Mechanistic Studies on the cis-[VO₂(H₂O)₄]⁺ and [Mo(CN)₈]³⁻ Oxidations of the Reᴵⱽ₂ Complex [(C₂O₄)₂-Re(μ-O)₂Re(C₂O₄)₂]⁴⁻ †

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Rate constants (25 °C) have been determined for the oxidation of the Re^{IV}_2 complex di-μ-oxo-bis[dioxalatorhenate(iv)], $[(C_2O_4)_2Re(μ-O)_2Re(C_2O_4)_2]^{4-}$, $I = 1.00$ M (ClO_4^- or Cl^-). Whereas the complex is itself stable in air at pH 7 over many days, at lower pH there is a slow decay of the 446 nm peak ($\varepsilon = 6840$ M^{-1} cm^{-1} per Re^{IV}_2) to give in air the colourless perrhenate(vii) $[ReO_4]^-$ product, peak at 225 nm ($\varepsilon = 3400$ M^{-1} cm^{-1}). The kinetics indicate a protonation step, equilibrium constant $K = 2.4$ M^{-1}, followed by the decay process $k = 4.3 \times 10^{-5}$ s^{-1}. With the one-equivalent oxidants cis-$[VO_2(H_2O)_4]^+$ (1.0 V) and $[Mo(CN)_8]^{3-}$ (0.80 V), stoichiometries of 6 mol of oxidant per Re^{IV}_2 are obtained indicating conversion through to Re^{VII}. Two kinetic stages have been monitored with the oxidant in large excess. For the reaction with V^V as oxidant the first stage is dependent on $[V^V]$ and $[H^+]$ as well as $[Re^{IV}_2]$, giving the rate constant $k_1 = 3.31 \times 10^4$ M^{-2} s^{-1}. Since in the corresponding reaction with Mo^V as oxidant the reaction is independent of $[H^+]$ ($k_{Mo} = 2.27 \times 10^4$ M^{-1} s^{-1}), it is concluded that the V^V reactant introduces the $[H^+]$-dependent term. The second stage of the V^V reaction gives the rate law dependence $k_{2obs} = k_2[V^V] + k_0$, but with the less strong Mo oxidant $k_{2obs} = k_0$ which is ≈ 0.20 s^{-1}. The spectrum of the $Re^{IV}Re^V$ intermediate, peak at 529 nm ($\varepsilon = 3800$ M^{-1} cm^{-1}), was obtained by stopped-flow rapid-scan spectrophotometry. Reactions of less than full stoichiometric amounts of V^V with Re^{IV}_2, followed by QAE-Sephadex chromatography at 0 °C, gave orange-pink (peak at ≈ 495 nm) and maroon (≈ 550 nm) intermediates, which undergo spontaneous decay.

Earlier reports on the preparation of a dark brown Re^{IV}–oxalato complex have appeared.[1-4] A single crystal X-ray structure determination has demonstrated the dinuclear di-μ-oxo nature of the product, $K_4[(C_2O_4)_2Re(μ-O)_2Re(C_2O_4)_2]\cdot 3H_2O$ **1**, with in this instance a *meso*-ΔΛ arrangement of the oxalato ligands.[5] The short Re–Re distance of 2.362 Å is consistent with a multiple metal–metal bond, and the compound is diamagnetic. An X-ray crystal structure of the Re^{IV}_2–edta (edta = ethylenediaminetetraacetate) complex has demonstrated that here also a di-μ-oxo structure [(edta)Re(μ-O)₂Re(edta)]⁴⁻ is obtained, which incorporates two tetradentate edta ligands. The latter has been the subject of previous studies with cis-$[VO_2(H_2O)_4]^+$ as a one-equivalent oxidant.[6] The kinetics implicate two isomers of Re^{IV}_2, and protonation of the unco-ordinated carboxylates of the edta ligands is evident. Steps involving inhibition by V^{IV} (implicated in the back reaction), and competition between V^{IV} and H^+ for the free carboxylate groups is observed. Although these observations require intermediate formation of $Re^{IV}Re^V$ no spectrophotometric evidence for the existance of such an intermediate was obtained.[6] We now report corresponding studies with the Re^{IV}_2–oxalato complex from which different features have emerged, particularly with respect to the identification of intermediates. Comparisons with a third di-μ-oxo Re^{IV}_2 complex [L(X)Re(μ-O)₂Re(X)L]²⁺, where L is the 1,4,7-triazacyclononane ligand are also made.[7] The latter work is of interest because mononuclear forms provide the lead-in to the preparation of the dinuclear complexes described.

