Mechanism of the Oxidation of the Molybdenum(V)–Ethylenediaminetetra-acetato Dimer by Hexachloroiridate(IV) and Tris(1,10-phenanthroline)iron(III)

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The kinetics of the oxidation of μ-*NN'*-ethylenediaminetetra-acetato-di-μ-oxo-bis[oxomolybdenum(V)], $[Mo_2O_4(edta)]^{2-}$, by hexachloroiridate(IV), $[IrCl_6]^{2-}$, have been studied in aqueous perchloric acid solutions, $I = 1.0$M ($LiClO_4$), at 15–30 °C. The reaction is first-order in both reactants and is independent of $[H^+]$ in the range 0.01–0.50M investigated. Pseudo-first-order rate constants, k_{obs}, obtained by monitoring the disappearance of $[IrCl_6]^{2-}$ are substantially lower in the presence of added hexachloroiridate(III), $[IrCl_6]^{3-}$. The experimental data give a good fit to (i),

$$\frac{-d[Ir^{IV}]}{dt} = k_{obs}[Ir^{IV}] = \frac{2k_1k_2[(Mo^V)_2][Ir^{IV}]}{k_{-1}[Ir^{III}] + k_2} \qquad (i)$$

where the rate constants k_1, k_{-1}, and k_2 are as defined in the reaction scheme (ii)–(iv).

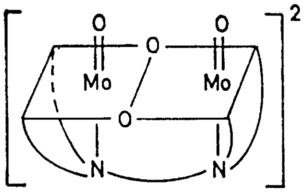
$$(Mo^V)_2 + Ir^{IV} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo^VMo^{VI} + Ir^{III} \qquad (ii)$$

$$Mo^VMo^{VI} \xrightarrow{k_2} Mo^V + Mo^{VI} \qquad (iii)$$

$$Mo^V + Ir^{IV} \xrightarrow{\text{fast}} Mo^{VI} + Ir^{III} \qquad (iv)$$

At 25 °C, $k_1 = 6.6$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger}_1 = 13.3 \pm 0.3$ kcal mol^{-1}, $\Delta S^{\ddagger}_1 = -10.0 \pm 1.0$ cal K^{-1} mol^{-1}, and $k_{-1}/k_2 = 1.74 \times 10^3$ l mol^{-1}. The corresponding oxidation with tris(1,10-phenanthroline)iron(III), $[Fe(phen)_3]^{3+}$, exhibits similar features with (at 25 °C) $k_1 = 1.9 \times 10^3$ l mol^{-1} s^{-1}, $\Delta H^{\ddagger}_1 = 16.6 \pm 0.4$ kcal mol^{-1}, $\Delta S^{\ddagger}_1 = 12.2 \pm 1.3$ cal K^{-1} mol^{-1}, and $k_{-1}/k_2 = 1.17 \times 10^4$ l mol^{-1}. No reaction of $[Mo_2O_4(edta)]^{2-}$ with the strong two-equivalent, oxidant hexachloroplatinate(IV), $[PtCl_6]^{2-}$, was observed during a period of 1 day at 25 °C.

DIMERIC ethylenediaminetetra-acetate (edta) complexes of molybdenum(III),[1] molybdenum(V),[2] and molybdenum(VI)[3] containing two molybdenum centres per edta ligand have been prepared and characterised. Recently the formation and dissociation kinetics of the edta complex of molybdenum(V) have been reported.[4] Preliminary results of an *X*-ray crystal study[5] have indicated a structure as shown, with features similar to other molybdenum(V) complexes, notably those with cysteine[6] and histidine[7] as ligands. The Mo_2O_4 sub-unit, is present in the aquo-dimer, and is retained on co-ordination of edta.[4] A di-bridged structure has been proposed for the molybdenum(III) dimer containing edta,[1] and also for the tungsten(V)–edta[8] dimer. In the case of the molybdenum(VI) dimer the metal centres are more remote.[9]



Kinetic studies on the oxidation of $[Mo_2O_4(edta)]^{2-}$ by hexachloroiridate(IV) and tris(1,10-phenanthroline)iron(III) are reported in this paper. By choosing reactants which have no aquo-ligands complexing with the molybdenum(VI) product is avoided.

RESULTS

Dissociation of the edta ligand from the molybdenum(V) dimer, is known to occur within the range $[H^+] = 0.5$–2.0M,[4] and investigations of the redox reactions of this complex were therefore limited to acidities $\leqslant 0.5$M.

