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Kinetic Studies on the Reactions of the Molybdenum(V)–Aquo Dimer, $Mo_2O_4^{2+}$, with $IrCl_6^{2-}$, $Fe(phen)_3^{3+}$, and Other Oxidants

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Details of the kinetics of the oxidation of the molybdenum(V)–aquo dimer, $Mo_2O_4^{2+}$, to Mo(VI) with $IrCl_6^{2-}$ and $Fe(phen)_3^{3+}$ have been investigated, at $I = 1.00$ M ($LiClO_4$). With $IrCl_6^{2-}$ as oxidant the rate law rate $= k_1[Mo_2O_4^{2+}][H^+]^{-1} + (k_2 + k_3[H^+]^{-1})[Mo_2O_4^{2+}][IrCl_6^{2-}]$ has been established at 25 °C for a wide range of reactant concentrations, $[H^+] = 0.02$–1.00 M. Rate constants are $k_1 = 2.95 \times 10^{-6}$ M s^{-1}, $k_2 = 0.114$ M^{-1} s^{-1}, and $k_3 = 0.052$ s^{-1}. The same rate law applies with $Fe(phen)_3^{3+}$ as oxidant when rate constants and activation parameters (ΔH^*, kcal mol^{-1}; ΔS^*, cal K^{-1} mol^{-1}) for the corresponding pathways are $k_4 = 3.09 \times 10^{-6}$ M s^{-1} (17.6, −24.9), $k_5 = 31.0$ M^{-1} s^{-1} (8.9, −21.7), and $k_6 = 6.0$ s^{-1} (10.9, −18.4). Agreement of data for the oxidant-independent pathways k_1 and k_4 suggests that the same rate-determining process is involved. This is believed to involve oxo-bridge cleavage, where the only detectable route involves a conjugate-base form of $Mo_2O_4^{2+}$. The reactions with I_3^-, NO_3^-, and $PtCl_6^{2-}$ as oxidants are very much slower and were only briefly studied. The results obtained support a pattern of redox behavior in which monomeric Mo(V) species are more reactive than dimeric Mo(V).

The molybdenum(V)–aquo ion has been characterized as a dimeric di-μ-oxo species, $Mo_2O_4^{2+}$, with two terminal oxo groups.[1,2] A study of the 1:1 equilibration with NCS^- has yielded information regarding the substitution lability of the H_2O ligands.[3] Kinetic studies on the $IrCl_6^{2-}$ and $Fe(phen)_3^{3+}$ oxidation of $Mo_2O_4(edta)^{2-}$ (where edta is ethylenediaminetetraacetate) have recently been carried out[4] and provide evidence for the involvement of a Mo(V,VI) dimer as a kinetically significant intermediate. The rate laws now obtained for the aquo ion $Mo_2O_4^{2+}$ are of an entirely different form. Moreover earlier studies on redox reactions of the molybdenum(V)–aquo ion with I_3^- and NO_3^- were carried out in phosphate and tartrate buffers, respectively,[5,6] which appear to interact with the Mo(V). The present studies were carried out in noncomplexing perchlorate media using a higher range of hydrogen ion concentrations, $[H^+] > 0.02$ M.

Experimental Section

Reactants. The molybdenum(V)–aquo dimer $Mo_2O_4^{2+}$ was prepared by three different methods. These involved aquation of the pyridinium pentachlorooxomolybdate(V) complex $[PyH]_2[MoOCl_5]$ in 0.05 M perchloric acid,[3] the reduction of sodium molybdate in 10 M HCl with hydrazine hydrochloride at 80 °C for 2–3 h,[7] and reaction of sodium molybdate with potassium hexachloromolybdate(III). Ion-exchange procedures[3,7] were used to remove chloride and pyridinium ions and yielded stock solutions where typically $[Mo_2O_4^{2+}] = 7 \times 10^{-3}$ M in $[HClO_4] = 0.5$ M. All such solutions were stored under nitrogen or argon. The reagents $Fe(phen)_3^{3+}$ and $Fe(phen)_3^{2+}$ (both as perchlorate salts), $IrCl_6^{2-}$ and $IrCl_6^{3-}$ (both as sodium salts), $HClO_4$, and $LiClO_4$ were as used previously.[4] AnalaR $NaNO_3$ and $Na_2MoO_4 \cdot 2H_2O$ and K_2PtCl_6 (Johnson Matthey) were used without further purification. Iodine was purified by sublimation.

Preparation of Solutions. Standard Atlas nylon syringes, Teflon (plastic) and stainless steel syringe needles, and rubber serum caps were used to prepare solutions under N_2 or Ar gas. Stock solutions of $Fe(phen)_3^{3+}$ were prepared freshly each day by dissolving the perchlorate salt in 5 M $HClO_4$ and storing at 0 °C. Solutions of $IrCl_6^{2-}$ (and $PtCl_6^{2-}$) were also prepared each day. It was necessary to use Teflon and not stainless steel needles to transfer the latter solutions. Aquation of $IrCl_6^{2-}$ was negligible over 3–4-h periods at 25 °C. All I_2 solutions were made up in NaI (final concentration 0.1 M), thus converting the I_2 into I_3^-; $K = [I_3^-]/[I_2][I^-] = 782$ M^{-1}.[8] Iodine solutions were made up in a glovebag in an atmosphere of N_2, and spectrophotometric cells were completely filled (plastic stoppers) to avoid sublimation of I_2. All reactant solutions were made up to ionic strength 1.0 M with $LiClO_4$.