Experimental

Preparation of the Re^{IV}_2–Oxalato Complex.—The synthesis

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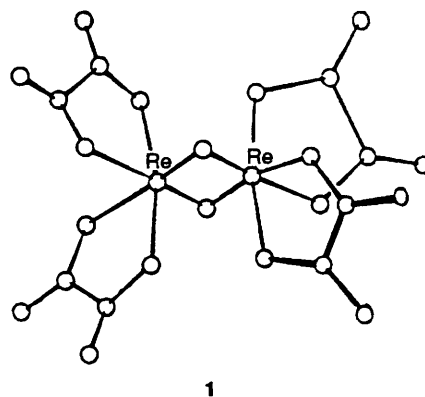
of the Re^{IV}_2–oxalato complex has been the subject of a number of papers.[2-5] Indications are that all the procedures are not entirely reproducible and that several products can be isolated. A significant step was the determination of the crystal and molecular structure of $K_4[(C_2O_4)_2Re(μ-O)_2Re(C_2O_4)_2]\cdot 3H_2O$.[5] The following procedure yields chromatographically clean product. Hexachlororhenate(iv) (1.0 g, K^+ salt; 2.09×10^{-3} M), prepared by H_3PO_2 or I^- reduction of ammonium perrhenate(vii) (Johnson Matthey) in concentrated HCl,[8] was dissolved in H_2O (40 cm³) at room temperature, and solid oxalic acid, $H_2C_2O_4\cdot 2H_2O$, (1.6 g; 12.7×10^{-3} M) added. The stirred solution was warmed to 60 °C, and $K_2C_2O_4\cdot H_2O$ (1.15 g; 6.25×10^{-3} M) added. The colour changes from pale lime green to dark yellow-brown during heating which was continued for 1 h. Exposure to atmospheric O_2 may be relevant, and the product is cleaner if low pH conditions are maintained.

Table 1 Comparison of peak positions for the visible absorbance spectra of di-μ-oxo Re^{IV}_2 complexes $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ **1**, $[(edta)Re(\mu\text{-}O)_2Re(edta)]^{4-}$ **2** and $[L(Cl)Re(\mu\text{-}O)_2Re(Cl)L]^{2+}$ **3** (L = 1,4,7-triazacyclononane) in H_2O, units λ/nm (ε/M^{-1} cm^{-1} per dimer)

| Complex	λ (ε)	λ (ε)	λ (ε)	λ (ε)
1	446 (6840)	525 (sh) (—)	624 (592)	744 (353)
2	450 (7880)	582 (sh) (588)	608 (sh) (267)	751 (260)
3	461 (4500)	520 (sh) (—)	621 (272)	757 (217)

The solution was evaporated to dryness at room temperature and the black solid slurried with water (30 cm³). Following filtration and washing with water (5 cm³), an equal volume of ethanol was carefully added, with stirring, to the combined filtrate and washings. Brown-olive green crystals were deposited in ≈50% yield, and these were collected from the ice-cooled solution (2 h), washed with acetone and dried in air. A further recrystallisation was induced by addition of alcohol to an aqueous solution (30 cm³). A single band of pure complex was then obtained by column chromatography from a Sephadex QAE resin on elution with 2 M KCl. The visible absorption spectrum in H_2O gave peaks at λ/nm (ε/M $^{-1}$ cm^{-1} per dimer): 744 (353), 624 (592), 446 (6840). Comparisons with corresponding data for the edta and the 1,4,7-triazacyclononane (L) complexes, Table 1,[6,7] indicate similar features for these di-μ-oxo complexes. The very intense absorption maximum in the visible for the d^3–d^3 metal pair is assigned to a symmetry allowed π→π* transition.

Preparation of Oxidants.—Solutions of the V^V aqua ion as cis-$[VO_2(H_2O)_4]^+$ were prepared by dissolving the required amount of ammonium vanadate NH_4VO_3 (BDH, Analar) in hot water, followed by addition of an equal volume of acid, typically 1.0 M. The concentration of the yellow V^V solutions was determined by titration against a freshly prepared standard solution of iron(II) ammonium sulfate, using ferroin as indicator. The V^V absorbance at 350 nm (ε = 128 M^{-1} cm^{-1}), not a peak position, was used to determine concentrations. The reduction potential for the cis-$[VO_2(H_2O)_4]^+$–$[VO(H_2O)_5]^{2+}$ couple is 1.0 V in 1 M H$^+$.[9] A sample of the light yellow octacyanomolybdate(V) as $Cs_3[Mo(CN)_8]\cdot 2H_2O$,[10,11] was a gift from Professor J. G. Leipoldt. It has negligible absorbance at the Re^{IV}_2–oxalato 446 nm peak (and above) used in these studies, with absorbance increasing steeply at <400 nm. The $[Mo(CN)_8]^{4-}$ product has a peak at 365 nm (ε = 164 M^{-1} cm^{-1}), and shoulder at 425 nm (ε ≈ 36 M^{-1} cm^{-1}). Precautions were taken to avoid any contributions arising from the photochemistry of $[Mo(CN)_8]^{3-}$.[12] Solutions of the latter stored in the dark were stable for >6 h. The reduction potential for the $[Mo(CN)_8]^{3-}$–$[Mo(CN)_8]^{4-}$ couple is 0.80 V.[13]

Preparation of Other Reagents.—Solutions of V^{IV} were prepared from hydrated vanadium(IV) sulfate (Aldrich) by Amberlite IR(H) 120 cation-exchange chromatography in 1.0 M $HClO_4$. The solution was standardised from its known UV/VIS absorbance spectrum, with ε = 17.0 M^{-1} cm^{-1} at the 765 nm peak.[14] Other reagents including LiCl, NaCl, $LiClO_4$ and $HClO_4$ were of AnalaR grade purity.