Reaction with Hexachloroiridate(IV).—Preliminary experiments were carried out with $[Mo_2O_4(edta)]^{2-}$ in excess and the decrease in the absorption due to the complex at 297 nm indicated that 2 mol equiv. of iridium(IV) are consumed per mol equiv. of dimer (1). The reaction was studied by

$$[Mo_2O_4(edta)]^{2-} + 2[IrCl_6]^{2-} \longrightarrow 2Mo^{VI} + edta + 2[IrCl_6]^{3-} \qquad (1)$$

conventional spectrophotometry with the dimer in large excess, $I = 1.0$M ($LiClO_4$), the decrease in absorption at the 487 nm peak position of $[IrCl_6]^{2-}$ (ε 4 075 l mol^{-1} cm^{-1})[10] was used to monitor the reaction. The products do not have a significant absorption at this wavelength and first-order plots of log (O.D.$_t$ − O.D.$_\infty$) against time were linear to >90% completion. From the gradient of such plots ($k_{obs}/2.303$) values for the rate constant k_{obs} (Table 1) were

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evaluated. These were independent of hydrogen-ion concentration over the range 0.10—0.50M, and showed a first-order dependence on the concentration of molybdenum(v) dimer as illustrated in Figure 1. The rate law is therefore as in (2) where k_1 is the rate constant for the reaction of the first $[\mathrm{IrCl_6}]^{2-}$ with the dimer.

$$-\mathrm{d}[\mathrm{Ir^{IV}}]/\mathrm{d}t = k_{\mathrm{obs}}[\mathrm{Ir^{IV}}] = 2k_1\,[(\mathrm{Mo^V})_2][\mathrm{Ir^{IV}}] \qquad (2)$$

Further runs were performed with a large excess of $[\mathrm{IrCl_6}]^{3-}$ (over $[\mathrm{IrCl_6}]^{2-}$), $[\mathrm{H^+}] = 0.01 - 0.3$M, when values of k_{obs} were significantly lower than those in which $[\mathrm{IrCl_6}]^{3-}$ was not present initially, Table 2. A good fit to (3) was

$$\frac{-\mathrm{d}[\mathrm{Ir^{IV}}]}{\mathrm{d}t} = k_{\mathrm{obs}}\,[\mathrm{Ir^{IV}}] = \frac{2k_1k_2[(\mathrm{Mo^V})_2][\mathrm{Ir^{IV}}]}{k_{-1}[\mathrm{Ir^{III}}] + k_2} \qquad (3)$$

obtained, where the rate constants k_1, k_{-1}, and k_2 are as defined in equations (4)—(6)

TABLE 1

Pseudo-first-order rate constants (k_{obs}) for oxidation of the $[\mathrm{Mo_2O_4(edta)}]^{2-}$ with $[\mathrm{IrCl_6}]^{2-}$, $I = 1.0$M $(\mathrm{LiClO_4})$

Temp. °C	$[\mathrm{H^+}]$ M	$10^5[\mathrm{IrCl_6}^{2-}]$ M	$10^4[(\mathrm{Mo^V})_2]$ M	10^3k_{obs} [a] s^{-1}
15.0	0.10	3.0	4.0	2.38
	0.10	3.0	6.0	3.46
	0.10	3.0	8.0	4.81
	0.20	3.0	10.0	5.96
20.0	0.20	3.0	4.0	3.60
	0.10	3.0	8.0	7.31
	0.10	3.0	10.0	9.10
25.0	0.10	1.5	2.0	2.86
	0.20	3.0	3.0	3.69
	0.10	30.0	0.30	3.76 [b]
	0.30	3.0	4.50	6.10
	0.10	3.0	6.0	7.56
	0.30	3.0	6.0	7.51
	0.50	3.0	7.5	9.70 [c]
	0.20	3.0	8.0	10.6 [d]
	0.50	12.0	9.0	12.5
30.0	0.10	3.0	2.0	4.00
	0.10	3.0	3.0	6.00
	0.30	3.0	4.5	9.34
	0.10	3.0	6.0	12.0
	0.10	3.0	7.5	15.1

[a] Obtained by monitoring the decay of $[\mathrm{IrCl_6}]^{2-}$ at 487 nm. [b] Obtained by monitoring the decay of $[\mathrm{IrCl_6}]^{2-}$ at 575 nm. [c] $[\mathrm{Mo^{VI}}] = 7.5 \times 10^{-3}$M present. [d] $[\mathrm{Mo^{VI}}] = 1.5 \times 10^{-2}$M present.