Stability of $Mo_2O_4^{2+}$. Stock solutions were kept for periods of up to 2 weeks. Solutions of $Mo_2O_4^{2+}$ (ca. 10^{-4} M) at $[H^+] = 0.012$ M were stable for >8 h. Variations in $[H^+]$ from 0.01 to 1.00 M had no measurable effect on the UV–visible spectrum and an acid dissociation constant $<10^{-2}$ M is indicated. A yellow to orange color change was observed at $[H^+] = 5 \times 10^{-3}$ M followed by precipitation. It was observed that addition of 0.1–0.5 M phosphate, at $[H^+] = 5 \times 10^{-2}$–10^{-3} M, produces spectrophotometric changes and prevents precipitation and that spectrophotometric changes occur with 0.1 M tartrate, at $[H^+] =$ ca. 2×10^{-3} M.

Stoichiometries and Products. Stoichiometries were determined for the $IrCl_6^{2-}$ and $Fe(phen)_3^{3+}$ oxidations by spectrophotometric determination of reactants and products in the UV–visible range. Relevant peak positions and absorption coefficients (λ, nm; ϵ, M^{-1} cm^{-1}) as used here and elsewhere are as follows: $Mo_2O_4^{2+}$, 295, 3546; $IrCl_6^{2-}$, 487, 4075; $Fe(phen)_3^{3+}$, 355, 5200; 510, ca. 300; $Fe(phen)_3^{2+}$, 510, 1.11×10^4. Details of spectra of $IrCl_6^{3-}$ [9] and Mo(VI)[10,11] (absorbances not relevant at wavelengths used) have also been reported. The reactions conform to eq 1 and 2. The Ir(III) product has been

$$Mo^V_2 + 2Ir^{IV} \rightarrow 2Mo^{VI} + 2Ir^{III} \quad (1)$$

$$Mo^V_2 + 2Fe^{III} \rightarrow 2Mo^{VI} + 2Fe^{II} \quad (2)$$

shown to be $IrCl_6^{3-}$ (>90%) and not $IrCl_5H_2O^{2-}$ by reoxidation with Cl_2. It has been demonstrated previously that the Ir(III) coordination sphere is retained in the Ir(IV) product.[12] Spectra of $IrCl_6^{2-}$ and $IrCl_5H_2O^-$ differ significantly and allow a clear-cut distinction to be made.[9] Reactant concentrations and therefore reaction time for the $Fe(phen)_3^{3+}$ oxidation were adjusted so that aquation of $Fe(phen)_3^{2+}$ and the Fe^{2+}-catalyzed aquation of $Fe(phen)_3^{3+}$ were negligible.[13] Samples of $Fe(phen)_3^{3+}$ contained varying amounts of $Fe(phen)_3^{2+}$ (<30%).

Kinetics. For runs with $IrCl_6^{2-}$ reactant in large (>10-fold) excess the $Mo_2O_4^{2+}$ absorbance was monitored at wavelengths in the 295–325-nm range. Plots of absorbance change log $(A_t - A_\infty)$ against time were linear to >85% completion. From the slope (×2.303) rate constants k_{obsd} were obtained. With $Mo_2O_4^{2+}$ in large excess the $IrCl_6^{2-}$ was monitored at the 487-nm peak. The oxidation with $Fe(phen)_3^{3+}$ was monitored at the 510-nm peak for the $Fe(phen)_3^{2+}$ product, and with I_3^- as oxidant it was monitored at the I_3^- peak at 353 nm (ϵ 26 400 M^{-1} cm^{-1}). The $Mo_2O_4^{2+}$ peak at 384 nm (ϵ 103 M^{-1} cm^{-1}) was used for the NO_3^- oxidation, and with $PtCl_6^{2-}$ the 454-nm peak of the latter (ϵ 48 M^{-1} cm^{-1}) was used.

Results

Oxidation with $IrCl_6^{2-}$. The shape of absorbance against time traces for runs with excess $Mo_2O_4^{2+}$ (Unicam SP8000 spectrophotometer), in particular the abrupt cutoff in absorbance changes, Figure 1, suggests a mixed zero- and first-order dependence on $[IrCl_6^{2-}]$. A rate law of the form (3) was tested by carrying out an unweighted least-squares

$$-d[IrCl_6^{2-}]/2dt = k_0[Mo_2O_4^{2+}] + k_{Ir}[Mo_2O_4^{2+}][IrCl_6^{2-}] \quad (3)$$

fit of absorbance–time data to the integrated equation (4)

$$\ln \{(k_0/k_{Ir}) + [IrCl_6^{2-}]_t\} = -2[Mo_2O_4^{2+}]k_{Ir}t + \text{constant} \quad (4)$$

which can be written as (5), where $[IrCl_6^{2-}]_t$ is given by

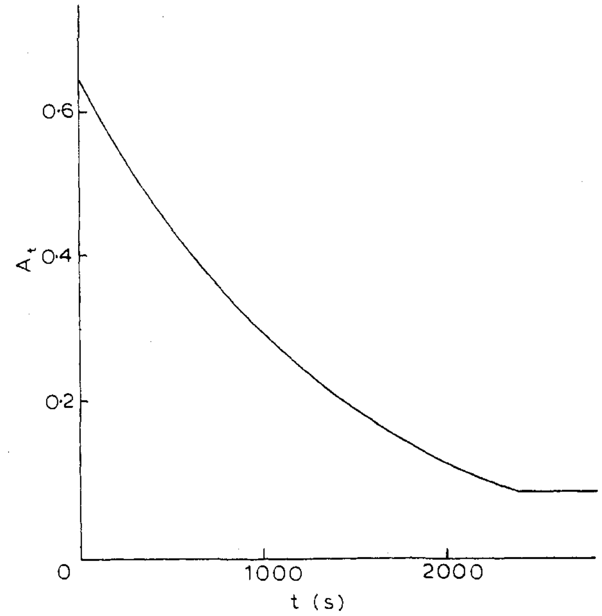

Figure 1. Absorbance changes at 487 nm (1-cm cell, no cell correction applied), for the $IrCl_6^{2-}$ (1.41×10^{-4} M) oxidation of $Mo_2O_4^{2+}$ (6.0×10^{-4} M) at 25 °C, $[H^+] = 0.13$ M, and $I = 1.00$ M ($LiClO_4$). The shape of the curve (in particular the abrupt cessation of reaction) indicates contributions from a path zero order in oxidant.