Stability of Re^{IV}_2 Complex.—Solutions of the oxalato complex (2.6 × 10^{-4} M) in water gave ≈3% decrease in absorbance at 446 nm over 20 d at room temperature. On addition of 0.3 M acid ($HClO_4$, H_2SO_4 or trifluoromethanesulfonate) solutions became colourless within 1 d of preparation. In acid the UV spectrum of the final product indicates formation of the perrhenate(VII) ion, $[ReO_4]^-$, peak at 225 nm (ε = 3400 M^{-1} cm^{-1}).

Stoichiometries.—The absorbance at 446 nm (ε = 6840 M^{-1} cm $^{-1}$) was monitored on addition of aliquots of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ from a Hamilton microsyringe to cis-$[VO_2(H_2O)_4]^+$ in a spectrophotometer cell. A stoichiometry of 6:1 as in equation (1) was indicated. With $[Mo(CN)_8]^{3-}$ as

$$Re^{IV}_2 + 6V^V \longrightarrow 2Re^{VIII} + 6V^{IV} \qquad (1)$$
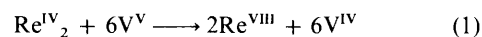
oxidant similar observations were made, giving the stoichiometry for reaction as in equation (2).

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

Kinetic Studies.—Kinetic studies were carried out at 25.0 ± 0.1 °C, and ionic strength I = 1.00 ± 0.001 M adjusted by appropriate amounts of LiCl, $LiClO_4$ or NaCl. In order to study the decomposition of the Re^{IV}_2 complex HCl–LiCl solutions were used. The same conditions were used for the reaction with $[Mo(CN)_8]^{3-}$ as oxidant, where check runs using NaCl were also carried out. With cis-$[VO_2(H_2O)_4]^+$ as oxidant the conditions I = 1.0 M ($LiClO_4$) were used so as to avoid complexing anions. To meet the stoichiometry requirements concentrations of oxidant were in >60-fold excess. A Dionex D-110 stopped-flow spectrophotometer with on-line data system (OLIS, Bogart, GA, USA) utilising an IBM AT computer with suitable interface and data storage facilities was used. Rate constants were calculated using an exponential fitting routine from OLIS, who also supplied the rapid wavelength scan attachment.

Rapid-scan Spectra.—These were recorded for the reaction of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ with cis-$[VO_2(H_2O)_4]^+$. A pink coloured intermediate is observed by eye at various reactant concentrations including 1:1 and 2:1 oxidant to Re^{IV}_2 ratios. Formation of an intermediate with an absorbance peak at 529 nm is indicated (Fig. 2). A slower (stopped-flow) decay of this absorbance follows.

Other Intermediates.—Partial separation of two other intermediates was achieved using anion-exchange QAE Sephadex column chromatography. The first approach was to react $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ (1 mol) with a restricted amount of cis-$[VO_2(H_2O)_4]^+$ (4.4 mol), and then load onto the column under air-free conditions (N_2). An alternative method was to load the Re^{IV}_2 complex as a tight band at the top of a Sephadex column, and oxidise with less than a stoichiometric amount of the V^V reactant. On elution with 2 M KCl a band of unreacted (4−) Re^{IV}_2–oxalato complex (peak at 446 nm), followed by an orange-pink band (most of which decayed during the elution procedure), and a more stable pink band were obtained. We had difficulty in isolating both these bands in a pure state at 0 °C, but can report peak positions at ≈495 nm (orange-pink) and ≈550 nm (maroon) for the products. The latter is, on the evidence obtained, different from the intermediate detected by rapid-scan spectrophotometry (peak at 529 nm). The decay of the maroon coloured complex gives a less intense absorbance at ≈775 nm.

Using a batch technique Sephadex resin was saturated with Re^{IV}_2 complex (≈1 × 10^{-4} mol), and then reacted with excess cis-$[VO_2(H_2O)_4]^+$ (≈5 × 10^{-4} mol) in 0.3 M $HClO_4$. The Sephadex became a red colour. From the amount of V^V remaining, absorbance at 350 nm (ε = 128 M^{-1} cm^{-1}), a 2:1 stoichiometry with Re^V_2 formation was indicated.

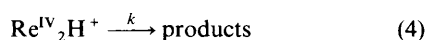*Treatment of Data.*—An unweighted least-squares treatment of kinetic data was used.

Results

Decomposition of Re^{IV}_2.—From the absorbance (A) decay of the 446 nm peak of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ kinetic

Table 2 Effect of $[H^+]$ on rate constants k_{dec} (25 °C) for the spontaneous decomposition of the Re^{IV}_2 complex $[(C_2O_4)_2Re(\mu-O)_2Re(C_2O_4)_2]^{4+}$, $I = 1.00$ M (LiCl)