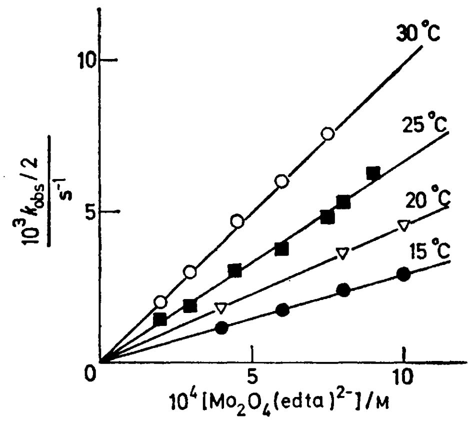

FIGURE 1 Dependence of $k_{\mathrm{obs}}/2$ on the concentration of molybdenum(v) dimer for the oxidation of $[\mathrm{Mo_2O_4(edta)}]^{2-}$ by $[\mathrm{IrCl_6}]^{2-}$, $I = 1.0$M $(\mathrm{LiClO_4})$. The computed lines are shown

TABLE 2

Pseudo-first-order rate constants (k_{obs}) for the oxidation of $[\mathrm{Mo_2O_4(edta)}]^{2-}$ with $[\mathrm{IrCl_6}]^{2-}$ (3×10^{-5}M) in the presence of $[\mathrm{IrCl_6}]^{3-}$, $I = 1.0$M $(\mathrm{LiClO_4})$

Temp. °C	$[\mathrm{H^+}]$ M	$10^4[(\mathrm{Mo^V})_2]$ M	$10^4[\mathrm{IrCl_6}^{3-}]$ M	10^3k_{obs} [a] s^{-1}
15.0	0.10	6.0	2.0	2.58
	0.20	8.0	4.0	2.64
	0.10	10.0	6.0	2.81
	0.10	8.0	8.0	1.70
	0.20	10.0	10.0	1.88
20.0	0.10	6.0	2.0	3.77
	0.10	6.0	4.0	3.06
	0.10	8.0	7.5	2.98
	0.20	8.0	9.0	2.63
25.0	0.01	4.0	1.0	4.65
	0.10	4.0	2.0	3.67
	0.20	4.0	5.0	2.94
	0.10	4.0	7.5	2.26
	0.30	8.0	10.0	3.83
	0.20	4.0	10.0	1.95
30.0	0.10	4.0	2.0	6.40
	0.20	4.0	3.5	4.73
	0.10	4.0	5.0	4.25
	0.10	6.0	7.5	5.31
	0.20	6.0	10.0	4.73
	0.20	6.0	11.0	4.35

[a] Obtained by monitoring the disappearance of $[\mathrm{IrCl_6}]^{2-}$ at 487 nm.

$$(\mathrm{Mo^V})_2 + \mathrm{Ir^{IV}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mo^VMo^{VI}} + \mathrm{Ir^{III}} \qquad (4)$$

$$\mathrm{Mo^VMo^{VI}} \xrightarrow{k_2} \mathrm{Mo^V} + \mathrm{Mo^{VI}} \qquad (5)$$

$$\mathrm{Mo^V} + \mathrm{Ir^{IV}} \xrightarrow{\text{fast}} \mathrm{Mo^{VI}} + \mathrm{Ir^{III}} \qquad (6)$$

Equation (3) may be rearranged to give (7),

$$\frac{2[(\mathrm{Mo^V})_2]}{k_{\mathrm{obs}}} = \frac{k_{-1}}{k_1k_2}\,[\mathrm{Ir^{III}}] + \frac{1}{k_1} \qquad (7)$$

and plots of the left-hand side of (7) against the concentration of $[\mathrm{IrCl_6}]^{3-}$ are shown in Figure 2, where the intercepts correspond to and are in good agreement with reciprocal