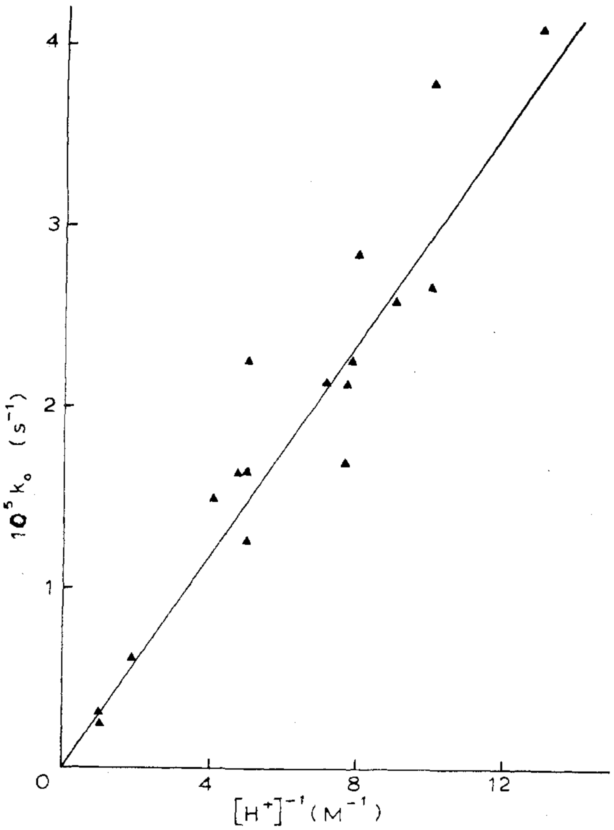

Figure 2. Dependence of k_0 on $[H^+]^{-1}$ for the $IrCl_6^{2-}$ oxidation of $Mo_2O_4^{2+}$, with $Mo_2O_4^{2+}$ in large excess, at 25 °C and $I = 1.00$ M ($LiClO_4$).

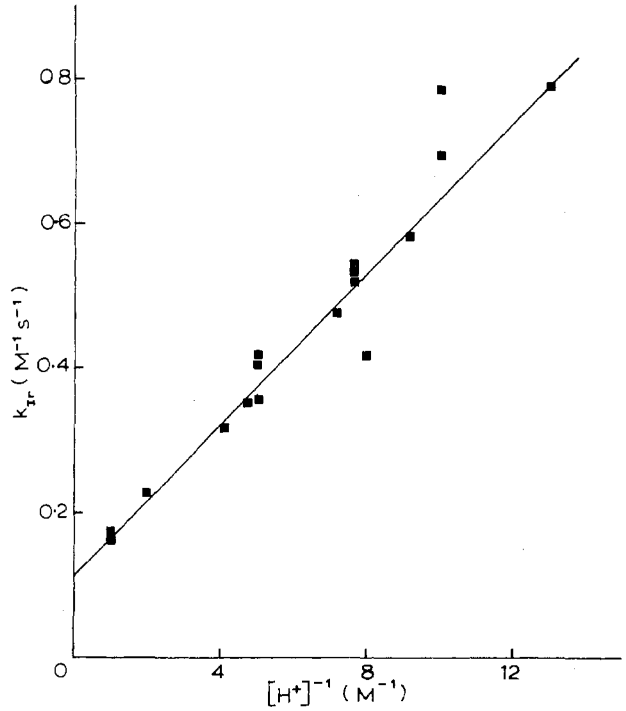

Figure 3. Dependence of k_{Ir} on $[H^+]^{-1}$ for the $IrCl_6^{2-}$ oxidation of $Mo_2O_4^{2+}$, with $Mo_2O_4^{2+}$ in large excess, at 25 °C and $I = 1.00$ M ($LiClO_4$).

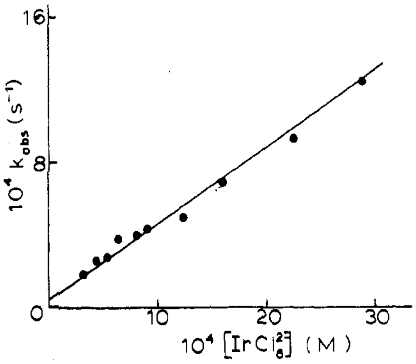

Figure 4. Dependence of k_{obsd} on $[IrCl_6^{2-}]$ for the oxidation of $Mo_2O_4^{2+}$ with $IrCl_6^{2-}$, the latter in large excess, at 25 °C and $I = 1.00$ M ($LiClO_4$).

$$[IrCl_6^{2-}]_t = \{(k_0/k_{Ir}) + [IrCl_6^{2-}]_0\} \exp(-2[Mo_2O_4^{2+}]k_{Ir}t) - (k_0/k_{Ir}) \qquad (5)$$

absorbance changes $(A_t - A_\infty)/\Delta\epsilon$. With $Mo_2O_4^{2+}$ in large excess, concentrations $(0.54–4.94) \times 10^{-3}$ M, a good fit to (5) was obtained.[14] Values of k_0 and k_{Ir} are listed in Table I.[15] The $[H^+]^{-1}$ dependences of k_0 and k_{Ir}, $[H^+] = 0.077–1.00$ M, Figures 2 and 3, respectively, indicate a full rate law dependence (6). At 25 °C and $I = 1.00$ M ($LiClO_4$), rate

$$-d[IrCl_6^{2-}]/2dt = k_1[Mo_2O_4^{2+}][H^+]^{-1} + (k_2 + k_3[H^+]^{-1})[Mo_2O_4^{2+}][IrCl_6^{2-}] \qquad (6)$$

constants obtained are $k_1 = (2.95 \pm 0.13) \times 10^{-6}$ M s^{-1}, $k_2 = 0.114 \pm 0.012$ M^{-1} s^{-1}, and $k_3 = 0.052 \pm 0.003$ s^{-1}.

