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Kinetics and mechanisms of the reduction of a *cis*-dioxoruthenium(VI) complex by $[Ni(tacn)_2]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ †

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The kinetics of the reduction of *cis*-$[Ru^{VI}L(O)_2]^{2+}$ (L = *N*,*N*,*N*′,*N*′-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine) by $[Ni(tacn)_2]^{2+}$ (tacn = 1,4,7-triazacyclononane) and $[Fe(H_2O)_6]^{2+}$ have been studied in aqueous acidic solutions. Both reactions have the following stoichiometry: $2M^{II}$ + *cis*-$[Ru^{VI}L(O)_2]^{2+}$ + $2H^+$ ⟶ $2M^{III}$ + *cis*-$[Ru^{IV}L(O)(OH_2)]^{2+}$ (M = Ni or Fe). Two distinct steps were observed for both reactions and these are assigned to $Ru^{VI} \longrightarrow Ru^{V}$ and $Ru^{V} \longrightarrow Ru^{IV}$. Both steps are first order in $[Ru^{VI}]$ and $[M^{II}]$. For the reduction by $[Ni(tacn)_2]^{2+}$, the activation parameters ($I = [H^+] = 0.1$ mol dm^{-3}) for the first step are $\Delta H^‡ = 13.4 \pm 1.0$ kJ mol^{-1} and $\Delta S^‡ = -111 \pm 10$ J mol^{-1} K^{-1}; for the second reaction, $\Delta H^‡ = 28.5 \pm 1.5$ kJ mol^{-1} and $\Delta S^‡ = -110 \pm 10$ J mol^{-1} K^{-1}. The rate constant for the first step is independent of acid concentration, an outer-sphere mechanism is proposed and a self-exchange rate of 2×10^4 dm^3 mol^{-1} s^{-1} for the *cis*-$[Ru^{VI}L(O)_2]^{2+}$/*cis*-$[Ru^{V}L(O)_2]^{+}$ couple is estimated using the Marcus cross-relation. The rate constant of the second step increases with $[H^+]$ and it reaches saturation at high $[H^+]$. A mechanism involving a pre-equilibrium protonation of *cis*-$[Ru^{V}L(O)_2]^{+}$ followed by outer-sphere electron transfer is proposed. For the reduction by $[Fe(H_2O)_6]^{2+}$, rate constants for both steps are independent of acid concentration in the range of pH = 1–3. The activation parameters ($I = 1.0$ mol dm^{-3}, pH = 1.0) for the first step are $\Delta H^‡ = 32.5 \pm 1.5$ kJ mol^{-1} and $\Delta S^‡ = -52.5 \pm 7$ J mol^{-1} K^{-1}; while for the second step, $\Delta H^‡ = 17.3 \pm 1.2$ kJ mol^{-1} and $\Delta S^‡ = -140 \pm 13$ J mol^{-1} K^{-1}. An outer-sphere mechanism is proposed for the first step and an inner-sphere mechanism is proposed for the second step.