$[H^+]$/M	$10^5\ k_{dec}/s^{-1}$
0.20	1.41
0.30	1.91
0.40	2.18
0.50	2.11
0.60	2.50
0.60	2.60
0.70	2.75
0.90	2.95
1.00	3.08
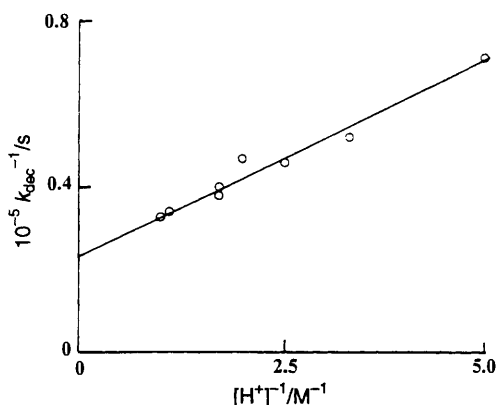
Fig. 1 Linear dependence of k_{dec}^{-1} against $[H^+]^{-1}$ for the spontaneous (25 °C) decay of $[(C_2O_4)_2Re(\mu-O)_2Re(C_2O_4)_2]^{4-}$, $I = 1.0$ M (LiCl)

plots of ln $(A_t - A_\infty)$ against time were carried out. In air such plots are linear to $\approx 60\%$ completion (7–8 h), and rate constants k_{dec} obtained with $[H^+]$ in the range 0.20–1.00 M are as listed in Table 2. Under air-free conditions there was little absorbance change over the first ≈ 2 h indicating that O_2 is an essential component to take the reaction through to completion. A graph of k_{dec} vs. $[H^+]$ (including a value zero at pH 7) exhibits saturation kinetic behaviour consistent with equations (3) and (4). Applying mass balance the de-

$$Re^{IV}_2 + H^+ \underset{}{\overset{K}{\rightleftharpoons}} Re^{IV}_2H^+ \qquad (3)$$

$$Re^{IV}_2H^+ \overset{k}{\longrightarrow} \text{products} \qquad (4)$$

pendence (5) is obtained. A plot of k_{dec}^{-1} against $[H^+]^{-1}$ is

$$k_{dec} = \frac{Kk[H^+]}{1 + K[H^+]} \qquad (5)$$

shown in Fig. 1, from which values of $K = 2.4 \pm 0.2$ M^{-1}, and $k = (4.3 \pm 0.5) \times 10^{-5}$ s^{-1} are obtained.

Oxidation of Re^{IV}_2 *by* cis-$[VO_2(H_2O)_4]^+$.—Stopped-flow rapid-scan spectra indicate formation of an intermediate at 529 nm ($\varepsilon \approx 3800$ M^{-1} cm^{-1}), with isosbestic points at 385, 490 and 617 nm, Fig. 2. Identical first-order rate constants k_{1obs} are obtained from the 446 nm decay, and the absorbance increase at 529 nm with V^V in large excess. The rate constants k_{1obs}, Table 3, are dependent on $[V^V]$ and $[H^+]$, Fig. 3. The rate law can be written as in equation (6). At 25 °C, $I = 1.00$ M (LiClO$_4$), $k_1 =$

$$\text{Rate} = k_{1obs}[Re^{IV}_2] = k_1[Re^{IV}_2][V^V][H^+] \qquad (6)$$

Table 3 First-order rate constants k_{1obs} and k_{2obs} at 25 °C from stopped-flow studies on the cis-$[VO_2(H_2O)_4]^+$ oxidation of the Re^{IV}_2 complex $[(C_2O_4)_2Re(\mu-O)_2Re(C_2O_4)_2]^{4-}$ (1.0–5.0) $\times$ 10^{-5} M monitored at 529 nm, $I = 1.00$ M (LiClO$_4$)

$[H^+]$/M	$10^3\ [V^V]$/M	k_{1obs}/s^{-1}	k_{2obs}/s^{-1}
0.50	1.0	18	0.24
	2.0	34	0.28
	3.1	52	0.29
	4.7	72	0.34
	6.2	102	0.38
	7.8	126	0.41
	9.3	154	0.45
0.40	1.0	15	0.22
	3.5	44	0.28
	6.0	84	0.34
	7.5	107	0.41
0.30	1.0	12	0.23
	2.5	28	0.28
	5.0	55	0.36
	7.5	88	0.43
0.10	1.0	4.1	0.23
	1.5	6.4	0.24
	2.0	7.3	0.28
	2.5	9.5	0.30
	3.5	11.7	0.27
	3.5	9.9^a	0.27^a
	3.5	11.5^b	0.25^b

^{a} $[V^{IV}] = 4.9 \times 10^{-3}$ added. ^{b} $[V^{IV}] = 10.0 \times 10^{-3}$ M added.
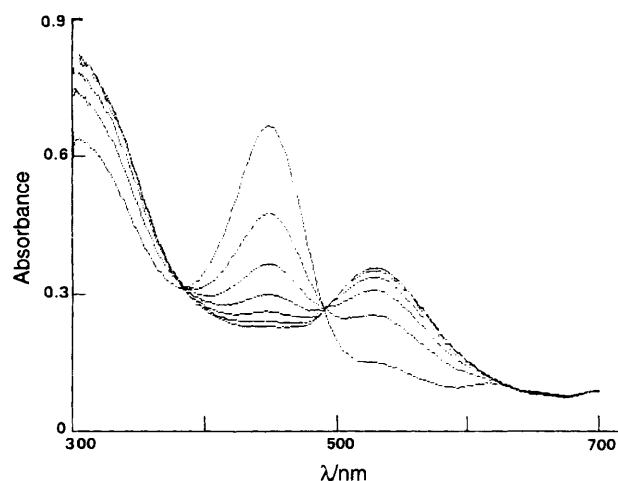
Fig. 2 UV/VIS stopped-flow rapid-scan spectra at 0.15 s intervals for the first stage of the reaction of $[(C_2O_4)_2Re(\mu-O)_2Re(C_2O_4)_2]^{4-}$ with cis-$[VO_2(H_2O)_4]^+$. The decay of the Re^{IV}_2 absorbance (A) at 446 nm is matched by the formation of an intermediate (B) absorbing at 529 nm