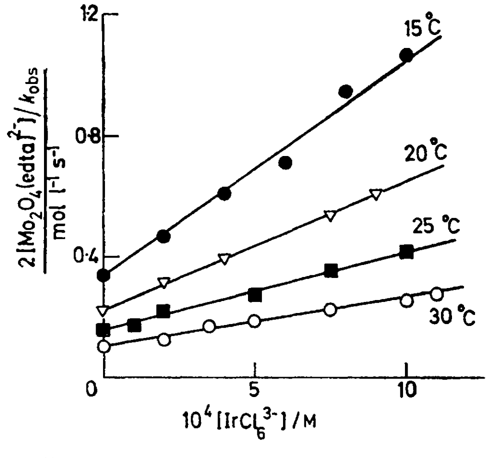

FIGURE 2 Dependence of the left-hand side of equation (7) on the concentration of $[\mathrm{IrCl_6}]^{3-}$ for the oxidation of $[\mathrm{Mo_2O_4(edta)}]^{2-}$ by $[\mathrm{IrCl_6}]^{2-}$, $I = 1.0$M $(\mathrm{LiClO_4})$. The computed lines are shown

gradients in Figure 1. The term in k_{-1} is negligible for runs performed in the absence of added $[IrCl_6]^{3-}$ under which condition (3) reduces to (2).

Addition of molybdenum(VI), in the form of the molybdate, did not have any effect on k_{obs} (Table 1) although when high concentrations of molybdenum(VI) were used the formation of ' molybdenum blue ' was apparent before completion of the reaction. Rate constants for these runs were evaluated from the initial portion of absorbance-time plots using the Guggenheim treatment.[11]

Values of the rate constant k_1 (Table 3) were obtained by a non-linear least-squares fit of the data in Tables 1 and 2 to (3),[12] with each datum point being given a weighting factor of k_{obs}^{-2}. A value $[Ir^{III}] = 0$ was assumed for runs in Table 1. From this treatment $10^{-3}k_{-1}/k_2$(l mol⁻¹), which is also given by the ratio of slope to intercept in Figure 2, is equal to 2.06 (15 °C), 1.89 (20 °C), 1.74 (25 °C), and 1.61 (30 °C). From the temperature dependence log (k_1/T) against $1/T, \Delta H_1^\ddagger = 13.3 \pm 0.3$ kcal mol⁻¹ and $\Delta S_1^\ddagger = -10.0 \pm 1.0$ cal K^{-1} mol⁻¹.

TABLE 3

Values of k_1 for the oxidation of $[Mo_2O_4(edta)]^{2-}$ with $[IrCl_6]^{2-}$, $I = 1.0$M $(LiClO_4)$

Temp. °C	k_1 l mol⁻¹ s⁻¹
15.0	3.03 ± 0.09
20.0	4.59 ± 0.04
25.0	6.77 ± 0.25
30.0	10.07 ± 0.19

Attempts were also made to study reaction (1) in the presence of an excess of $[IrCl_6]^{2-}$ at lower wavelengths, but values of the final absorbance (O.D.$_\infty$) were difficult to obtain owing to the redox reaction between free edta and $[IrCl_6]^{2-}$. A similar reaction between cerium(IV) and edta has previously been reported.[13]

Reaction with Tris(1,10-*phenanthroline*)*iron*(III).—Experiments with the dimer in excess indicated that 2 mol equiv. of $[Fe(phen)_3]^{3+}$ are consumed per mol equiv. of dimer [equation (8)].

$$[Mo_2O_4(edta)]^{2-} + 2[Fe(phen)_3]^{3+} \longrightarrow 2Mo^{VI} + edta + [Fe(phen)_3]^{2+} \quad (8)$$

The kinetics of reaction (8) were studied with a large excess of $[Mo_2O_4(edta)]^{2-}$, $[H^+] = 0.02$—0.40M, and with $I = 1.0$M $(LiClO_4)$. Absorption charges at 510 nm due to the formation of $[Fe(phen)_3]^{2+}$ (ε 10 900 l mol⁻¹ cm⁻¹) were monitored.[14] The reaction was considerably faster than with $[IrCl_6]^{2-}$ as oxidant and a lower range of temperatures and smaller dimer concentrations were necessary in order to follow the reaction by conventional spectrophotometry.

A first-order dependence on both reactants was observed and values of k_{obs} evaluated from the first-order plots (Table 4) were independent of $[H^+]$ over the range 0.02—0.40M investigated.