Introduction

There exists an extensive series of ruthenium oxo complexes with oxidation states ranging from IV to VIII.[1–2] The most common classes of ruthenium oxo complexes are monooxoruthenium(IV) and *trans*-dioxoruthenium(VI), which are in general potent oxidants and there have been numerous reports on their reactions with organic substrates.[1–4] We have been studying the oxidation of *inorganic* substrates by ruthenium oxo complexes, since much less is known on this aspect. We have reported the kinetics and mechanisms of the oxidation of $[Fe(H_2O)_6]^{2+}$,[5] iodide,[6] sulfite,[7] hypophosphite and phosphite[8] by two *trans*-dioxoruthenium(VI) complexes, *trans*-$[Ru(tmc)(O)_2]^{2+}$ and *trans*-$[Ru(N_2O_2)(O)_2]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; N_2O_2 = 1,12-dimethyl-3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclopentadecane). These complexes are found to react *via* a variety of pathways including outer-sphere one-electron, inner-sphere one-electron, oxygen-atom transfer and hydride abstraction. Compared to *trans*-dioxoruthenium(VI) complexes, *cis*-dioxoruthenium(VI) complexes are relatively rare, and there are only two well characterized examples that were reported by Che and coworkers, $[Ru^{VI}Cn^*(CF_3CO_2)(O)_2]ClO_4$ (Cn* = 1,4,7-trimethyl-1,4,7-triazacyclononane)[9] and *cis*-$[Ru^{VI}L(O)_2](ClO_4)_2$ (L = *N*,*N*,*N*′,*N*′-tetramethyl-3,6-dimethyl-3,6-diazaoctane-1,8-diamine).[10] These complexes are potent oxidants and their reactions with organic substrates have been studied.[11,12] Herein the kinetics and mechanisms of the reduction of *cis*-$[Ru^{VI}L(O)_2]^{2+}$ (Fig. 1) by two inorganic reductants, $[Ni^{II}(tacn)_2](ClO_4)_2$ (tacn = 1,4,7-triazacyclononane) and $[Fe(H_2O)_6]^{2+}$ are reported. The reactivities of these complexes would make a nice comparison with that of *trans*-$[Ru(tmc)(O)_2]^{2+}$,[13] since both tmc and L are tetradentate tertiary amine ligands. The redox potentials of these two ruthenium oxo complexes, which have been determined by cyclic voltammetry,[10,13] are shown below (at pH = 1.0, in volts *vs*. NHE, L′ = tmc):

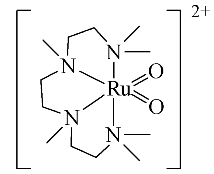

Fig. 1 Structure of *cis*-$[Ru^{VI}L(O)_2]^{2+}$.

$$\textit{cis}\text{-}[Ru^{VI}L(O)_2]^{2+} \xrightarrow{+1.01} \textit{cis}\text{-}[Ru^{V}L(O)_2]^{+} \xrightarrow{+1.07}$$
$$\textit{cis}\text{-}[Ru^{IV}L(O)(OH_2)]^{2+} \xrightarrow{+0.87}$$
$$\textit{cis}\text{-}[Ru^{III}L(OH)(OH_2)]^{2+} \xrightarrow{+0.50} \textit{cis}\text{-}[Ru^{II}L(OH_2)_2]^{2+}$$

$$\textit{trans}\text{-}[Ru^{VI}L'(O)_2]^{2+} \xrightarrow{+0.56} \textit{trans}\text{-}[Ru^{V}L'(O)_2]^{+} \xrightarrow{+1.24}$$
$$\textit{trans}\text{-}[Ru^{IV}L'(O)(OH_2)]^{2+} \xrightarrow{+0.60} \textit{trans}\text{-}[Ru^{III}L'(OH)(OH_2)]^{2+}$$

$[Ni(tacn)]^{2+}$ is chosen as the reductant because its redox potential (E^0 for $[Ni(tacn)_2]^{3+/2+}$ = 0.94 V)[13] is close to that of *cis*-$[Ru^{VI}L(O)_2]^{2+}$, hence the reaction should occur at a convenient rate. It is also a one-electron outer-sphere reductant so that self-exchange rates of the ruthenium system may be estimated using Marcus theory. On the other hand, with $[Fe(H_2O)_6]^{2+}$ as reductant, both outer-sphere and inner-sphere pathways are possible.[5]

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† Electronic supplementary information (ESI) available: spectrophotometric titration of *cis*-$[Ru^{VI}L(O)_2]^{2+}$ with $[Fe(H_2O)_6]^{2+}$. See http://www.rsc.org/suppdata/dt/b2/b202230c/

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Experimental

Materials

The complexes *cis*-[Ru^{VI}L(O)$_2$](ClO$_4$)$_2$ and [Ni^{II}(tacn)$_2$](ClO$_4$)$_2$ were prepared by the literature methods.[10,14] Ammonium iron(II) sulfate was obtained from RDH and was used as received. Solutions of iron(II) were standardized with potassium permanganate. Water for kinetic experiments was distilled twice from alkaline permanganate. Ionic strength was maintained with sodium trifluoroacetate.