$(3.31 \pm 0.07) \times 10^4$ M^{-2} s^{-1}. At $[H^+] = 1.00$ M the $[H^+]$ term can be incorporated along with k_1 to give $k_V = 3.31 \times 10^4$ M^{-1} s^{-1}, thus enabling comparison to be made with k_{Mo}. The second (stopped-flow) phase of the reaction, in which there is a decay of the 529 nm peak, is shown in Fig. 4. First-order rate constants, k_{2obs}, are also listed in Table 3. For k_{2obs} there are two contributing terms, equation (7), both

$$k_{2obs} = k_2[V^V] + k_0 \qquad (7)$$

independent of $[H^+]$, and with k_0 also independent of $[V^V]$, Fig. 5. From the slope and intercept $k_2 = 26.6 \pm 1.4$ M^{-1} s^{-1}, and $k_0 = 0.21 \pm 0.01$ s^{-1}. Addition of $[V^{IV}]$ up to 10 mM produces no inhibition of the reaction.

Oxidation of Re^{IV}_2 *by* $[Mo(CN)_8]^{3-}$.—Biphasic kinetics were monitored at the Re^{IV}_2 peak at 446 nm. The same rate constants were obtained for a check run monitored at 529 nm.
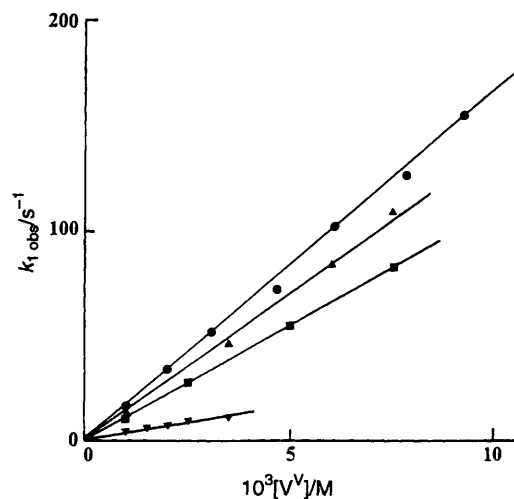
Fig. 3 Dependence of first-order rate constants, k_{1obs} (25 °C) for the first stage of the oxidation of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ with cis-$[VO_2(H_2O)_4]^+$ monitored at 529 nm with $[H^+]/M = 0.50$ (●), 0.40 (▲), 0.30 (■) and 0.10 M (▼), $I = 1.00$ M $(LiClO_4)$
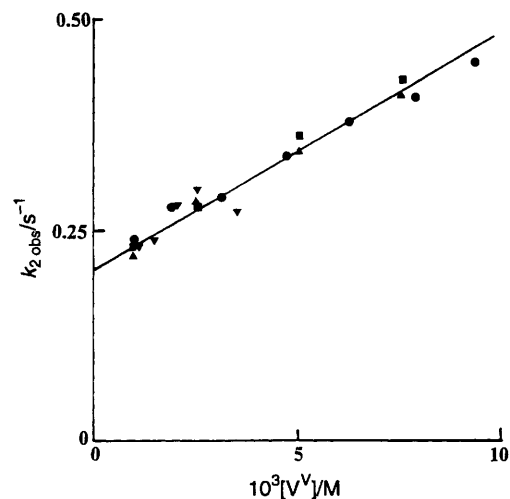

Fig. 5 Dependence of first-order rate constants, k_{2obs} (25 °C), for the second stage of the oxidation of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ with cis-$[VO_2(H_2O)_4]^+$ on the concentration of oxidant with $[H^+]/M = 0.50$ (●), 0.40 (▲), 0.30 (■) and 0.10 (▼), $I = 1.00$ M $(LiClO_4)$
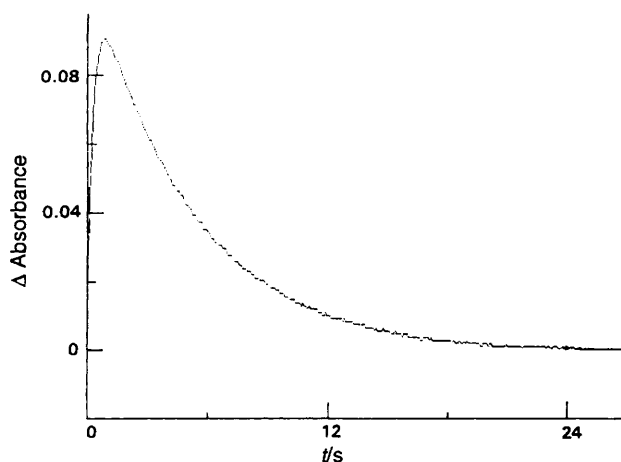

