Reaction Paths and Kinetics in the Cr^{2+} Reduction of the Mo^{V}_2 and Mo^{IV}_3 Ions $[Mo_2O_4(H_2O)_6]^{2+}$ and $[Mo_3O_4(H_2O)_9]^{4+}$ †

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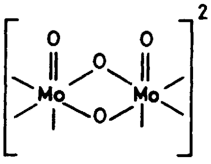
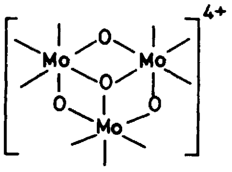
Inner-sphere paths are observed in the Cr^{2+} reduction of 10^{-4}—10^{-3} M solutions of Mo^{V}_2, $[Mo_2O_4(H_2O)_6]^{2+}$, and Mo^{IV}_3, $[Mo_3O_4(H_2O)_9]^{4+}$, at 25 °C, I = 2.0 M [Na(pts)]. In 1.9 M Hpts (*p*-toluenesulphonic acid) and with $[Cr^{2+}]$ in >10-fold excess the reaction of Mo^{V}_2 proceeds *via* a grey-green Cr-containing intermediate ($\approx$1 min), to give a product with the Mo^{III}_2 spectrum ($\approx$24 h). The rate law for formation of the intermediate is of the form $k_1[Cr^{2+}]^2[Mo^{V}_2][H^+]$, with $k_1 = 9.1 \times 10^3$ M^{-3} s^{-1}. The decay of the intermediate is independent of $[Cr^{2+}]$ and can be expressed as k_2[Intermediate]$[H^+]$, with $k_2 = 2.0 \times 10^{-5}$ M^{-1} s^{-1} believed to correspond to a process involving loss of Cr^{III}. With a 2:1 Cr^{2+} : Mo^{V}_2 ratio of reactants, evidence for two intermediates is obtained ($\approx$1 min), one (green in colour) giving a Cr:Mo ratio of 1:1, and the other the same as that generated in the reaction of excess of Cr^{2+} with Mo^{V}_2 giving a Cr:Mo ratio of 2:1. Some 30% of the Mo is separated as Mo^{V}_2. Over longer periods ($\approx$22 h) 60—70% overall conversion to Mo^{IV}_3 is observed, and 24—30% of the Mo is present as Mo^{V}_2. In separate experiments, with Cr^{2+} in >10-fold excess, Mo^{IV}_3 is reduced to $Mo^{III,III,IV}$ in a two-stage process, complete within 1 min, and then through to Mo^{III}_3 ($\approx$40 min). Reduction of Mo^{V}_2 to either Mo^{III}_2 or Mo^{III}_3 is observed therefore, depending on whether a single addition of excess of Cr^{2+} or successive additions of Cr^{2+} are made.

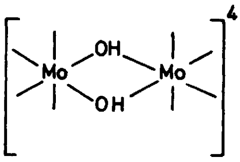
In aqueous acidic solutions, here $[H^+]$ = 0.1—2.0 M, Mo^{V} is present as the orange-yellow dimer $[Mo_2O_4(H_2O)_6]^{2+}$, (**A**),[1] Mo^{IV} as the red trimer $[Mo_3O_4(H_2O)_9]^{4+}$, (**B**),[2] and Mo^{III} can exist as the pale yellow $[Mo(H_2O)_6]^{3+}$,[3] a green dimer established as $[Mo_2(OH)_2(H_2O)_8]^{4+}$, (**C**),[4] or a trimer of 4+ or 5+ charge with a μ-hydroxo structure, similar to (**B**), which is also green.[5] Monomeric Mo^{V} has only transient existence,[6] and monomeric and dimeric forms of Mo^{IV} have not yet been identified.[7] The quite different structures of successive oxidation states are noted, where these give rise to an interesting and varied redox chemistry. Kinetic studies for a number of oxidation reactions have been reported. These include: $[Mo(H_2O)_6]^{3+}$ with $[IrCl_6]^{2-}$, $[Co(C_2O_4)_3]^{3-}$, $[VO(H_2O)_5]^{2+}$, and O_2;[8,9] $[Mo_2(OH)_2(H_2O)_8]^{4+}$ with $[Co(C_2O_4)_3]^{3-}$;[10] and $[Mo_3O_4(H_2O)_9]^{4+}$ and $[Mo_2O_4(H_2O)_6]^{2+}$ with both $[IrCl_6]^{2-}$ and $[Fe(phen)_3]^{3+}$ (phen = 1,10-phenanthroline).[11,12] To date there have been no corresponding studies of reactions involving reduction, and it was decided therefore to investigate the Cr^{2+} reductions of the Mo^{V}_2 and Mo^{IV}_3 aqua ions (**A**) and (**B**). One possible outcome of interest was the formation of stable mixed-metal Cr- and Mo-containing complexes.



(**A**)



(**B**)



(**C**)

Because of the reactivity of Mo^{III}_2 with ClO_4^-,[13] *p*-toluenesulphonic acid, Hpts (Sigma Chemicals), a strong acid and poor donor, was used as supporting electrolyte.