Kinetics

Kinetic experiments were performed under pseudo-first-order conditions using a Hi-Tech SF-61 stopped-flow spectrophotometer equipped with a diode-array detector. Pseudo-first-order rate constants, k_{obs}, were obtained by non-linear least-squares fits of A_t to time t according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbances, respectively.

Results and discussion

Reaction with [Ni^{II}(tacn)$_2$]$^{2+}$

Spectral changes and stoichiometry. Preliminary repetitive scanning (Fig. 2a) of a solution of *cis*-[Ru^{VI}L(O)$_2$]$^{2+}$ (5 × 10^{-5} mol dm^{-3}) with an excess of [Ni(tacn)$_2$]$^{2+}$ (1 × 10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} CF$_3$CO$_2$H revealed rapid growth of a peak at around 315 nm, consistent with the formation of [Ni(tacn)$_2$]$^{3+}$ (λ_{max} = 312 nm, $\varepsilon = 1.01 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[14] From the final absorbance at 312 nm and taking into account the absorbance of the ruthenium product, it can be deduced that two moles of Ni^{III} were produced from one mole of Ru^{VI}. The overall reaction can be represented by eqn. (1):

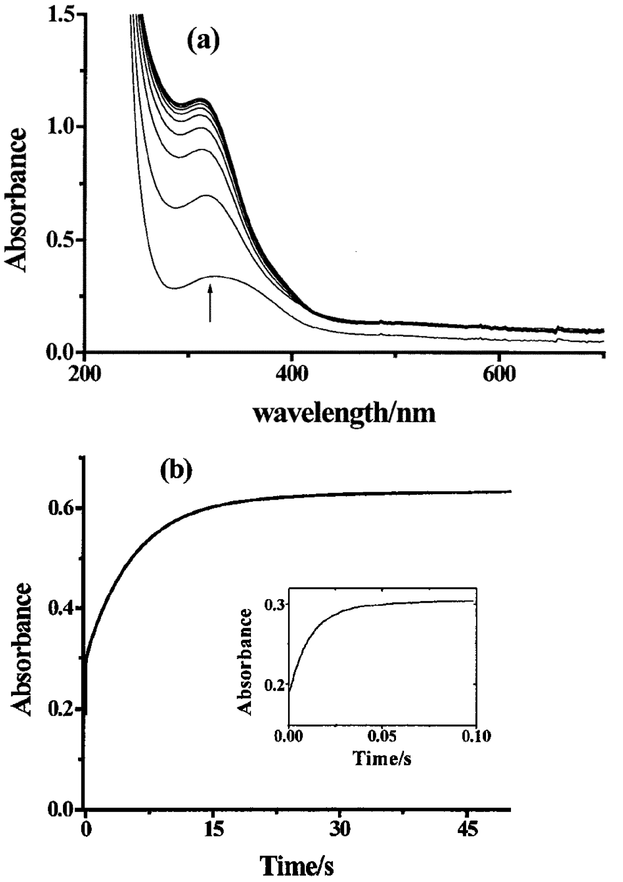

Fig. 2 (a) Spectral changes at 5 s intervals during the reduction of *cis*-[Ru^{VI}L(O)$_2$]$^{2+}$ (5 × 10^{-5} mol dm^{-3}) by excess [Ni(tacn)$_2$]$^{2+}$ (1 × 10^{-3} mol dm^{-3}) at T = 298 K, I = 0.1 mol dm^{-3} and pH = 1.0. (b) Absorbance changes *vs.* time at 320 nm. The inset shows the first step.

$$2[\mathrm{Ni^{II}(tacn)_2}]^{2+} + cis\text{-}[\mathrm{Ru^{VI}L(O)_2}]^{2+} + 2\mathrm{H^+} \longrightarrow 2\,[\mathrm{Ni^{III}(tacn)_2}]^{3+} + cis\text{-}[\mathrm{Ru^{IV}L(O)(OH)_2}]^{2+} \quad (1)$$