The effect of the $[Fe(phen)_3]^{2+}$ product on the rate was investigated by monitoring the reaction at 350 nm, at which wavelength the ratio of ε values for $[Fe(phen)_3]^{3+}$ and

TABLE 4

Pseudo-first-order rate constants(k_{obs}) for the oxidation of $[Mo_2O_4(edta)]^{2-}$ with $[Fe(phen)_3]^{3+}$, $I = 1.0$M $(LiClO_4)$

Temp. °C	$[H^+]$ M	$10^6[Fe(phen)_3{}^{3+}]$ M	$10^5[(Mo^V)_2]$ M	10^3k_{obs} [a] s⁻¹
0.75	0.02	1.25	1.00	3.00
	0.40	1.25	1.50	5.40
	0.02	1.25	1.50	4.00
	0.04	2.50	2.00	6.40
	0.40	2.50	2.00	6.50
	0.04	2.50	2.50	6.60
	0.04	2.50	2.50	6.80
	0.40	2.50	2.50	8.00
	0.04	2.50	2.50	7.00
	0.24	3.12	2.50	8.20
	0.20	4.69	3.75	11.3
	0.24	6.25	5.00	14.6
	0.20	5.00	5.00	13.2
	0.20	5.00	5.00	15.4
	0.20	4.69	5.63	17.4
	0.20	4.69	7.50	20.4
	0.24	6.25	7.50	20.2
5.0	0.02	2.50	1.10	6.40
	0.02	2.50	2.04	10.80
	0.20	5.00	3.30	15.6
	0.20	5.00	3.30	16.6
	0.40	5.00	4.08	19.4
	0.20	10.00	4.08	17.6
	0.20	5.00	5.37	22.8
	0.20	10.00	5.37	23.0
	0.04	5.00	6.60	28.0
	0.08	10.00	6.60	30.6
10.0	0.04	5.00	1.27	10.8
	0.40	5.00	1.52	14.0
	0.04	5.00	2.54	19.0
	0.20	5.00	3.05	24.0
	0.20	5.00	3.81	31.4
	0.08	10.00	5.08	36.4
15.0	0.20	5.0	1.27	18.6
	0.20	5.0	1.52	22.4
	0.04	5.0	2.03	26.0
	0.04	5.0	2.03	30.2
	0.10	5.0	2.54	36.0
	0.08	10.00	3.05	40.6
	0.08	10.00	3.56	50.2

[a] Obtained by monitoring the formation of $[Fe(phen)_3]^{2+}$ at 510 nm.

TABLE 5

Pseudo-first-order rate constants (k_{obs}) for the oxidation of the $[Mo_2O_4(edta)]^{2-}$ with $[Fe(phen)_3]^{3+}$ (5×10^{-6} to 10^{-5}M) in the presence of $[Fe(phen)_3]^{2+}$, $I = 1.0$M $(LiClO_4)$

Temp. °C	$[H^+]$ M	$10^5[(Mo^V)_2]$ M	$10^5[Fe(phen)_3{}^{2+}]$ M	10^3k_{obs} [a] s⁻¹
0.75	0.20	2.5	1.5	5.2
	0.20	5.0	1.5	12.0
	0.20	5.0	2.5	9.4
	0.20	5.0	3.75	8.0
	0.20	5.0	5.0	7.6
	0.20	2.0	5.0	2.8
	0.20	2.0	6.0	2.6
	0.20	5.0	7.5	5.6
5.0	0.20	3.3	1.5	12.0
	0.20	2.04	2.5	6.2
	0.20	3.3	5.0	7.6
10.0	0.08	5.08	1.5	31.6
	0.04	2.54	2.5	14.0
	0.20	3.05	3.75	15.0
	0.40	1.52	5.0	6.4
	0.40	1.52	6.0	6.0
15.0	0.10	2.54	1.5	29.6
	0.10	2.54	2.5	26.0
	0.08	3.05	3.75	28.8
	0.04	1.27	6.0	9.8

[a] Obtained by monitoring the disappearance of $[Fe(phen)_3{}^{3+}]$ at 350 nm.

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[12] Los Alamos Report LA 2367 (1959) and Addenda by R. H. Moore and R. K. Ziegler.

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[14] R. Davies, B. Kipling, and A. G. Sykes, *J. Amer. Chem. Soc.*, 1973, **95**, 7250.