Fig. 4 Stopped-flow plots of absorbance against time at 529 nm indicating the formation and decay of the intermediate observed in Fig. 2 for the oxidation of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ ($\approx 2 \times 10^{-5}$ M) with cis-$[VO_2(H_2O)_4]^+$ (10 mM), $[H^+] = 0.10$ M
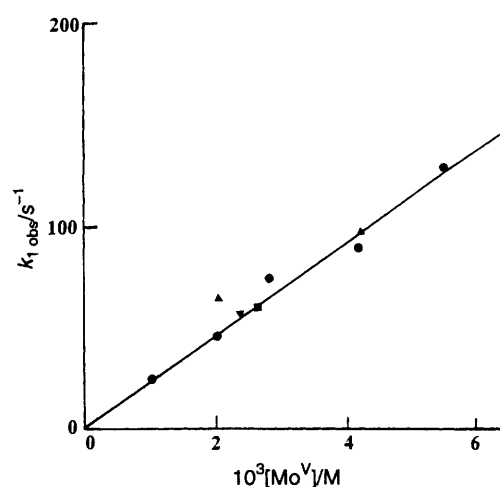

Fig. 6 Dependence of first-order rate constants k_{1obs} (25 °C) for the oxidation of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ with $[Mo(CN)_8]^{3-}$ on the concentration of oxidant at $[H^+] = 0.40$ M (■), 0.20 M (▼), 0.10 M (●), $I = 1.00$ M (LiCl), and $[H^+] = 0.10$ M (▲), $I = 1.00$ M (NaCl)

Table 4 First-order rate constants k_{1obs} and k_{2obs} at 25 °C from stopped-flow studies on the $[Mo(CN)_8]^{3-}$ oxidation of the Re^{IV}_2 complex $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ [(2.3–4.6) $\times 10^{-5}$ M] monitored at 446 nm, $I = 1.00$ M (LiCl)

$[H^+]/M$	$10^3 [Mo^V]/M$	k_{1obs}/s^{-1}	k_{2obs}/s^{-1}
0.40	2.63	59	0.130
0.20	2.39	56	0.140
0.10	1.00	24	0.145
	2.00	46	0.155
	2.05	69*	0.199*
	2.80	74	0.150
	4.11	98*	0.187*
	4.15	90	0.169
	5.50	129	0.163

* $I = 1.00$ M (NaCl).

First-order rate constants k_{1obs} and k_{2obs} are listed in Table 4. The rate law for the first stage is independent of $[H^+]$, Fig. 6, and is given by equation (8), where $k_{Mo} = (2.27 \pm 0.14) \times 10^4$ M^{-1} s^{-1}. The second stage is also independent of $[Mo^V]$, Fig. 7. Therefore the corresponding oxidant-

$$\text{Rate} = k_{1obs}[Re^{IV}_2] = k_{Mo}[Re^{IV}_2][Mo^V] \qquad (8)$$

dependent k_2 term in (7) makes no contribution, and $k_{2obs} = 0.17$ s^{-1} corresponds to k_0. The 15% smaller k_0 value here appears to stem from effects of Li^+, e.g. the association of Li^+ with the $Re^{IV}Re^V$ anion. Thus on adjusting the ionic strength with NaCl instead of LiCl, a value of $k_0 = 0.20$ s^{-1} is obtained, in good agreement with the value $k_0 = 0.21$ s^{-1} for the V^V study.

Discussion

The spontaneous decay of the Re^{IV}_2-oxalato complex $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ is extremely slow ($\approx 3\%$ in 20 d) at neutral pH, but more rapid in acidic solutions. This suggests a mechanism for decay involving cleavage of the oxo bridges and/or aquation of $C_2O_4^{2-}$.[15] The reaction studied in air with $[H^+]$ in the range 0.20–1.00 M, using different acids ($I = 1.00$ M), progresses to colourless perrhenate(VII) within 24 h at 25 °C. If air-free conditions are adopted the reaction is slow initially with $< 3\%$ absorbance decay over 2 h (cf. 20% decay in
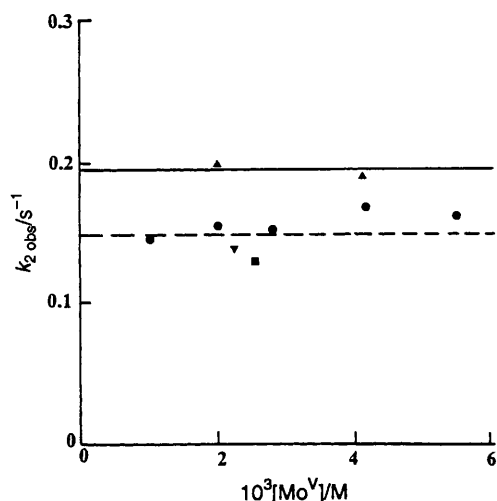
Fig. 7 Non-dependence of first-order rate constants k_{2obs} (25 °C) for the oxidation of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ with $[Mo(CN)_8]^{3-}$ on the concentration of oxidant with $[H^+] = 0.40$ M ($\blacksquare$), 0.20 M ($\blacktriangledown$), 0.10 M ($\bullet$), $I = 1.00$ M (LiCl), and $[H^+] = 0.10$ M ($\blacktriangle$) at $I = 1.00$ M (NaCl)

air). Over longer periods the reaction speeds up possibly due to traces of O_2 entering the system, where O_2 is required to take the reaction through to the Re^{VII} product. In air the saturation kinetic behaviour observed is in accordance with a protonation equilibrium ($K = 2.4$ M^{-1}), followed by a rate-determining decay process (4.3×10^{-5} s^{-1}). Subsequent steps involving O_2 appear to be relatively rapid.