Kinetics. The kinetics of the reaction were monitored at 320 nm, and two well separated consecutive steps were observed (Fig. 2b). In the presence of at least a 20-fold excess of [Ni^{II}(tacn)$_2$]$^{2+}$, both steps obeyed pseudo-first-order kinetics. The pseudo-first-order rate constants were independent of [Ru^{VI}] (5 × 10^{-5}–2 × 10^{-4} mol dm^{-3}), but depended linearly on [Ni^{II}(tacn)$_2$]$^{2+}$ (5 × 10^{-4}–5 × 10^{-3} mol dm^{-3}). Representative second-order rate constants for the first (k_{Ni}) and the second (k_{Ni}' steps are shown in Table 1. An increase in the ionic strength was found to enhance the rates of both steps.

The effects of acidity on the rate constants were investigated in the concentration range [H$^+$] = 0.005–0.1 mol dm^{-3}. At constant ionic strength (0.1 mol dm^{-3}) the rate of the first step was insensitive to changes in acid concentration, but the rate of the second step increased with [H$^+$], and it reached saturation at high [H$^+$] (Fig. 3). A plot of 1/k_{Ni}' *versus* 1/[H$^+$] gives a straight line (Fig. 3), this is consistent with the following relationship:

$$k_{Ni}' = K_p k_{et}[\mathrm{H^+}]/(1 + K_p[\mathrm{H^+}]) \quad (2)$$

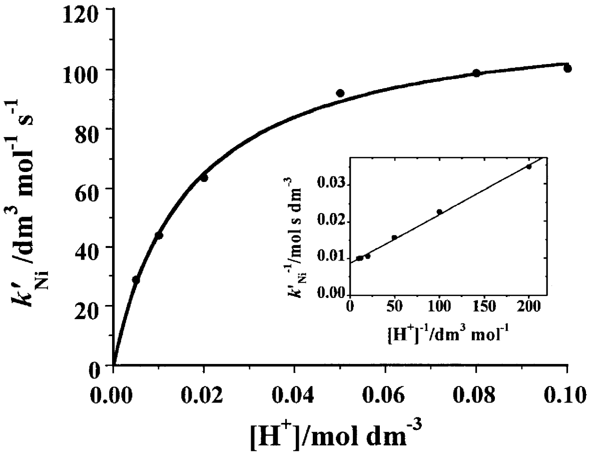

Fig. 3 Plot of k_{Ni}' *vs.* [H$^+$] for the reduction of *cis*-[Ru^{VI}L(O$_2$)]$^{2+}$ by [Ni(tacn)$_2$]$^{2+}$ at I = 0.1 mol dm^{-3} and T = 298 K. The inset shows the corresponding plot of 1/k_{Ni}' *vs.* 1/[H$^+$].

At 298 K and I = 0.1 mol dm^{-3}, k_{et} = (1.19 ± 0.29) × 10^2 dm^3 mol^{-1} s^{-1} and K_p = 60.1 ± 3.9 dm^3 mol^{-1}, using a non-linear least-squares fit to eqn. (2).

Activation parameters were obtained from plots of ln(k_{Ni}/T) and ln(k_{Ni}'/T) *versus* 1/T according to the Eyring equation. At I = [H$^+$] = 0.1 mol dm^{-3} the values for the first step are $\Delta H^\ddagger$ = 13.4 ± 1.0 kJ mol^{-1} and $\Delta S^\ddagger$ = −111 ± 10 J mol^{-1} K^{-1}, and for the second reaction, $\Delta H^\ddagger$ = 28.5 ± 1.5 kJ mol^{-1} and $\Delta S^\ddagger$ = −110 ± 10 J mol^{-1} K^{-1}.