$[\mathrm{Fe(phen)_3}]^{2+}$ is *ca.* 8. A similar lowering of k_{obs} to that obtained on the addition of $[\mathrm{IrCl_6}]^{3-}$ in the previous section was observed, and the data (Table 5) give a good fit to equation (9), where the rate constants k_1, k_{-1}, and k_2 are as

$$\frac{-\mathrm{d}(\mathrm{Fe^{III}})}{\mathrm{d}t} = k_{obs}[\mathrm{Fe^{III}}] = \frac{2k_1k_2[(\mathrm{Mo^V})_2][\mathrm{Fe^{III}}]}{k_{-1}[\mathrm{Fe^{II}}] + k_2} \qquad (9)$$

previously defined in the sequence (4)—(6).

Values of the rate constant k_1 (Table 6) were obtained using a non-linear least-squares treatment [12] of the data in Tables 4 and 5, each datum point being given the weighting k_{obs}^{-2}. Values of 10^{-4} k_{-1}/k_2 (l mol^{-1}) are 2.11 (0.75 °C), 1.91 (5.0 °C), 1.67 (10 °C) and 1.48 (15 °C). From the temperature dependence of k_1, $\Delta H_1^‡ = 16.6 \pm 0.4$ kcal mol^{-1} and $\Delta S_1^‡ = 12.2 \pm 1.3$ cal K^{-1} mol^{-1}. Kinetic data are summarised in Table 7.

TABLE 6

Summary of rate constants obtained for the oxidation of $[\mathrm{Mo_2O_4(edta)}]^{2-}$ with $[\mathrm{Fe(phen)_3}]^{3+}$, $I = 1.0$M (LiClO$_4$)

Temp. °C	$10^{-2}k_1$ l mol^{-1} s^{-1}
0.75	1.35 ± 0.05
5.0	2.00 ± 0.10
10.0	3.44 ± 0.25
15.0	6.68 ± 0.42

Reaction with Hexachloroplatinate(IV).—Attempts were made to study the reaction between $[\mathrm{Mo_2O_4(edta)}]^{2-}$ and hexachloroplatinate(IV), $[\mathrm{PtCl_6}]^{2-}$, $I = 1.0$M (LiClO$_4$). Absorbance changes were monitored at 300 nm, where $[\mathrm{PtCl_6}]^{2-}$ has ε = 4 609 l mol^{-1} cm^{-1}, $[\mathrm{Mo_2O_4(edta)}]^{2-}$ has ε = *ca.* 9 000, and $[\mathrm{PtCl_4}]^{2-}$ and Mo$^{\mathrm{VI}}$ have negligible absorbance. All reactions were carried out under air-free conditions and in the presence of 0.01M-chloride to limit the dissociation of $[\mathrm{PtCl_6}]^{2-}$. Runs were with $[\mathrm{H^+}] = 0.01$ and 0.10M, $[\mathrm{PtCl_6}^{2-}] = 2.5 \times 10^{-5}$M, and $[(\mathrm{Mo^V})_2] = 1 \times 10^{-4}$M. In all cases there was no detectable reaction over a period of 1 day, and assuming a bimolecular process it can be concluded that rate constants are $<10^{-2}$ l mol^{-1} s^{-1} at 25 °C. An additional run was performed at the elevated temperature of 40 °C with $[\mathrm{H^+}] = 0.01$M, $I = 1.0$M (LiClO$_4$), when no significant spectrophotometric changes were observed over a period of 5 h.

DISCUSSION

Recent studies [15] on the complexation of thiocyanate to the molybdenum(V) aquo-dimer, $[\mathrm{Mo_2O_4(H_2O)_6}]^{2+}$, suggest that the $\mathrm{Mo_2O_4}$ sub-unit reacts by a dissociative mechanism. It is unlikely therefore that in the present study hexachloroiridate(IV) is able to co-ordinate to molybdenum unless the edta ligand is partially displaced before reaction. The oxidant tris(1,10-phenanthroline)-iron(III) cannot co-ordinate, and, on this basis, we are able to conclude that in both cases electron transfer occurs by an outer-sphere mechanism.

It has previously been suggested [16] that a necessary pre-requisite for the transfer of two electrons is that a reaction should be of the inner-sphere type. This provides a possible explanation as to why the reaction of $[\mathrm{Mo_2O_4(edta)}]^{2-}$ with the strong two-equivalent oxidant $[\mathrm{PtCl_6}]^{2-}$ is negligible over periods of a day at 25 °C. A one-electron process is necessarily slow because of the need to generate unstable platinum(III).