Experimental

Reactions.—The Mo^{V}_2 ion, $Mo_2O_4^{2+}$, was prepared by the procedure previously described.[14] Final elution of $Mo_2O_4^{2+}$ from a Dowex column was with 0.5—2.0 M Hpts. Solutions were standardised spectrophotometrically at peak positions 384 (ε 52) and 295 nm (ε 1 770 M^{-1} cm^{-1}),[12] ε values per Mo. The preparation of Mo^{IV} as $Mo_3O_4^{4+}$ has also been described.[14] Final solutions eluted from a Dowex column with 2.0 M Hpts were typically 0.01 M in Mo^{IV}_3. These were standardised spectrophotometrically at the 505 nm peak (ε 63 M^{-1} cm^{-1} per Mo).[11]

Solutions of Cr^{2+} ($\approx$0.05 M) were obtained by electrochemical reduction of $[Cr(H_2O)_6]^{3+}$ in 0.5 M Hpts at a Hg-pool cathode as in previous papers from this laboratory. When solutions of higher concentration were required $[Cr(H_2O)_6]^{2+}$ in 0.5 M $HClO_4$ was loaded onto an air-free Dowex 50W-X2 column, the ClO_4^- removed by washing with 0.1 M Hpts (100 cm^3), and Cr^{2+} eluted with 2.0 M Hpts. Using this method stock solutions of $[Cr^{2+}]$ > 0.2 M were obtained. Standardisation was at the 715 nm peak of Cr^{2+} (ε 4.8 M^{-1} cm^{-1}); any $[Cr(H_2O)_6]^{3+}$ present gave peaks at 408 (15.8) and 574 nm (13.3 M^{-1} cm^{-1}).[15] Subsequently solutions were also obtained from solid $CrCl_2{\cdot}6H_2O$.[16]

p-Toluenesulphonic acid (Sigma Chemicals) was converted into the sodium salt, Na(pts), by neutralising with NaOH and recrystallising twice. Solutions were standardised by exchanging onto an IR(H)120 Amberlite resin column, and titrating the H^+ released with standard 0.10 M NaOH.

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† *Non-S.I. unit employed:* M = mol dm^{-3}.

Table 1. Product analyses after ≈22 h for the reaction of Cr^{2+} (0.039 M) with Mo^{V}_2 (0.0017 M) following Sephadex C25-120 column separation

$[H^+]$/M	Mo as Mo^{V}_2 (%)	Mo as Mo^{IV}_3 (%)
1.0	24	70
1.0	30	60
2.0	25	65

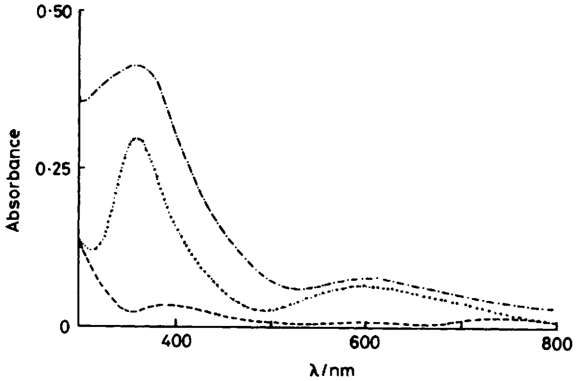

Figure 1. U.v.-visible spectra for the Cr^{2+} (2.9×10^{-2} M) reduction of Mo^{V}_2 (1.6×10^{-3} M) at 25 °C, $[H^+] = 1.00$ M, $I = 2.00$ M [Na(pts)] (path length 2 mm). The initial spectrum (– – – –) was calculated from known absorbances of the reactants, that of the intermediate (– · – · – · –) was recorded ≈1 min after mixing, and the final spectrum (· · · ·) after ≈24 h

All the reactions with Cr^{2+} require rigorous air-free techniques. These were using N_2 gas, further purified by passing through Cr^{+} solutions, rubber seals, Teflon tubing, and nylon syringes.

Products of the Reaction of Cr^{2+} *with* Mo^{V}_2.—Reduction of Mo^{V}_2 with Cr^{2+} [>10-fold excess, equation (1)] gave an intermediate (≈1 min) followed by the slow formation ($t_{\frac{1}{2}}$ 5—24 h depending on $[H^+]$) of a product with the spectrum of aqua Mo^{III}_2, (C), Figure 1.[4b,10] The spectrum of the