Mechanism. E^0 for the [Ru^{VI}L(O)$_2$]$^{2+}$/[Ru^{V}L(O)$_2$]$^+$ couple is pH independent but E^0 for the [Ru^{V}L(O)$_2$]$^+$/[Ru^{IV}L(O)(OH$_2$)]$^{2+}$ couple shifts cathodically by 0.118 V for each increase in pH unit. The E^0 of [Ni(tacn)$_2$]$^{3+}$ is reported to be 0.94 V[13] in the pH range of 1–3. Thermodynamically both [Ru^{VI}L(O)$_2$]$^{2+}$ and [Ru^{V}L(O)$_2$]$^+$ (at pH ≲ 2) are capable of oxidizing [Ni(tacn)$_2$]$^{2+}$ to [Ni(tacn)$_2$]$^{3+}$. Thus the two steps observed are assigned to Ru^{VI} ⟶ Ru^{V} and Ru^{V} ⟶ Ru^{IV}:

$$cis\text{-}[\mathrm{Ru^{VI}L(O)_2}]^{2+} + [\mathrm{Ni^{II}(tacn)_2}]^{2+} \longrightarrow cis\text{-}[\mathrm{Ru^{V}L(O)_2}]^{+} + [\mathrm{Ni^{III}(tacn)_2}]^{3+} \quad (3)$$

$$cis\text{-}[\mathrm{Ru^{V}L(O)_2}]^{+} + [\mathrm{Ni^{II}(tacn)_2}]^{2+} + 2\mathrm{H^+} \longrightarrow cis\text{-}[\mathrm{Ru^{IV}L(O)(OH_2)}]^{2+} + [\mathrm{Ni^{III}(tacn)_2}]^{3+} \quad (4)$$

Table 1 Representative second-order rate constants for the reduction of *cis*-$[RuL(O)_2]^{2+}$ by $[Ni^{II}(tacn)_2]^{2+}$

T/K	$[H^+]$/mol dm^{-3}	I/mol dm^{-3}	k_{Ni}/dm^3 mol^{-1} s^{-1}	k_{Ni}'/dm^3 mol^{-1} s^{-1}
298.0	0.005	0.10	$(4.54 \pm 0.08) \times 10^4$	$(2.86 \pm 0.04) \times 10^1$
298.0	0.010	0.10	$(5.29 \pm 0.18) \times 10^4$	$(4.39 \pm 0.11) \times 10^1$
298.0	0.020	0.10	$(4.64 \pm 0.94) \times 10^4$	$(6.36 \pm 0.13) \times 10^1$
298.0	0.050	0.10	$(4.78 \pm 0.11) \times 10^4$	$(9.20 \pm 0.09) \times 10^1$
298.0	0.080	0.10	$(4.43 \pm 0.16) \times 10^4$	$(9.89 \pm 0.08) \times 10^1$
298.0	0.100	0.10	$(4.52 \pm 0.02) \times 10^4$	$(1.00 \pm 0.06) \times 10^2$
298.0	0.010	0.01	$(2.09 \pm 0.05) \times 10^4$	$(2.06 \pm 0.06) \times 10^1$
298.0	0.010	0.04	$(2.97 \pm 0.05) \times 10^4$	$(3.08 \pm 0.03) \times 10^1$
298.0	0.010	0.07	$(3.42 \pm 0.03) \times 10^4$	$(3.88 \pm 0.02) \times 10^1$
278.1	0.100	0.10	$(2.74 \pm 0.06) \times 10^4$	$(4.73 \pm 0.02) \times 10^1$
288.0	0.100	0.10	$(3.46 \pm 0.06) \times 10^4$	$(7.31 \pm 0.04) \times 10^1$
308.0	0.100	0.10	$(5.36 \pm 0.12) \times 10^4$	$(1.30 \pm 0.04) \times 10^2$