For runs with Ir(IV) in large excess rate constants k_{obsd}, Table II,[15] were evaluated from first-order plots. A linear dependence on $[IrCl_6^{2-}]$ with small contributions from an oxidant-independent path are clearly indicated from a graph of k_{obsd} against $[IrCl_6^{2-}]$, Figure 4. From these data $k_1 = (7.5 \pm 3.4) \times 10^{-6}$ M s^{-1}, $k_2 = 0.19 \pm 0.04$ M^{-1} s^{-1}, and $k_3 = 0.047 \pm 0.007$ s^{-1}. Agreement with rate constants as determined above is satisfactory bearing in mind that with Ir(IV) in excess k_1 contributes less and therefore becomes less precise.

Runs with and without addition of a 20-fold excess of $IrCl_6^{3-}$ (over $IrCl_6^{2-}$) gave identical kinetic behavior, with $[Mo_2O_4^{2+}]$

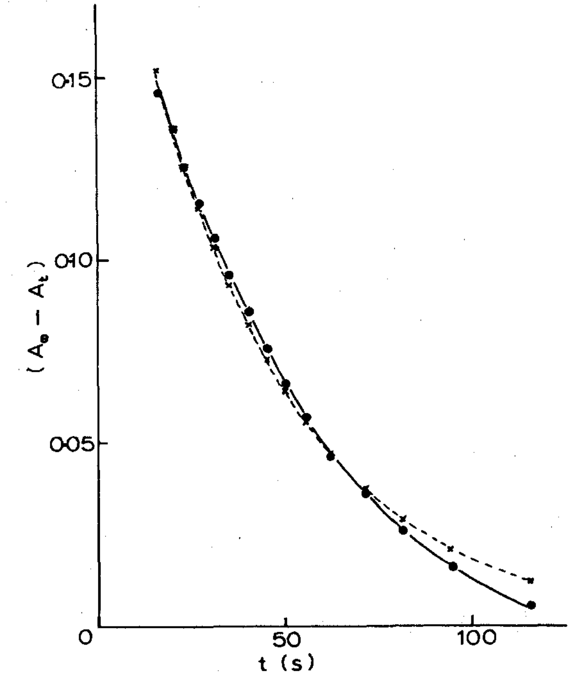

Figure 5. Absorbance differences $A_\infty - A_t$ at 510 nm (Fe(phen)$_3^{2+}$ peak), for the Fe(phen)$_3^{3+}$ ((5.3 ± 0.2) × 10^{-6} M) oxidation of $Mo_2O_4^{2+}$ (9.02 × 10^{-5} M) at 30 °C. The closed circles are the experimental points where the solid line is the best fit assuming terms zero order (k_0 = 5.15 × 10^{-5} s^{-1}) and first order (k_{Fe} = 113 ± 3.6 M^{-1} s^{-1}) in oxidant are effective. Comparative points (×) indicate the best fit if only k_{Fe} (145 ± 4.2 M^{-1} s^{-1}) is effective; [H$^+$] = 0.1 M.

= 5.8 × 10^{-4} M, [IrCl$_6^{2-}$] = 3 × 10^{-5}, and [H$^+$] = 0.10 M. The reaction is however catalyzed by addition of molybdenum(VI) which under the conditions of [H$^+$] investigated is present predominantly as monomer and dimer forms.[10,11] The effect of Mo(VI) was investigated at [H$^+$] = 0.125 M with concentrations (0.68–3.42) × 10^{-3} M in large excess over the Mo(VI) built up in runs listed in Table I. Two runs were also carried out at [H$^+$] = 0.276 M. It was not possible to decrease [H$^+$] and increase Mo(VI) concentrations due to the formation of molybdenum blue. Analysis of data ($Mo_2O_4^{2+}$ in excess) was carried out as for runs without added Mo(VI), where k_0 and k_{Ir} are given in Table III.[15] By assuming a monomer–dimer equilibrium constant of K = 55 M^{-1} to apply for Mo(VI),[11] a pattern of behavior emerges in which the k_0 catalytic pathway appears to be dependent on concentration of dimer (rate constant ca. 0.13 M^{-1} s^{-1}) and the k_{Ir} catalytic pathway appears to depend on concentration of monomer (rate constant ca. 1.39 × 10^3 M^{-2} s^{-1}). Both catalytic pathways are retarded by increasing [H$^+$]. It is concluded from these studies that the effect of Mo(VI) generated during the reaction is small and makes <7% contribution for comparable runs in Table I.