$$4Cr^{2+} + Mo^{V}_2 \longrightarrow 4Cr^{III} + Mo^{III}_2 \qquad (1)$$

intermediate is independent of $[Cr^{2+}]$ (2.1—5.4) $\times 10^{-2}$ M, and $[H^+]$, 0.50—1.92 M, and has a peak at 360 nm, $\varepsilon = 639 \pm 15$ M^{-1} cm^{-1} per Mo, Figure 1. The reaction of Cr^{2+} with Mo^{V}_2 (2:1 ratio) gave for the same Mo^{V}_2 concentration an intermediate of about half the intensity of that in Figure 1 as shown in Figure 2 with a peak at 400 nm (≈1 min), and after ≈22 h a final solution (red in colour) indicating substantial amounts of Mo^{IV}_3, (**B**). Addition of excess of Cr^{2+} after 1 min resulted in a more intense absorption approaching that obtained for a 10-fold Cr^{2+} excess. For the 2:1 addition the existence of Mo^{IV}_3 was confirmed by separating the products on a Sephadex C25-120 column under air-free conditions which yielded three bands: the first (orange-yellow) eluted with 0.10 M Hpts + 0.10 M Li(pts) was identified as Mo^{V}_2, the second (blue) eluted with 0.10 M Hpts + 0.40 M Li(pts) as $[Cr(H_2O)_6]^{3+}$, and the third (red) with 0.10 M Hpts + 1.9 M Li(pts) as Mo^{IV}_3. Details of product analyses are as indicated in Table 1, with >90% Mo recovery and no apparent dependence on $[H^+]$. No unreacted Cr^{2+} or green Cr^{III}_2 formed by air oxidation of Cr^{2+} was observed in these experiments.[17]

Composition of Intermediates.—Some 5 min after mixing the reactants, with the Cr^{2+} in large excess, $[Mo^{V}_2] = 0.0173$, $[Cr^{2+}] = 0.56$ M, and in 2:1 excess, $[Mo^{V}_2] = 0.046$, $[Cr^{2+}] = 0.096$, [Hpts] = 0.60—9.96 M, solutions were loaded onto air-free ice-cooled Sephadex G10-120 gel filtration columns (90 × 1 cm) pre-equilibrated in 0.5 M HCl. The columns were washed with 0.5 M HCl, and gave (≈5 h) in the first case grey-green and blue bands merging into each other. Three fractions of the grey-green band were collected. The first gave a spectrum very similar in appearance to Cr^{III}_2 with peaks at 415 and 580 nm. The peak ratio of 1.9:1, compared to the literature value of 1.2:1,[18] suggested that the band is predominantly but not pure Cr^{III}_2. This component is most likely formed by reaction of Cr^{2+} with traces of O_2. Analysis of the second and third fractions of the grey-green band gave Cr:Mo ratios of 3.3:1 and 3.2:1. Ratios >2:1 are regarded as unrealistic, in view of the overall $Mo^{V}_2 \longrightarrow Mo^{III}_2$ change, and suggest some contamination by Cr^{III}_2. Analyses for Cr and Mo were carried out by oxidising both metals to the VI state by heating with concentrated HNO_3, and then Br_2. The solution (in HCl) was then analysed on a model 2380 Perkin-Elmer atomic absorption spectrometer, to give ratios having an estimated accuracy of ±15%. From its spectrum, the blue band was identified as Cr^{2+}. From runs with

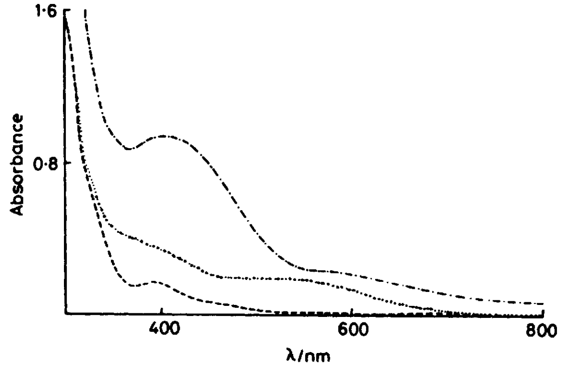

Figure 2. U.v.-visible spectra for the Cr^{2+} (3.7×10^{-2} M) reduction of Mo^{V}_2 (1.7×10^{-2} M) at 25 °C, $[H^+] = 2.0$ M (path length 1 mm). The initial spectrum (– – – –) was calculated from known absorbances of reactants, that of the intermediate (– · – · – · –) was recorded ≈1 min after mixing, and the final spectrum (· · · ·) after ≈20 h

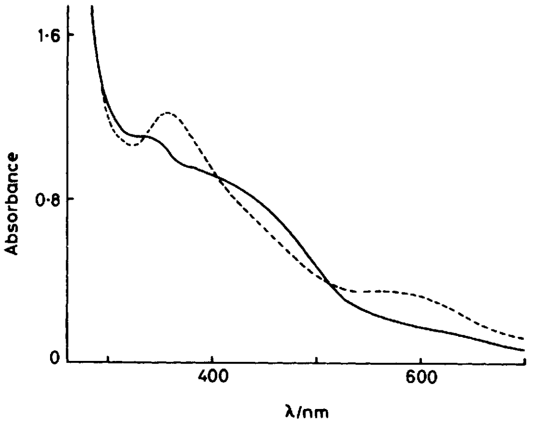

Figure 3. U.v.-visible spectra of fractions obtained following the separation of intermediates obtained in the reaction of Cr^{2+} (9.6×10^{-2} M) with Mo^{V}_2 (4.6×10^{-2} M) (2:1 ratio) at 25 °C, in 2.00 M Hpts (path length 1 cm). The column was loaded after 5 min reaction and the spectra correspond to the first (——) and second intermediates (– – – –)