$Ru^{VI} \longrightarrow Ru^{V}$. No acidity dependence (pH 1–3) was observed in this step, suggesting that a pathway involving the protonated dioxoruthenium(VI) species, $[Ru^{VI}L(O)(OH)]^{3+}$, is insignificant. The UV-Vis spectrum of *cis*-$[Ru^{VI}L(O)_2]^{2+}$ was found to remain unchanged in acid concentrations of up to 5 mol dm^{-3}, and the pK_a of $[Ru^{VI}L(O)(OH)]^{3+}$ is estimated to be $\leqslant 3$. The mechanism for this step [eqn. (3)] is most likely a simple outer-sphere electron transfer, since both reactants are substitution inert. The self-exchange rate for the $[Ru^{VI}L(O)_2]^{2+}/[Ru^{V}L(O)_2]^{+}$ couple (k_{11}) can therefore be estimated from the rate data and the overall free energy change using the Marcus cross-relation (neglecting work term):[15,16]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \qquad (5)$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4\log(k_{11}k_{22}/Z^2)} \qquad (6)$$

The equilibrium constant of the reaction $K_{12} = 15.3$, is calculated from E^0 for the $[Ru^{VI}L(O)_2]^{2+}/[Ru^{V}L(O)_2]^{+}$ (1.01 V)[10] and $[Ni^{III}(tacn)_2]^{3+}/[Ni^{II}(tacn)_2]^{2+}$ (0.94 V)[15] couples. The self-exchange rate for $[Ni^{III}(tacn)_2]^{3+}/[Ni^{III}(tacn)_2]^{2+}$, k_{22}, is taken as 6.0×10^3 dm^3 mol^{-1} s^{-1}.[14] The average value of k_{12} for the cross reaction at $I = 0.1$ mol dm^{-3} and pH 1–3 is 4.6×10^4 dm^3 mol^{-1} s^{-1}. The value of k_{11} so obtained is 2×10^4 dm^3 mol^{-1} s^{-1}. This is slightly lower than the value of 1×10^5 dm^3 mol^{-1} s^{-1} for that of the *trans*-$[Ru(tmc)(O)_2]^{2+}$/*trans*-$[Ru(tmc)(O)_2]^{+}$ couple. This calculated value is also consistent with X-ray structural data,[10] which indicate that *cis*-$[Ru^{VI}L(O)_2]^{2+}$ and *cis*-$[Ru^{V}L(O)_2]^{+}$ have similar geometries, with only small differences in Ru=O bond lengths (0.04 Å) and O–Ru–O angles (3°).

$Ru^{V} \longrightarrow Ru^{IV}$. The variation of k_{Ni}' with pH is consistent with a pre-equilibrium protonation of *cis*-$[Ru^{V}L(O)_2]^{+}$ followed by electron transfer, eqns. (7)–(9):

$$cis\text{-}[Ru^{V}L(O)_2]^{+} + H^{+} \underset{}{\overset{K_p}{\rightleftharpoons}} cis\text{-}[Ru^{V}L(O)(OH)]^{2+} \qquad (7)$$

$$cis\text{-}[Ru^{V}L(O)(OH)]^{2+} + [Ni(tacn)_2]^{2+} \xrightarrow{k_{et}} cis\text{-}[Ru^{IV}L(O)(OH)]^{+} + [Ni(tacn)_2]^{3+} \qquad (8)$$

$$cis\text{-}[Ru^{IV}(L)(O)(OH)]^{+} + H^{+} \xrightarrow{\text{fast}} cis\text{-}[Ru^{IV}L(O)(OH_2)]^{2+} \qquad (9)$$

According to this scheme, the pK_a of *cis*-$[Ru^{V}L(O)(OH)]^{2+}$ is found to be 1.8, which is lower than the value of 2.8 for *trans*-$[Ru^{V}(tmc)(O)(OH)]^{2+}$. The mechanism for the subsequent electron-transfer [eqn. (8)] is most likely also outer-sphere, as in the reduction of Ru^{VI} to Ru^{V}. However, in this case the self-exchange rate for the *cis*-$[Ru^{V}L(O)(OH)]^{2+}$/*cis*-$[Ru^{IV}L(O)(OH)]^{+}$ couple cannot be readily calculated using the Marcus equations, since E^0 for this couple cannot be determined without knowing the pK_a of *cis*-$[Ru^{IV}L(O)(OH_2)]^{2+}$. An experimental determination of this pK_a is not straightforward, however, since *cis*-$[Ru^{IV}L(O)(OH_2)]^{2+}$ disproportionates at pH > 4.5.[10]

Reaction with Fe^{2+}

Spectral changes and stoichiometry. Rapid spectral changes were observed when a solution of *cis*-$[Ru^{VI}L(O)_2]^{2+}$ was mixed with an excess of $[Fe(H_2O)_6]^{2+}$ in acidic solution (Fig. 4a).