Oxidation with Fe(phen)$_3^{3+}$. A large excess of $Mo_2O_4^{2+}$, (4.2–18) × 10^{-5} M, was used in all runs. The need for the k_0 term was not at first apparent since plots of log ($A_\infty - A_t$) against time were linear to ca. 65% reaction. However without contribution from k_0 there was an obvious anomaly in our interpretation (namely why should the oxidant-independent path k_0 not contribute when k_{Fe} is not sufficiently big to exclude contributions?), and computer fitting to an equation of the form (5) was again carried out. Figure 5 illustrates the fit of experimental data points to different calculated (rate law) dependences. Because of the small contributions of k_0 the imprecision of these values is quite large. The hydrogen ion concentration was varied from 0.10 to 1.00 M and the temperature was varied from 15 to 30 °C. Rate constants k_0 and k_{Fe}, as defined by an equation of the same form as (3), were obtained by computer fit of absorbance–time data to (5). Both k_0 and k_{Fe} were allowed to float initially. The hydrogen ion dependences of k_0 and of k_{Fe}, Figure 6, were as before and the full rate law is (7). The rate constant k_4 = 3.09 × 10^{-6}

$$d[Fe(phen)_3^{2+}]/2dt = k_4[Mo_2O_4^{2+}][H^+]^{-1} + (k_5 + k_6[H^+]^{-1})[Mo_2O_4^{2+}][Fe(phen)_3^{3+}] \qquad (7)$$

M s^{-1} at 25 °C and I = 1.00 M (LiClO$_4$) is in excellent agreement with k_1 from the IrCl$_6^{2-}$ investigation, with $\Delta H_4^{\ddagger}$ = 17.6 ± 2.8 kcal mol^{-1} and $\Delta S_4^{\ddagger}$ = −24.9 ± 9.3 cal K^{-1} mol^{-1}. Using fixed k_0 values as obtained from these parameters, k_{Fe} values, as in Table IV,[15] were recomputed. Kinetic parameters derived from k_{Fe} are k_5 = 31.0 M^{-1} s^{-1}, $\Delta H_5^{\ddagger}$ = 8.9 ± 1.1 kcal mol^{-1}, $\Delta S_5^{\ddagger}$ = −21.7 ± 3.8 cal K^{-1} mol^{-1}, and k_6 = 6.0 s^{-1}, $\Delta H_6^{\ddagger}$ = 10.9 ± 1.3 kcal mol^{-1}, $\Delta S_6^{\ddagger}$ = −18.4 ± 4.5 cal K^{-1} mol^{-1}. Addition of an ca. 10-fold excess of Fe(phen)$_3^{2+}$ had no effect on the rate.

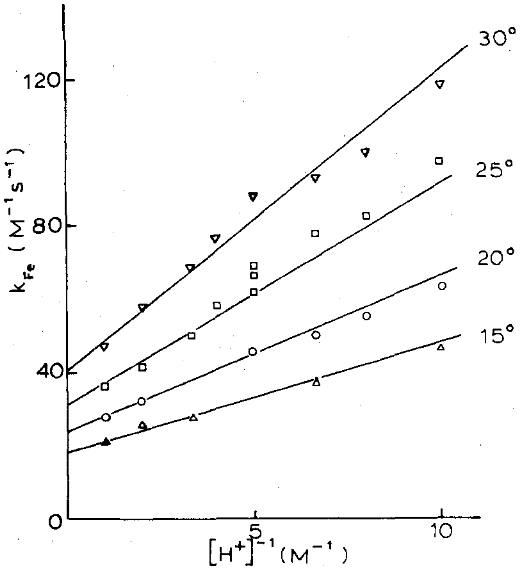

Figure 6. Dependence of k_{Fe} on [H$^+$]$^{-1}$ for the Fe(phen)$_3^{3+}$ oxidation of $Mo_2O_4^{2+}$ at 15–30 °C and I = 1.00 M (LiClO$_4$).

Other Oxidants. The reaction with I_3^- is slower than with IrCl$_6^{2-}$ but otherwise exhibits similar features. The precise form of the rate law was not established. For concentrations [$Mo_2O_4^{2+}$] = 5 × 10^{-4} M, [I_3^-] = 3 × 10^{-5} M, and [H$^+$] = 0.05 M, ca. 20 h was required for completion of the reaction at 25 °C.

With nitrate as oxidant at 25 °C, [H$^+$] = 0.06 M, and [NO_3^-] = 0.01 and 0.05 M, 18% and 37% reaction, respectively, are observed over a 20-h period. Assuming a rate law of the form [$Mo_2O_4^{2+}$][NO_3^-]/[H$^+$] (and NO_2^- to be the product), we find rate constants are in the range (3–8) × 10^{-6} s^{-1}. The reaction with PtCl$_6^{2-}$ was similarly slow.

Discussion

The kinetics of the oxidations of $Mo_2O_4^{2+}$ with IrCl$_6^{2-}$ and Fe(phen)$_3^{3+}$ conform to the rate laws (6) and (7), and no retardation is observed on addition of products IrCl$_6^{3-}$ and Fe(phen)$_3^{2+}$. Rate laws for the IrCl$_6^{2-}$ and Fe(phen)$_3^{3+}$ oxidations of Mo_2O_4(edta)$^{2-}$ are of an entirely different form, the reactions exhibiting a marked retardation by products IrCl$_6^{3-}$ and Fe(phen)$_3^{2+}$, respectively. The edta is believed to hold together the Mo(V,VI) dimer for a sufficient length of time to make it a kinetically significant intermediate. The inference with $Mo_2O_4^{2+}$ is that there is rapid dissociation of Mo(V,VI), and that the reaction sequence is as in (8)–(10).

$$\mathrm{Mo^{V}}_2 + \mathrm{Ir^{IV}} \rightarrow \mathrm{Mo^{V,VI}} + \mathrm{Ir^{III}} \tag{8}$$

$$\mathrm{Mo^{V,VI}} \xrightarrow{\text{rapid}} \mathrm{Mo^{V}} + \mathrm{Mo^{VI}} \tag{9}$$

$$\mathrm{Mo^{V}} + \mathrm{Ir^{IV}} \xrightarrow{\text{rapid}} \mathrm{Mo^{VI}} + \mathrm{Ir^{III}} \tag{10}$$

Alternatively (8) may be followed by Ir(IV) oxidation of Mo(V,VI). A similar mechanism applies with $\mathrm{Fe(phen)_3}^{3+}$ as oxidant. We are uncertain as to the origin of the Mo(VI) catalysis but have quantified this effect sufficiently to be able to conclude that it does not represent a major contributing pathway in the absence of added Mo(VI).

