13.6
0.83	8.0	7.7
1.00	8.0	6.4
1.00	6.5	5.4
1.00	4.75	3.6
1.00	2.50	1.65
1.00	1.20	0.77
1.50	8.0	3.2
1.75	8.0	1.58
2.00	4.0	0.24

10^{-4} M^{-1} s^{-1} which was difficult to determine with accuracy, Figure 8.

Discussion

Previous studies [26] have indicated that $[Co(C_2O_4)_3]^{3-}$ and O_2 oxidise the green aquamolybdenum(III) dimer some 10^2 times faster than monomeric aquamolybdenum(III), consistent with structural similarities of Mo^{III}_2 [27] and Mo^{V}_2.* The oxidant-independent rate-law term $k_d[Mo^{III}]^2$, which contributes to the reaction of the two less powerful oxidants $[Co(C_2O_4)_3]^{3-}$ and VO^{2+}, suggests a process in which dimer formation is rate determining and is followed by rapid oxidation. Such a path is able to compete with that involving direct oxidation of Mo^{III}. On replacing pts^- by $tfms^-$ k_d becomes zero which suggests that pts^- is involved in the formation of Mo^{III}_2. This study therefore casts doubt on the use of pts^- as an inert electrolyte and indicates that use of $tfms^-$ is to be preferred.† Examples in which $tfms^-$ (and perchlorate) co-ordinate to metal ions are also known.[28]

The oxidant-independent term k_e presumably also involves complexing of Mo^{III} to pts^-, the monomer generated having increased redox activity. Identical k_d and k_e values are indicated in both the $[Co(C_2O_4)_3]^{3-}$ and VO^{2+} studies, and no dependence on the identity of the oxidant is observed. This is a particularly important point since in the case of the $[Co(C_2O_4)_3]^{3-}$ oxidant a number of side reactions as in (2), (3), and (5) could have made some contribution.

No kinetic or spectrophotometric evidence was obtained for Mo^{IV} as other than a transient intermediate. Rate-law dependences, clearly established in the case of $[IrCl_6]^{2-}$ and $[Co(C_2O_4)_3]^{3-}$, point to rate-determining processes as in equation (10). All subsequent reactions are rapid, at least two

$$Mo^{III} + Ir^{IV} \longrightarrow Mo^{IV} + Ir^{III} \qquad (10)$$

further stages being required to give the Mo^{V}_2 product. Interestingly, addition of the product $[IrCl_6]^{3-}$ (5×10^{-3} M) did not effect reaction (10), or the overall progress of the reaction, and addition of aquavanadium(III) likewise had no effect on the VO^{2+} reaction. Rate constants (M^{-1} s^{-1}) at 25 °C [5,7] which have been reported for 1 : 1 substitution reactions of aquamolybdenum(III) with Cl^- (0.0046), NCS^- (0.27), $HC_2O_4^-$ (0.49) strongly suggest that k_a (3.4×10^4 M^{-1} s^{-1}) for the $[IrCl_6]^{2-}$ oxidation of Mo^{III} is outer sphere. The acid-dissociation constant of Mo^{3+} has not as yet been determined. Assuming a pK_a of 3.0, the rate constant for the $[IrCl_6]^{2-}$ oxidation of $MoOH^{2+}$ is *ca.* 2.9×10^7 M^{-1} s^{-1}, indicating a very favourable outer-sphere reaction. This presumably reflects the more extensive acid dissociation of the molybdenum(IV) state. Previously [29] it has been demonstrated that the $[IrCl_6]^{2-}$ oxidation of hexa-aquavanadium(III) proceeds solely by an $[H^+]^{-1}$-dependent path, rate constant 52 s^{-1}, and is probably outer sphere. The occurrence of k_a and k_b suggests that Mo^{IV} is unlikely to be as extensively hydrolysed as V^{IV} (possibly $MoOH^{3+}$ rather than MoO^{2+}) consistent with the greater ionic radius of Mo^{IV}. Also relevant is the magnitude of k_b (2.9×10^4 s^{-1}) for the molybdenum(III) reaction, which is considerably faster than the corresponding rate constant for the vanadium(III) reaction (52 s^{-1}). One possible implication is that Mo^{III} is a much stronger reductant, but this is not borne out by the slowness of the molybdenum(III) reduction of VO^{2+}. The reduction potential for the Mo^{IV}–Mo^{III} couple is probably very similar to, possibly slightly less (say 0.3 V) than, that for the V^{IV}–V^{III} couple.

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* See, for example, ref. 25, and footnote ref. 13 therein.

† Studies on substitution reactions of hexa-aquamolybdenum(III) [5,7] were carried out in pts^- solutions, $I = 1.0$ M [Li(pts)]. In view of the present findings it was decided to check results for the NCS^- substitution using $tfms^-$ for pts^-. Five runs in 1.0 M Htfms gave a rate constant of 0.36 M^{-1} s^{-1} for the 1 : 1 formation of the thiocyanato-complex compared to the previous value of 0.27 M^{-1} s^{-1} in pts^-.[5] A similar small effect is observed for the reaction with Cl^-.

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