The differences in $\Delta H^‡$ and $\Delta S^‡$ respectively for the composite term k_1 ($= kK_{\mathrm{IP}}$) in the reaction of $[\mathrm{Mo_2O_4(edta)}]^{2-}$ with $[\mathrm{IrCl_6}]^{2-}$ and $[\mathrm{Fe(phen)_3}]^{3+}$ (Table 7) become smaller if ion-pairing of the reactants (K_{IP}) is taken into account. Thus the Fuoss treatment [17] indicates that contributions from ion-pairing to the observed enthalpy and entropy of activation are both negative for $[\mathrm{IrCl_6}]^{2-}$ (2−, 2− reactants), and positive for the reaction of $[\mathrm{Fe(phen)_3}]^{3+}$ (3+, 2− reactants). The activation parameters for k_1 will be more similar therefore after allowance for K_{IP}.

TABLE 7

Summary of activation parameters for the oxidation of $[\mathrm{Mo_2O_4(edta)}]^{2-}$ with $[\mathrm{IrCl_6}]^{2-}$ and $[\mathrm{Fe(phen)_3}]^{3+}$, $I = 1.0$M (LiClO$_4$).

Oxidant	Rate constant (25 °C)	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal K^{-1} mol^{-1}
$[\mathrm{IrCl_6}]^{2-}$	$k_1 = 6.6$	13.3 ± 0.3	−10.0 ± 1.0
$[\mathrm{Fe(phen)_3}]^{3+}$	$k_1 = 1.9 \times 10^3$	16.6 ± 0.4	12.3 ± 1.3
$[\mathrm{IrCl_6}]^{2-}$	$k_{-1}/k_2 = 1.74 \times 10^3$	−2.9 ± 0.7 [a]	5.1 ± 2.5 [b]
$[\mathrm{Fe(phen)_3}]^{3+}$	$k_{-1}/k_2 = 1.17 \times 10^4$	−4.0 ± 1.5 [a]	5.2 ± 5.5 [b]

[a] Corresponds to $\Delta H^‡_{-1} - \Delta H^‡_2$. [b] Corresponds to $\Delta S^‡_{-1} - \Delta S^‡_2$.

The ratio k_1k_2/k_{-1} for $[\mathrm{Fe(phen)_3}]^{3+}$ to that for $[\mathrm{IrCl_6}]^{2-}$ as reactant (k_2 is common to both reactions) is 43 at 25 °C, whereas a value of *ca.* 6 is calculated from the standard reduction potential for $[\mathrm{IrCl_6}]^{2-}/[\mathrm{IrCl_6}]^{3-}$ (1.017 V) [18] and $[\mathrm{Fe(phen)_3}]^{3+}/[\mathrm{Fe(phen)_3}]^{2+}$ (1.06 V).[19] While exact correspondence would not be anticipated since different solution media, ionic strengths, *etc.*, apply, the discrepancy is partly explained by taking into account the different ion-pairing constants between 2− and 3+ oxidants and the 2− dimer. The calculated ratio of *ca.* 6 does not allow for this factor.

It is interesting to note that in the oxidation of the molybdenum(V) aquo-dimer, $[\mathrm{Mo_2O_4(H_2O)_6}]^{2+}$ by $[\mathrm{Fe(phen)_3}]^{3+}$ a k_{-1} term is not observed, and no retardation of rate is observed on the addition of $[\mathrm{Fe(phen)_3}]^{2+}$ product.[20] It appears, therefore, that in the present case the edta ligand is able to hold the molybdenum(V)-(VI) dimer together for sufficiently long for it to become a kinetically significant species. Also, since the reaction with both oxidants is independent of hydrogen-ion concentration, the k_2 step in both reaction sequences most likely corresponds to rate-determining cleavage of the first carboxylate ring of the edta, which is independent of $[\mathrm{H^+}]$. It has been shown that in the chelation of quadridentate edta to give the quinquidentate chromium(III)-edta complex the path involving unprotonated

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[15] Y. Sasaki, R. S. Taylor, and A. G. Sykes, *J.C.S. Dalton*, 1975, 396.

[16] See, for example, M. G. Ondrus and G. Gordon, *Inorg. Chem.*, 1971, **10**, 474; M. Green and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 3221; 1971, 3067.

[17] See, for example, M. R. Hyde and A. G. Sykes, *J.C.S. Chem. Comm.*, 1972, 1340.