Second-order rate constants k_{Ir} and k_{Fe} both exhibit hydrogen ion dependences of the form $a + b[\mathrm{H^+}]^{-1}$. The $[\mathrm{H^+}]^{-1}$-dependent paths cannot in this case be of the inner-sphere type with $\mathrm{OH^-}$ bridging because of the substitution inertness of both oxidants. Rather, they represent favorable pathways (involving a conjugate-base form of $\mathrm{Mo_2O_4}^{2+}$), which are the consequences of the Mo(VI) product being more extensively hydrolyzed. The ratio of rate constants ($\mathrm{Fe(phen)_3}^{3+}$:$\mathrm{IrCl_6}^{2-}$) for the a term (k_5/k_2) is 272 and for b (k_6/k_3) is 116, whereas the corresponding ratio for the oxidation of $\mathrm{Mo_2O_4(edta)}^{2-}$ (no $[\mathrm{H^+}]$ dependence is observed) is 288. All reactions of $\mathrm{Fe(phen)_3}^{3+}$ must be outer sphere. An inner-sphere pathway seems unlikely for the $\mathrm{IrCl_6}^{2-}$ oxidation of $\mathrm{Mo_2O_4(edta)}^{2-}$, and in view of the similarity of the above ratios it seems likely that $\mathrm{IrCl_6}^{2-}$ oxidation of $\mathrm{Mo_2O_4}^{2+}$ is also outer sphere. On electrostatic grounds the ratios for the oxidation of the aquo dimer might have been expected to favor more $\mathrm{IrCl_6}^{2-}$ over $\mathrm{Fe(phen)_3}^{3+}$. A trend favoring $\mathrm{IrCl_6}^{2-}$ is also expected if the $\mathrm{IrCl_6}^{2-}$ oxidation of $\mathrm{Mo_2O_4}^{2+}$ makes use of an inner-sphere pathway.

An important feature of the $\mathrm{Mo_2O_4}^{2+}$ reactions is the existence of an oxidant-independent term, where this exhibits a $[\mathrm{H^+}]^{-1}$ dependence as the only effective pathway. Rate constants k_1 for $\mathrm{IrCl_6}^{2-}$ (2.95×10^{-6} M s^{-1}) and k_4 for $\mathrm{Fe(phen)_3}^{3+}$ (3.09×10^{-6} M s^{-1}) are in excellent agreement at 25.0 °C and indicate a common process. This we believe corresponds to oxo-bridge cleavage, where a $[\mathrm{H^+}]^{-1}$ rather than a direct $[\mathrm{H^+}]$ dependence is somewhat surprising. The $[\mathrm{H^+}]^{-1}$ dependence implicates the conjugate-base form of $\mathrm{Mo_2O_4}^{2+}$, resulting from acid dissociation of an aquo ligand. It is not necessary to postulate formation of mononuclear Mo(V) for reaction by k_1 and k_4, and were such a path effective, $\mathrm{NO_3}^-$ might be expected to take advantage of it. This is not apparent from the data presented where whatever rate law is assumed for $\mathrm{NO_3}^-$ the reaction is unusually slow. It is possible that the single-bridge μ-oxo ion $\mathrm{Mo_2O_3}^{4+}$ (a species which has not as yet been identified) is formed. Whether this is itself more reactive than $\mathrm{Mo_2O_4}^{2+}$ with $\mathrm{IrCl_6}^{2-}$ and $\mathrm{Fe(phen)_3}^{3+}$ or whether it undergoes rapid disproportionation to Mo(IV) and the Mo(VI) remains to be tested.[16] Under similar conditions the rate constant for the $\mathrm{IrCl_6}^{2-}$ oxidation of the molybdenum(IV)–aquo ion is known to be greater than that for the oxidation of $\mathrm{Mo_2O_4}^{2+}$.[17]

Interestingly, with the μ-superoxo complex $\mathrm{(NH_3)_5Co{-}O_2{-}Co(NH_3)_5}^{5+}$, $[\mathrm{H^+}] = 1.0$ M, only the k_0 term (4.3×10^{-6} M s^{-1} at 25 °C, $I = 2.00$ M, $\Delta H^\ddagger = 18.5 \pm 1.4$ kcal mol^{-1}, $\Delta S^\ddagger = -21 \pm 4.7$ cal K^{-1} mol^{-1}) is observed.[18] The second-order pathway is presumably excluded on electrostatic grounds and by the inaccessibility of the electrons in $\mathrm{Mo_2O_4}^{2+}$ to the μ-$\mathrm{O_2}^-$ group. It would appear that the μ-superoxo complex is only a slightly weaker oxidant (ca. 1.0 V[19]) than $\mathrm{IrCl_6}^{2-}$ (1.017 V) and $\mathrm{Fe(phen)_3}^{3+}$ (1.06 V).[4,20] With stronger oxidants it is possible that the k_0 path will be completely dominated by the second-order rate law terms.