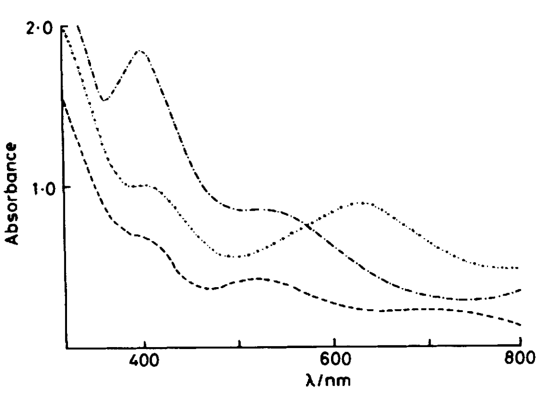

Figure 4. U.v.-visible spectra for the Cr^{2+} (5.0×10^{-2} M) reduction of Mo^{IV}_3 (2.5×10^{-3} M) at 25 °C, $[H^+] = 1.50$ M, $I = 2.00$ M [Na(pts)] (path length 10 mm). The initial spectrum (– – – –) was calculated from known absorbances of reactants, that of the intermediate (– · – · – · –) recorded ≈1 min after mixing corresponds to that of $Mo^{III,III,IV}$ at $[H^+] = 1.5$ M, and the final spectrum (· · · ·) after ≈40 min to Mo^{III}_3

a 2:1 ratio of the reactants, incompletely separated green and grey-green components were collected prior to a (small) red Mo^{IV}_3 and yellow Mo^{V}_2 bands. Analyses of the green and grey-green fractions gave Cr:Mo ratios of 1.1:1 and 2.2:1 respectively, thus identifying two intermediates. Spectra of these two fractions are shown in Figure 3. The spectrum of the grey-green 2.2:1 band corresponds to that of the intermediate shown in Figure 1.

Products of Reaction of Cr^{2+} *with* Mo^{IV}_3.—For the reaction of Cr^{2+} ($\geqslant$ 10-fold excess) with Mo^{IV}_3 spectra indicate Mo^{III}_3 as the sole Mo-containing product (40 min), with absorption peaks/nm (ε/M^{-1} cm^{-1} per Mo) at 420 (sh) (100), 635 (80), and 825 (45). The spectrum observed after ≈1 min, Figure 4, corresponds reasonably well to that of $Mo^{III,III,IV}$, 398 (230) and 495 nm (115 M^{-1} cm^{-1}),[5] bearing in mind that $[H^+] = 1.5$ M. The reaction can therefore be summarised by equations (2)—(3).

$$2Cr^{2+} + Mo^{IV}_3 \longrightarrow 2Cr^{III} + Mo^{III,III,IV} \qquad (2)$$

$$Cr^{2+} + Mo^{III,III,IV} \longrightarrow Cr^{III} + Mo^{III}_3 \qquad (3)$$

Previous work[5] has demonstrated that the Mo^{III}_3 product is difficult to elute from Dowex columns (a charge of 4+ or 5+ is indicated), and ion-exchange separation of the products was not attempted therefore. Also at $[H^+] < 4.0$ M, $Mo^{III,III,IV}$ disproportionates to give Mo^{III}_3 and Mo^{IV}_3.[5] This will have the effect of shifting the 495 nm peak to a higher wavelength as is observed in Figure 4. At $[H^+] < 0.5$ M, <30% of the $Mo^{III,III,IV}$ remains. No evidence has been obtained for the $Mo^{III,IV,IV}$ mixed-valence state.[5,6]

Kinetic Studies.—Reactions of Mo^{V}_2 and Mo^{IV}_3 with Cr^{2+} in > 10-fold excess were studied at 25 °C, $I = 2.00$ M [Na(pts)]. The formation of the intermediate in both cases was monitored in a Dionex D110 stopped-flow spectrophotometer using on-line procedures as described in other papers from this laboratory. In the case of the Mo^{V}_2 reaction the decay of the intermediate was studied using a Perkin-Elmer Lambda 5 spectrophotometer. Reactions were generally monitored at peak positions (as indicated). First-order plots of absorbance changes $\ln(A_\infty - A_t)$ against time were linear to at least three half-lives. The slopes of such plots gave first-order rate constants $k_{obs.}$ In the case of the Cr^{2+} reduction of Mo^{V}_2, when at the lower $[H^+]$ values the second stage of reaction can take up to 80 h to reach completion (and A_∞ values were difficult to determine), the Guggenheim method was also used to evaluate $k_{obs.}$.[19] Errors were determined using an unweighted linear least-squares program.