Not surprisingly in view of these observations, the stoichiometries for the oxidations of $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ with cis-$[VO_2(H_2O)_4]^+$ and $[Mo(CN)_8]^{3-}$ are both 6:1 mol of oxidant per Re^{IV}_2. The first stage of oxidation gives a product with an absorbance maximum at 529 nm, Fig. 2. The product is assigned as $Re^{IV}Re^V$ for a number of reasons. Firstly the kinetics give no evidence for two stages, and three isosbestic points are retained in the rapid-scan spectra. In the second phase of the reaction a spontaneous decay (k_0) is obtained consistent with an odd-electron $Re^{IV}Re^V$ product. Thirdly a maroon intermediate (peak at ≈ 550 nm), separated by chromatography after reacting Re^{IV}_2 with less than full stoichiometric amounts of V^V, is more likely to be Re^V_2 by analogy with the chemistry reported in ref. 7.

The stopped-flow studies on the V^V oxidation of Re^{IV}_2 give a single term rate law $k_1[Re^{IV}_2][V^V][H^+]$, equation (6). Protonation of Re^{IV}_2 is clearly one way in which the reaction might proceed. However this does not appear to be the case since the corresponding oxidation with $[Mo(CN)_8]^{3-}$ gives no $[H^+]$ dependence. We therefore associate the $[H^+]$ dependence with the $VO_2^+ \longrightarrow VO^{2+}$ conversion and protonation of the V^V reactant to give $VO(OH)^{2+}$. What is unusual is that for the second phase of the reaction, $k_{2obs} = k_2[V^V] + k_0$, the k_2 term is now independent of $[H^+]$. This suggests that V^V reacts with $Re^{IV}Re^V$ by a different mechanism, possibly one involving O-atom transfer to assist conversion of the second Re^{IV} to Re^V. Some caution is required however since in the V^V oxidation of $[Mo(CN)_8]^{4-}$ the kinetic rate law has $[H^+]$-dependant terms.[16] There are conflicting trends here which need to be addressed further.

At $[H^+] = 1.0$ M, the rate constant k_1 for the V^V oxidation of Re^{IV}_2 gives $k_V = 3.31 \times 10^4$ M^{-1} s^{-1}, which can be compared with the second-order rate constant $k_{Mo} = 2.27 \times 10^4$ M^{-1} s^{-1} for the Mo^V oxidation. The driving force is less in the case of the Mo^V oxidant, but reorganisation-energy considerations almost certainly favour Mo^V, thus helping to explain the similarity of the rate constants. Also the electron-self-exchange rate constant for the reaction of $[Mo(CN)_8]^{4-}$ with $[Mo(CN)_8]^{3-}$ has been
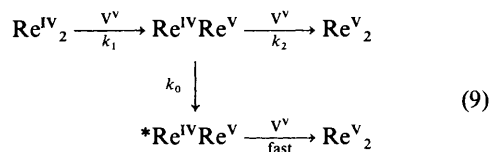
determined and is large at 3×10^4 M^{-1} s^{-1}.[17] The k_2 term for the second stage of the V^V oxidation is much smaller (26.6 M^{-1} s^{-1}) than k_V, while in the $[Mo(CN)_8]^{3-}$ reaction no $[Mo^V]$-dependant term corresponding to k_2 is observed. This supports the belief that a different mechanism is effective in the second stage of the V^V oxidation.

Similar UV/VIS spectra are noted for three Re^{IV}_2 complexes known to have di-μ-oxo structures, Table 1. Wieghardt and co-workers[7] have determined the structure of the analogous purple Re^V_2 complex (peak at 556 nm), which has two (anti) terminal oxo groups in addition to the di-μ-oxo ligands. A similar anti structure (I) may be formed in the case of the Re^V_2-oxalate complex, but at present the syn structure (II) cannot be ruled out.

I   II
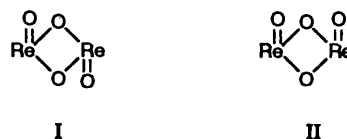
A key question with oxalate is whether the $Re^{IV}_2 \longrightarrow Re^V_2$ conversion is achieved with all four oxalates remaining chelated, in which case (with the additional oxo groups) the Re atoms become seven-co-ordinate, or whether two of the oxalates become monodentate. The (relative) difficulty in converting $Re^{IV}Re^V$ to Re^V_2 in the oxalate case may be related to the need for changes in ligation as the Re^V forms.