[18] W. M. Latimer, ' Oxidation States of the Elements and their Potentials in Aqueous Solutions,' Prentice-Hall, Englewood Cliffs, N.J., 1952, 2nd edn., p. 217.

[19] G. F. Smith and F. P. Richter, *Ind. Eng. Chem. Analyt.*, 1944, **16**, 580.

[20] G. R. Cayley, R. K. Wharton, and A. G. Sykes, to be published.

carboxylate is the most effective.[21] From the principles of microscopic reversibility dissociation of an unprotonated carboxylate function would, therefore, be expected to prevail. Some caution must be exercised in assuming that this assignment applies in all cases involving dissociation of a carboxylate function, since in the aquation of acetate from acetatopenta-aquochromium(III) the pathway involving protonated complex makes a significant contribution.[22] The determining factors are the tendency of the co-ordinated carboxylate to protonate, and relative values of the rate constants for dissociation of protonated and unprotonated species. Cleavage of the second or a subsequent chelate ring cannot be rate determining since this would introduce proton-dependent equilibria involving the unco-ordinated carboxylate.

Oxidation of the second molybdenum(V), equation (6), may occur before complete breakdown to monomeric molybdenum ions, equation (5). As an alternative to (6) it is possible that rapid dimerisation occurs, (10).

$$\mathrm{Mo^{V} + Mo^{V} \longrightarrow Mo_2{}^{V}} \qquad (10)$$

If this pathway is effective then the rate law (2) will require modifying and all values of k_1 will be twice those listed in the Tables.

EXPERIMENTAL

The μ-*NN'*-ethylenediaminetetra-acetato-di-μ-oxo-bis-[oxomolybdenum(V)] complex was prepared as a sodium salt using the procedure outlined in ref. 4 (Found: C, 20.3; H, 2.5; N, 4.7%. Calc. for $C_{16}H_{12}Mo_2N_2Na_2O_{12}$: C, 20.4; H, 2.05; N, 4.75%). Solutions of sodium molybdate (B.D.H. AnalaR) were in 1—3M-perchloric acid. It has been shown that under such conditions of acidity the molybdenum(VI) is present in both monomer and dimer forms which are in rapid equilibrium.

Sodium chloroiridate(IV) (Johnson Matthey Chemicals Limited), $Na_2IrCl_6{\cdot}H_2O$, was used without further purification. Aqueous solutions of the complex gave a spectrum ($\lambda_{\max.}$ 487 nm, $\varepsilon_{\max.}$ 4 070 l mol^{-1} cm^{-1}) in good agreement with that in the literature ($\lambda_{\max.}$ 487 nm, $\varepsilon_{\max.}$ 4 075 l mol^{-1} cm^{-1}).[23] However, sodium chloroiridate(III), $Na_3[IrCl_6]{\cdot}12H_2O$, from the same source required further purification since spurious absorptions were present in the u.v. region. The solid was purified by dissolution in water at room temperature and addition of absolute ethanol, the precipitate obtained being filtered off and washed with ether. This was repeated twice and the resultant solid gave a spectrum ($\lambda_{\max.}$ 358 nm, ε 78 l mol^{-1} cm^{-1}) in satisfactory agreement with that in the literature ($\lambda_{\max.}$ 358 nm, ε 74 l mol^{-1} cm^{-1}).[23]

Tris(1,10-phenanthroline)iron(III) perchlorate was prepared as described in the literature[24] (Found: C, 47.1; H, 3.15; N, 9.35%. Calc. for $Fe(C_{12}H_8N_2)_3(ClO_4)_3{\cdot}H_2O$: C, 47.3; H, 2.85; N, 9.2%). Tris(1,10-phenanthroline)-iron(II) perchlorate was prepared by the method described in ref. 25. Absorption coefficients were as determined previously.[14]

Lithium perchlorate was prepared by adding lithium carbonate (Hopkin and Williams, Laboratory Reagent) to perchloric acid (Hopkin and Williams, AnalaR); the product was recrystallised until free from anionic impurities. Perchloric acid was of AnalaR-grade purity.

Stock solutions of $[Fe(phen)_3]^{3+}$ were prepared freshly each day by dissolving the complex in 5M-$HClO_4$ and storing it at 0 °C. Solutions of $[IrCl_6]^{2-}$ were also prepared freshly for each set of kinetic runs and the stock solution stored in the dark.

Kinetic runs were followed using a Unicam SP 500 spectrophotometer fitted with a thermostatted cell housing.

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