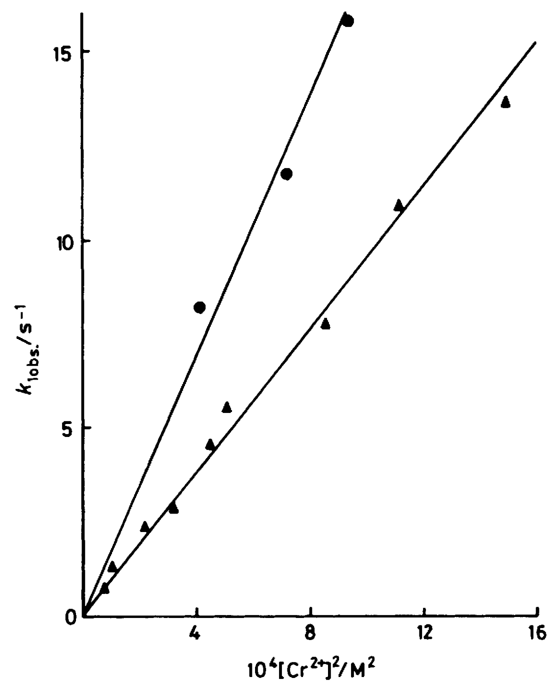

Figure 5. The dependence of first-order rate constants, $k_{1obs.}$ (25 °C), for the first stage (formation of the intermediate) of the Cr^{2+} (> 10-fold excess) reduction of Mo^{V}_2 (1.0—5.0) × 10^{-4} M on the concentration of Cr^{2+}, $[H^+] = 1.50$ (▲) and 1.95 M (●), $I = 2.00$ M [Na(pts)]

Results

Excess of Cr^{2+} *with* Mo^{V}_2.—First-order rate constants $k_{1obs.}$ are listed in Table 2. A linear second-order dependence on $[Cr^{2+}]$, (0.86—8.36) × 10^{-2} M, is observed, Figure 5. From the slope the third-order rate constant is (9.6 ± 0.6) × 10^3 M^{-2} s^{-1} at $[H^+] = 1.50$ M and (16.8 ± 2.0) × 10^3 M^{-2} s^{-1} at $[H^+] = 1.95$ M. Intercepts are small, *e.g.* 0.3 ± 0.4 s^{-1} at $[H^+] = 1.5$ M, and probably not meaningful. The first-order dependence of $k_{1obs.}$ (Table 3) on $[H^+]$ is illustrated in Figure 6. There was no dependence of $k_{1obs.}$ on the wavelength at which the reaction was monitored (Table 3). Equation (4) defines the

$$\text{Rate} = k_1[Cr^{2+}]^2[Mo^{V}_2][H^+] \qquad (4)$$

full rate law. At 25 °C, $I = 2.00$ M [Na(pts)], the rate constant k_1 is (9.1 ± 0.3) × 10^3 M^{-3} s^{-1}.

The much slower decay of the intermediate (intermediate 2 in this scheme) was studied by conventional spectrophotometry at 360 nm. First-order rate constants $k_{2obs.}$ (Table 4) give a linear dependence on $[H^+]$, Figure 7, but are independent of $[Cr^{2+}]$, (2.1—5.4) × 10^{-2} M. The rate law is as in equation (5), and at

$$\text{Rate} = k_2[\text{Intermediate}][H^+] \qquad (5)$$

25 °C, $I = 2.00$ M [Na(pts)], $k_2 = (2.0 \pm 0.3) \times 10^{-5}$ M^{-1} s^{-1}. From the least-squares treatment it is concluded that the intercept, $-(0.17 \pm 0.45) \times 10^{-6}$ s^{-1}, makes no contribution.

Table 2. Variation of first-order rate constants, $k_{1obs.}$ (25 °C), with $[Cr^{2+}]$ for the first stage of the reaction of Mo^{V}_2 with Cr^{2+}, $[Mo^{V}_2]$ = (1.0—5.0) × 10^{-4} M, I = 2.0 M [Na(pts)], λ = 298 nm (except as indicated)

$[H^+]$	$10^2[Cr^{2+}]$	
M		$k_{1obs.}$/s^{-1}
1.50	0.86	0.7
1.50	1.00	1.3
1.50	1.48	2.3
1.50	1.77	2.9
1.50	2.12	4.5
1.50	2.25	5.4
1.50	2.91	7.7
1.50	3.33	10.8
1.50	3.86	13.6
1.95	2.03	8.3*
1.95	2.67	11.8*
1.95	3.04	15.6*

* λ = 360 nm.

Table 3. Variation of the first-order rate constants, $k_{1obs.}$ (25 °C), with $[H^+]$ for the first stage of the reaction of Mo^{V}_2 with Cr^{2+}, $[Cr^{2+}]$ = 0.03 M, $[Mo^{V}_2]$ = (2.0—2.8) × 10^{-4} M, I = 2.0 M [Na(pts)]

λ/nm	$[H^+]$/M	$k_{1obs.}$/s^{-1}
360	0.50	4.8
298	0.57	4.7
360	0.65	6.2
400	0.70	6.6
360	0.85	7.5
400	1.15	9.7
400	1.40	12.5
360	1.60	13.5
400	1.65	14.8
400	1.95	16.1

Table 4. Variation of the first-order rate constants, $k_{2obs.}$ (25 °C), with $[H^+]$ for the second stage of the reaction of Mo^{V}_2 with Cr^{2+}, I = 2.0 M [Na(pts)], λ = 360 nm

$[H^+]$	$10^2[Cr^{2+}]$	$10^3[Mo^{V}_2]$	
	M	M	$10^6k_{2obs.}$/s^{-1}
0.50	2.1	1.2	9.7
0.75	2.3	2.0	15.8
1.00	2.9	1.6	19.9
1.50	3.9	2.1	30.7
1.80	5.4	3.0	36.7
1.93	2.2	1.1	39.1