The mechanism proposed here can be summarised as in equation (9), where $*Re^{IV}Re^V$ represents a second form of the

$$Re^{IV}_2 \xrightarrow{\ \ V^V\ \ }_{k_1} Re^{IV}Re^V \xrightarrow{\ \ V^V\ \ }_{k_2} Re^V_2$$
$$k_0 \downarrow$$
$$*Re^{IV}Re^V \xrightarrow[\text{fast}]{\ \ V^V\ \ } Re^V_2 \tag{9}$$

$Re^{IV}Re^V$ intermediate. Both stages of the V^V oxidation are unaffected by the addition of up to 10 mM V^{IV}. This amount of V^{IV} produces a significant inhibition in the corresponding oxidation of the Re^{IV}_2-edta complex 2. We have no information as to the identity of the orange-pink product detected in chromatographic separation of intermediates. However in the case of the maroon product spontaneous decay gives a further species with a less intense peak at ≈ 775 nm. Blue colours have previously been associated with the mononuclear Re^V state.[7] Since this process also gives a peak at 460 nm disproportionation to give Re^{IV} and Re^{VI} products is a further possibility. From studies on the pulse radiolysis reduction of perrhenate(VII) it would appear that rhenium(VI) as $[ReO_4]^{2-}$, peak at 290 nm ($\varepsilon = 1700$ M^{-1} cm^{-1}), is extremely unstable in neutral solution.[18] Cathodic reduction of the NMe_4^+ salt of $[ReO_4]^-$ in acetonitrile gives olive $[ReO_4]^{2-}$ which is very air sensitive.[19]

To summarise, as compared to studies on the Re^{IV}_2-edta complex[6] a rather different outcome is observed. The work described suggests that oxalate provides a better opportunity for studying in detail the progression of oxidation from Re^{IV}_2 with the formation of different intermediate states. In the studies on the 1,4,7-triazacyclononane-co-ordinated Re^{IV}_2 the emphasis has so far been on structural aspects.[7] The fact that strong oxidants are required for oxidation is in part due to the protection offered (in the present case) by the oxalate ligands, which impede changes in the degree of hydrolysis of Re. The special stability of di-μ-oxo Re^{IV}_2 complexes, and to a lesser extent Re^V_2 is a feature of

the chemistry observed. The latter stages of oxidation are achieved more easily than the earlier stages.

Finally, since comparison between Re and Tc are of interest,[20] we note that the oxalato complex $K_4[(C_2O_4)_2Tc(\mu-O)_2Tc(C_2O_4)_2]\cdot 3H_2O$ has been prepared, and the crystal structure determined. This is identical to the Re^{IV}_2-oxalato complex, with a Tc–Tc separation of 2.361 Å (cf. 2.362 Å for Re).[21]

Acknowledgements

References

1 K. A. Connor and R. A. Walton, in Comprehensive Coordination Chemistry, eds. G. Wilkinson, J. A. McCleverty and R. D. Gillard, vol. 4, pp. 125–213.
2 D. Sen and P. Ray, J. Indian Chem. Soc., 1953, 30, 171.
3 B. Jezowska-Trzebiatsoska and S. Wajda, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 1958, 6, 217.
4 S. M. Boshida and F. S. Shodiev, Proc. Int. Conf. Coord. Chem., 1973, 342.
5 T. Lis, Acta. Crystallogr., Sect. B, 1975, 31, 1594.
6 S. Ikari, T. Ito, W. McFarlane, M. Nasreldin, B.-L. Ooi, Y. Sasaki and A. G. Sykes, J. Chem. Soc., Dalton Trans., 1993, 2621.
7 G. Böhm, K. Wieghardt, B. Nuber and J. Weiss, Inorg. Chem., 1991, 30, 3464.
8 G. W. Watt and R. J. Thompson, Inorg. Synth., 1963, 7, 189.
9 W. Latimer, Oxidation States of the Elements and their Potentials in Aqueous Solution, 2nd edn., Prentice Hall Inc., Englewood Cliffs, NJ, 1952.
10 J. G. Leipoldt, L. D. C. Bok and P. J. Gilliers, Z. Anorg. Allg. Chem., 1974, 407, 350.
11 S. S. Basson, J. G. Leipoldt, L. D. C. Bok, J. S. van Vollenhoven and P. J. Gilliers, Acta. Crystallogr., Sect. B., 1980, 36, 1765.
12 J. G. Leipoldt, S. S. Basson and A. Roodt, Adv. Inorg. Chem., 1993, 40, 283.
13 R. J. Campion, N. Purdie and N. Sutin, Inorg. Chem., 1964, 3, 1091.
14 W. C. E. Higginson and A. G. Sykes, J. Chem. Soc., 1962, 2841.
15 See, for example, H.-F. Lee and W. C. E. Higginson, J. Chem. Soc. A, 1970, 2836.
16 L. Thomas and K. W. Hicks, Inorg. Chem., 1974, 13, 749.
17 K. W. Hicks and M. A. Hurless, Inorg. Chim. Acta., 1983, 74, 229.
18 G. A. Lawrance and D. F. Sangster, Polyhedron, 1985, 4, 1095.
19 L. Astheimer and K Schwochau, J. Inorg. Nucl. Chem., 1976, 38, 1131.
20 J. Baldas, Adv. Inorg. Chem., 1994, 41, 1–123.
21 R. Alberto, G. Anderegg and A. Albinato, Inorg. Chim. Acta., 1990, 178, 125.