Table V. Summary of Rate Constants and Activation Parameters for $\mathrm{IrCl_6}^{2-}$ and $\mathrm{Fe(phen)_3}^{3+}$ Oxidations of $\mathrm{Mo_2O_4(edta)}^{2-}$ and $\mathrm{Mo_2O_4}^{2+}$ [$I = 1.00$ M ($\mathrm{LiClO_4}$)]

Reactants	k(25 °C), M^{-1} s^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal K^{-1} mol^{-1}
$\mathrm{Mo_2O_4(edta)}^{2-} + \mathrm{IrCl_6}^{2-}$ [a]	6.6	13.3	−10
$\mathrm{Mo_2O_4(edta)}^{2-} + \mathrm{Fe(phen)_3}^{3+}$ [a]	1.9×10^3	16.6	12.2
$\mathrm{Mo_2O_4}^{2+} + \mathrm{Fe(phen)_3}^{3+}$ (k_5)	31	8.9	−21.7
$\mathrm{Mo_2O_4}^{2+} + \mathrm{Fe(phen)_3}^{3+}$ (k_6)	6.0 [b]	10.9	−18.4

[a] Rate constant k_1 as defined in ref 4. [b] Unit s^{-1}.

It has now been demonstrated that the $\mathrm{NO_3}^-$ oxidations of $\mathrm{Mo_2O_4}^{2+}$ and $\mathrm{Mo_2O_4(edta)}^{2-}$ are both extremely slow. When tartrate is added to $\mathrm{Mo_2O_4}^{2+}$, there is ESR evidence for formation of monomeric Mo(V). The kinetic rate law for the reaction with $\mathrm{NO_3}^-$ in tartrate solutions (dependence on $[\mathrm{Mo^V}_2]^{1/2}$, also provides evidence for involvement of monomeric Mo(V) in the rate-determining step.[6] The $\mathrm{NO_3}^-$ oxidation of the monomeric Mo(V) complex $\mathrm{MoOCl_3(OPPh_3)_2}$ in solvent $\mathrm{CH_2Cl_2}$ is also rapid.[21] There is therefore a strong case for monomeric Mo(V) being much more redox active than dimeric Mo(V), and this is also implied in the reaction scheme (8)–(10). It is possible to rationalize this behavior in terms of accessibility of electrons in the monomer as compared to the di-μ-oxo dimers, where the electrons in the latter are localized in the metal–metal bond.

A two-term rate law as for $\mathrm{IrCl_6}^{2-}$ and $\mathrm{Fe(phen)_3}^{3+}$ is probably applicable also in the $\mathrm{I_3}^-$ oxidation of $\mathrm{Mo_2O_4}^{2+}$. Guymon and Spence[5] have previously reported the term zero order in oxidant from their studies in phosphate buffer. An entirely satisfactory fit of data was not obtained in the present study, and stability of the $\mathrm{Mo_2O_4}^{2+}$ over >20-h periods for the low range of $[\mathrm{H^+}]$ investigated, as well as the effect of Mo(VI), is a possible explanation. It is also possible that for a weaker oxidant of this type the k_0 pathway is more complicated with bridge cleavage not being the only rate-determining process. The reaction with $\mathrm{PtCl_6}^{2-}$ is extremely slow. Standard reduction potentials for the $\mathrm{PtCl_6}^{2-}$ (0.68 V) and $\mathrm{I_3}^-/\mathrm{I}^-$ (0.54 V) couples are not too dissimilar.[20] With $\mathrm{PtCl_6}^{2-}$ it is concluded that no favorable one- or two-electron pathway exists.

Finally in Table V a comparison is made of activation parameters for reaction of $\mathrm{Mo_2O_4}^{2+}$ and $\mathrm{Mo_2O_4(edta)}^{2-}$. We note that positive $\Delta S^\ddagger$ values are observed in those cases in which the reactants are oppositely charged, whereas the converse holds for like-charged reactants. These trends are explained by considering solvent electrostriction effects arising from electrostatic interactions. Positive $\Delta S^\ddagger$ values are not a common feature of redox studies.

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Registry No. $\mathrm{Mo_2O_4(edta)}^{2-}$, 23187-54-4; $\mathrm{Mo_2O_4}^{2+}$(aquo), 52757-71-8; $\mathrm{IrCl_6}^{2-}$, 16918-91-5; $\mathrm{Fe(phen)_3}^{3+}$, 13479-49-7; $\mathrm{I_3}^-$, 14900-04-0; $\mathrm{NO_3}^-$, 14797-55-8.

Supplementary Material Available: Tables I–IV giving rate constants for the $\mathrm{IrCl_6}^{2-}$ and $\mathrm{Fe(phen)_3}^{3+}$ oxidations of $\mathrm{Mo_2O_4}^{2+}$ (5 pages). Ordering information is given on any current masthead page.

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Mechanism of the Reversible Oxidation of Vanadium(IV) by Hexachloroiridate(IV)[1]

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The reversible reaction between V(IV) and Ir(IV), $VO^{2+} + IrCl_6^{2-} + H_2O \rightleftharpoons VO_2^+ + IrCl_6^{3-} + 2H^+$, was studied at 25 °C and 1.00 M ionic strength. The equilibrium constant was determined to be 0.031 ± 0.004 M^2 from spectral changes and 0.029 ± 0.006 M^2 from kinetic measurements. The rate law is $-d[IrCl_6^{2-}]/dt = (A_{-1}[H^+]^{-1} + A_0)[IrCl_6^{2-}][VO^{2+}] - (B_1[H^+] + B_2[H^+]^2)[IrCl_6^{3-}][VO_2^+]$, with $A_{-1} = 0.0966 \pm 0.0021$ s^{-1}, $A_0 = 0.027 \pm 0.028$ M^{-1} s^{-1}, $B_1 = 3.30 \pm 0.11$ M^{-2} s^{-1}, and $B_2 = 0.59 \pm 0.19$ M^{-3} s^{-1}. Detailed mechanisms are presented and discussed.