Cr^{2+} *With* Mo^{V}_2 (2:1).—No kinetic studies were attempted on the first stages complete within 1 min. Decay of the intermediate was monitored at two wavelengths. At 505 nm a single bimolecular process complete in ≈5 h, and at 350 nm a bimolecular process complete in ≈20 h was observed. The first of these is believed to correspond to the reaction of the first intermediate to give Mo^{IV}_3

Excess of Cr^{2+} *with* Mo^{IV}_3.—The reaction is summarised in equations (2) and (3). Stopped-flow studies on (2) monitored at 575 nm, the cross-over point for $Mo^{III,III,IV}$ and Mo^{III}_3, gave an absorbance increase (complete in 0.1 s) followed by a decrease (complete in ≈5 s). The two are sufficiently well separated for most of the range to be studied as two distinct (first-order) processes. Rate constants $k_{3obs.}$ (Table 5) for the first stage are dependent on $[Cr^{2+}]$ and $[H^+]^{-1}$,* and the rate law is therefore as in equation (6). The $[H^+]$ dependence is illustrated in

$$\text{Rate} = k_3[Cr^{2+}][Mo^{IV}_3][H^+]^{-1} \qquad (6)$$

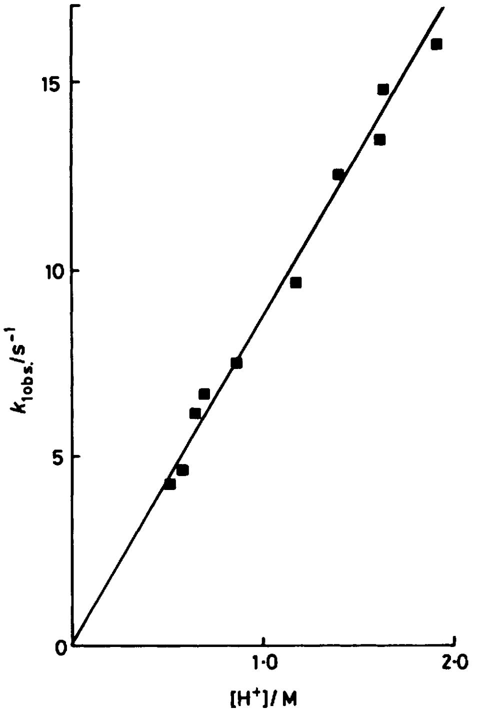

Figure 6. Dependence of first-order rate constants, $k_{1obs.}$ (25 °C), on $[H^+]$ for the first stage (formation of the intermediate) of the Cr^{2+} (0.030 M) reduction of Mo^{V}_2, (2.0—2.8) × 10^{-4} M, I = 2.00 M [Na(pts)]

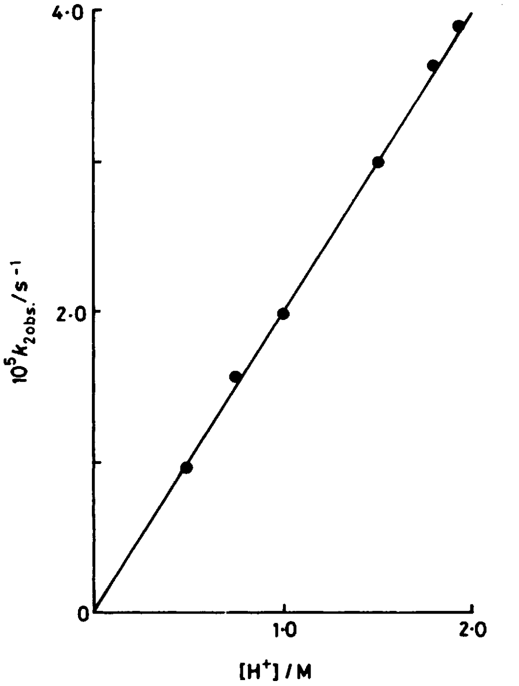

Figure 7. Dependence of first-order rate constants, $k_{2obs.}$ (25 °C), on $[H^+]$ for the second stage (decay of the intermediate) of the Cr^{2+} (2.1—5.4) × 10^{-2} M, reduction of Mo^{V}_2, (1.1—3.0) × 10^{-3} M, I = 2.00 M [Na(pts)]

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* An alternative $[H^+]$ dependence of the form $a + b[H^+]^{-2}$ is consistent with the data obtained, but seems less likely in view of the absence of an $[H^+]^{-1}$ contribution alongside the a and b terms.

Table 5. Rate constants $k_{3obs.}$ and $k_{4obs.}$ for the first and second stages (respectively) of the reduction of Mo^{IV}_3 by Cr^{2+}, $[Mo^{IV}_3] = 5 \times 10^{-4}$ M, $I = 2.0$ M [Na(pts)], $\lambda = 575$ nm

$10^2[Cr^{2+}]$	$[H^+]$	$k_{3obs.}$	$k_{4obs.}$
M		s^{-1}	
1.5	1.00	110	3.0
1.5	1.25	82	2.5
1.5	1.50	64	2.1
1.5	1.75	56	1.8
2.0	1.50	86	1.5
2.5	1.50	109	1.2
2.8	1.60		1.1

Figure 8. From a least-squares treatment $k_3 = (64 \pm 3) \times 10^2$ s^{-1} at 25 °C, $I = 2.00$ M [Na(pts)]. Rate constants $k_{4obs.}$ for the second stage (Table 5) also give an $[H^+]^{-1}$ dependence, with no meaningful dependence on $[Cr^{2+}]$. Since at $[H^+] < 4.0$ M, $Mo^{III,III,IV}$ is known to disproportionate to an equilibrium mixture as in equation (7),[5] we did not further investigate this or the reduction of $Mo^{III,III,IV}$ to Mo^{III}_3.

$$3Mo^{III,III,IV} \longrightarrow 2Mo^{III}_3 + Mo^{IV}_3 \qquad (7)$$

Discussion

At least two intermediates, Cr:Mo ratios 1:1 and 2:1, are formed in the Cr^{2+} reduction of Mo^V_2. Both are strongly held by Dowex (X2) columns indicating high charge, and are sufficiently long-lived to enable separation on Sephadex columns. Such column separations are not easy to carry out in the presence of Cr^{2+}, and require rigorous air-free conditions to limit formation of Cr^{III}_2, which is eluted at a similar rate to the intermediates. In the case of the Cr^{2+} excess runs we were unable to avoid some Cr^{III}_2 contamination. The most meaningful analyses were for the $Cr^{2+}:Mo^V_2$ experiments with 2:1 ratio of reactants. Although not completely separated on a 90-cm column two distinct fractions were obtained, the one green with Cr:Mo ratio 1:1 and the other grey-green with Cr:Mo ratio 2:1. The spectra of these two forms are indicated in Figure 3. In further experiments we attempted to explore the decay of these intermediates and reactions with Mo^V_2, but observed the formation of brown products of uncertain composition. It would appear that, over long time intervals in the absence of excess of Cr^{2+} (which serves to scavenge O_2), reactions of the intermediates with traces of O_2 impurity occur.

Although inner-sphere reductions by Cr^{2+} give products with substitution-inert Cr^{III} attached, the nature of the ligands involved and associated thermodynamic stabilities will determine whether the Cr^{III} is retained over long periods. Examples to note are the Cr^{2+} reductions of $[IrCl_6]^{2-}$ and $[Co(NH_3)_5(pfb)]^{2+}$ (in the latter case *p*-formylbenzoate is co-ordinated *via* the carboxylate, and the Cr^{2+} attacks the formyl group). In both reactions (at 25 °C) loss of Cr^{III} from the product occurs within a few minutes of formation.[20,21] We have no evidence in the studies here described for outer-sphere Cr^{2+} reduction, which is much less common and would give $[Cr(H_2O)_6]^{3+}$ directly as product.[22]

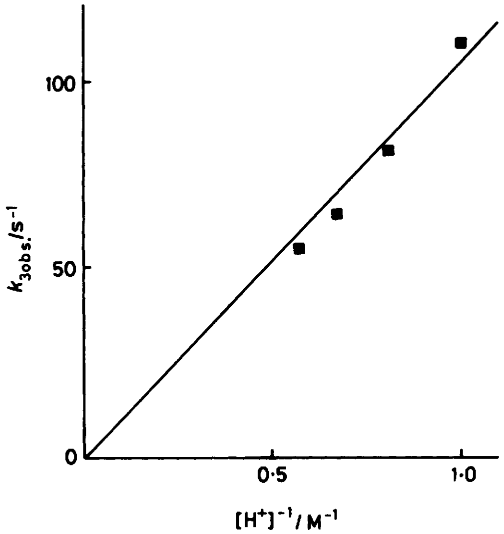
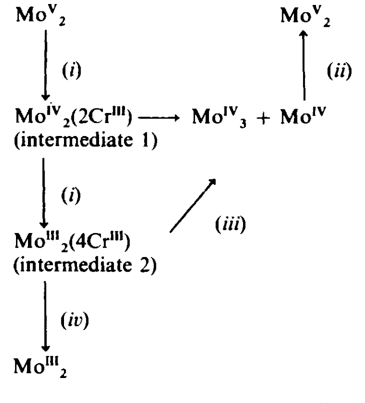


Figure 8. Dependence of first-order rate constants, $k_{3obs.}$ (25 °C), on $[H^+]$ for the first stage of the reduction of Mo^{IV}_3 (5.0×10^{-4} M) with Cr^{2+} (0.015 M), $I = 2.0$ M [Na(pts)]

The rate law (4) for the first stage of the reduction of Mo^V_2 with excess of Cr^{2+} is dependent on $[Cr^{2+}]^2$ and $[H^+]$. Therefore Mo^V_2 appears to be reduced to at least the Mo^{IV}_2 state. The grey-green intermediate generated in this process has the u.v.–visible spectrum of the 2:1 Cr:Mo product, suggesting further rapid reduction within the first phase of reaction (< 1 min) to the Mo^{III}_2 state. The product has a peak at 360 nm (ε 639 M^{-1} cm^{-1} per Mo), Figure 1, which is similar to that of the Mo^{III}_2, (C), peak at 360 nm (ε 455 M^{-1} cm^{-1} per Mo). The rate law for the slow conversion of this intermediate to a product having the Mo^{III}_2 spectrum gives a first-order $[H^+]$ dependence, consistent with proton-induced aquation of Cr^{III} at a μ-hydroxo (or μ-oxo) bridge. We were not able to ascertain how aquation of the other Cr^{III}'s takes place, and it is possible that this is in a statistical manner. Contributions of Cr^{III} to the spectrum are relatively small, and it is possible that some Cr^{III} remains attached and is not detectable in the final spectra.