Introduction

The reductions of chromium(VI)[2] and vanadium(V)[3,4] by substitution-inert iron(II) complexes exhibit striking similarities in reactivity and mechanism. Direct observation of successor complexes in the vanadium(V) reactions allowed the assignment of an inner-sphere mechanism in which the bridging ligand was supplied by the reducing agent. Similar observations were made for the Fe(II) reduction of Cr(IV),[2] and an inner-sphere mechanism was surmised for the reduction of Cr(VI) on the basis of reactivity patterns.[2,4] Similar results were also obtained in the $Mo(CN)_8^{4-}$ reduction of Cr(VI).[5] Attempts to identify the inner-sphere or outer-sphere nature of the Cr^{VI}–$IrCl_6^{3-}$ reaction failed,[6] due to the inability to distinguish between the absence of a successor complex and its rapid breakdown. Since this system provided some rather unique features in the mechanism of oxidations by Cr(VI) and since parallel studies of V(V) reactions proved fruitful in the past, we decided to undertake a study of the V^V–$IrCl_6^{3-}$ reaction.

This system is also pertinent to the studies of the $IrCl_6^{2-}$ oxidations of V^{2+} and of V^{3+}.[7] The V^{2+} reduction exceeded the capability of the stopped-flow apparatus, implying a second-order rate constant $>4 \times 10^6$ M^{-1} s^{-1}.[7] The reduction by V(III) followed the equation $-d[IrCl_6^{2-}]/dt = k[V(III)][IrCl_6^{2-}][H^+]^{-1}$ with $k = 52.2$ s^{-1} at 25 °C and 1.00 M ionic strength.[7] In each case, the redox rate exceeded the rate of substitution on the vanadium species, suggesting an outer-sphere mechanism. No reaction of V(IV) with $IrCl_6^{2-}$ was detected in these studies,[7] but the results to be presented here indicate that this reaction would have proceeded to only a small extent under most of the conditions investigated. The V(IV) reaction could have been observed in some experiments at low $[H^+]$ with [Ir(IV)] in excess over [V(III)], but the lower rate of the V(IV) reaction ($k \approx 1.0$ M^{-1} s^{-1} for V(IV) vs. 520 M^{-1} s^{-1} for V(III) at 0.1 M H^+) probably prevented its detection.

Experimental Section

Solutions of vanadium(V) perchlorate,[3] perchloric acid,[2] and lithium perchlorate[2] were prepared as previously described. Solutions of vanadium(IV) perchlorate were prepared by addition of an equivalent amount of barium perchlorate to a vanadyl sulfate solution[3] or by loading a column of Dowex 50W-X8 50–100 mesh cation-exchange resin with a $VOSO_4$ solution, followed by washing with 0.02 M $HClO_4$ and elution with 1.0 M $HClO_4$. The analysis of VO^{2+} solutions has been described.[3] Sodium hexachloroiridate(III) was prepared and stored as described;[6] it was prepared from Johnson, Matthey, and Co. sodium hexachloroiridate(IV), which was used without further purification. Stock solutions of Na_2IrCl_6 were prepared by weight and analyzed spectrally.[8] Solutions were stored at 0 °C or were frozen between experiments and were used only on the day they were prepared. Na_3IrCl_6 was added as the solid shortly before addition of VO_2^+ to the reaction solution in the thermostated cuvette. Removal of dissolved oxygen by purging with nitrogen had no effect on the kinetic or equilibrium behavior in several experiments, so oxygen was not excluded in most experiments.

Kinetics experiments were carried out with a Gilford Model 240 spectrophotometer, equipped with a Varian A-25 recorder and a thermostated cuvette holder. Most experiments were performed at 490 nm, a wavelength of maximum absorbance for Ir(IV) (ϵ 4000 M^{-1} cm^{-1}).[8] Solutions were thermostated to 25.0 °C and the ionic strength was adjusted to 1.00 M with $LiClO_4$. The concentrations of VO^{2+} and of VO_2^+ were maintained at least 10× in excess of the initial Ir(IV) or Ir(III) concentration to ensure pseudo-first-order conditions. Plots of log $(A_t - A_\infty)$ vs. time (where A is absorbance) were always linear through at least 95% reaction. Results were independent of the order of addition of the reagents.

Equilibrium constants were measured from the absorbance change observed in each experiment which had Ir(IV) as a reactant. The theoretical absorbance change for complete reaction was calculated as $\Delta A_c = l(\Delta\epsilon)[Ir(IV)]_0$ where $\Delta\epsilon$ was obtained from separately determined spectra of all species. Then $[Ir(III)]_{eq} = [Ir(IV)]_0\Delta A_{obsd}/\Delta A_c$ when $[Ir(III)]_0 = 0$. The equilibrium concentrations of all other species were determined from the value of $[Ir(III)]_{eq}$ and the reaction stoichimetry. Experiments under conditions leading to less than 5% reaction or more than 95% reaction were not used in equilibrium constant calculations because of the excessive errors involved in subtracting two similar numbers.

Results

Stoichiometry. The stoichiometry of the reaction between VO^{2+} and $IrCl_6^{2-}$ is described by

$$VO^{2+} + IrCl_6^{2-} + H_2O \rightleftharpoons VO_2^+ + IrCl_6^{3-} + 2H^+ \qquad (1)$$

This stoichiometry is confirmed by the reasonably constant values of $K = [VO_2^+][IrCl_6^{3-}][H^+]^2/[VO^{2+}][IrCl_6^{2-}]$ calculated from the absorbance changes as described above and by the kinetic behavior to be described below. Values of the equilibrium constant at various $[H^+]$ are presented in Table I. The equilibrium constant can also be calculated from standard oxidation potentials. Depending on the values of $E°$ used,[9–13] the calculated value of the equilibrium constant lies