For the experiments with 2:1 Cr^{2+} to Mo^V_2 an intermediate with a 1:1 Cr:Mo ratio has been identified. This suggests a product incorporating Mo^{IV}_2, although the absorption spectrum has no features which clearly support this rather than $Mo^{III,V}$, or some other combination of oxidation states in which the Cr is not necessarily in the III state. We believe this intermediate to be precursor of the 2:1 Cr:Mo intermediate, and the reaction Scheme shown is tentatively suggested. In this Scheme bimolecular decay of the first intermediate to give Mo^{IV}_3 is indicated. Such a process would lead to the formation of highly reactive monomeric Mo^{IV} which would be oxidised with either solvent water or traces of O_2 to give Mo^V_2, thus giving a maximum 75% yield of Mo^{IV}_3 as product along with Mo^V_2. A second stage in which Mo^V_2 reacts with the second intermediate to give (eventually) Mo^{IV}_3 is also possible although the evidence here is less well founded.



Scheme. (*i*) Cr^{2+}; (*ii*) O_2 or solvent water; (*iii*) Mo^V_2 (?); (*iv*) H^+

The rate law (4) obtained for the first stage of reaction with a large excess of Cr^{2+} provides further information. There are three possible sites on Mo^{V}_2 for inner-sphere Cr^{2+} reduction. Reaction at an H_2O is unlikely without an $[H^+]^{-1}$ dependence which is not observed. Also the bridging oxo ligands are unlikely sites because of their inaccessibility. Therefore the most likely site for Cr^{2+} attack is a terminal oxo ligand. The $[Cr^{2+}]^2$ dependence suggests that a single Cr^{2+} is not sufficiently strong to reduce Mo^{V}_2, and that the presence of a second Cr^{2+} is essential. Involvement of $[H^+]$ in the rate law indicates that one of the oxo groups which the Cr^{2+} attacks becomes protonated. The reaction sequence is accordingly as in (8) and (9) where the product (8) is believed to be with Cr^{2+} bound to Mo^{V}_2. The rate constant k_1 in (4) is equal to kK here defined. The product from two inner-sphere reductions will have a composition Mo^{IV}_2-Cr^{III}_2. Subsequently, rapid reduction by two further moles of Cr^{2+} is required to give an intermediate in the Mo^{III}_2 state. The high positive charge implied by the Cr:Mo ratio is consistent with the difficulty experienced in eluting the intermediate from Dowex columns.

$$Cr^{2+} + Mo^{V}_2 \overset{K}{\rightleftharpoons} Mo^{V}Cr^{II} \qquad (8)$$

$$Cr^{2+} + Mo^{V}_2Cr^{II} + H^+ \xrightarrow{k} \text{products} \qquad (9)$$

The kinetic law (6) for the first stage of the Cr^{2+} reduction of Mo^{IV}_3, with dependences on $[Cr^{2+}]$ and $[H^+]^{-1}$, is assigned to an inner-sphere process involving Cr^{2+} attack of a conjugate-base form of Mo^{IV}_3 obtained by acid dissociation of an H_2O ligand.[23] The nature of the second stopped-flow stage leading to $Mo^{III,III,IV}$ formation is uncertain. This study is complicated by the tendency of $Mo^{III,III,IV}$ to disproportionate at $[H^+] < 4.0$ M to Mo^{III}_3 and Mo^{IV}_3, with $<30\%$ $Mo^{III,III,IV}$ remaining at $[H^+] < 0.5$ M.[5] The other mixed-valence form $Mo^{III,IV,IV}$ has yet to be identified.

To summarise, it has been demonstrated that > 10-fold excess of Cr^{2+} reduces Mo^{V}_2 through to Mo^{III}_2 *via* a long-lived Cr-containing intermediate, Cr:Mo ratio of 2:1. With a 2:1 ratio of $Cr^{2+}:Mo^{V}_2$ two intermediates have been identified, and after $\approx$22 h 60—70% formation of Mo^{IV}_3 is observed. On further addition of Cr^{2+} the Mo^{IV}_3 is reduced to Mo^{III}_3. Thus, depending on whether the excess of Cr^{2+} is added in one or two amounts, the product obtained can be Mo^{III}_2 or Mo^{III}_3. Formation of Mo^{IV}_3 is particularly noteworthy since the oxidations of $[Mo(H_2O)_6]^{3+}$ and Mo^{III}_2, with *e.g.* $[IrCl_6]^{2-}$, proceed through to Mo^{V}_2 without detection of any Mo^{IV}_3. Similarly with O_2 as oxidant Mo^{V}_2 is obtained, although here it has been noted that when O_2 is bubbled through high concentrations of $[Mo(H_2O)_6]^{3+}$ (2.3×10^{-2} M) 10% of Mo^{IV}_3 is obtained.[9]

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