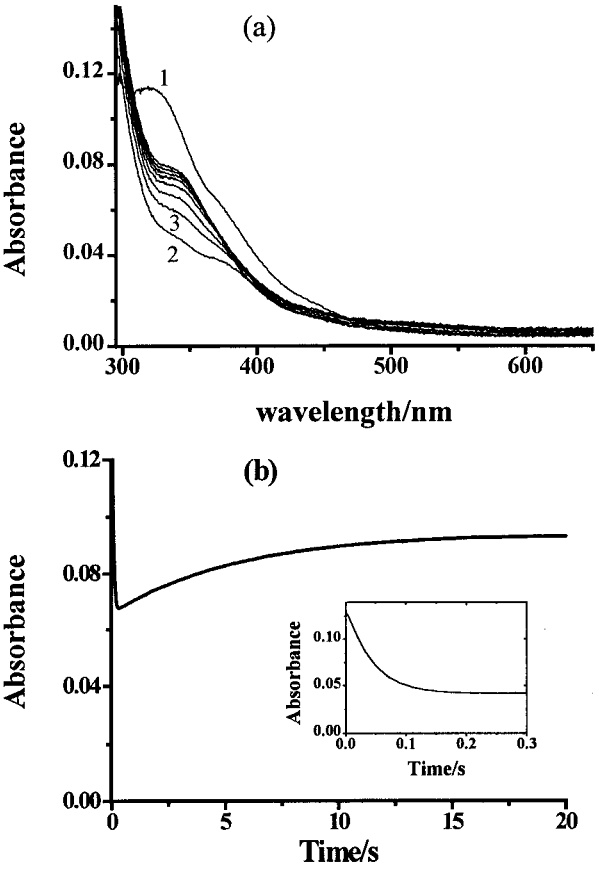

Fig. 4 (a) Spectral changes at 2 s intervals during the reduction of *cis*-$[Ru^{VI}L(O)_2]^{2+}$ (1×10^{-4} mol dm^{-3}) by excess $[Fe(H_2O)_6]^{2+}$ (1×10^{-3} mol dm^{-3}) at T = 298 K, I = 1.0 mol dm^{-3} and pH = 1.0. (b) Absorbance changes *vs.* time at 325 nm. The inset shows the first step.

Spectrophotometric titration performed by the addition of small aliquots of $[Fe(H_2O)_6]^{2+}$ to *cis*-$[Ru^{VI}L(O)_2]^{2+}$ at pH = 1.0 showed that two moles of Fe^{2+} react with one mole of Ru^{VI} (Fig. S1, ESI). Thus the stoichiometry of the reaction can be represented by eqn. (10):

$$cis\text{-}[Ru^{VI}L(O)_2]^{2+} + 2[Fe(H_2O)_6]^{2+} + 2H^{+} \longrightarrow cis\text{-}[Ru^{IV}L(O)(OH_2)]^{2+} + 2[Fe(H_2O)_6]^{3+} \qquad (10)$$

Table 2 Representative second-order rate constants for the reduction of *cis*-$[Ru^{VI}L(O)_2]^{2+}$ by Fe^{2+}

T/K	I/mol dm^{-3}	$[H^+]$/mol dm^{-3}	k_{Fe}/dm^3 mol^{-1} s^{-1}	k_{Fe}'/dm^3 mol^{-1} s^{-1}
298.0	1.0	0.001	$(2.75 \pm 0.11) \times 10^4$	$(2.88 \pm 0.05) \times 10^2$
298.0	1.0	0.010	$(2.73 \pm 0.11) \times 10^4$	$(2.23 \pm 0.04) \times 10^2$
298.0	1.0	0.030	$(2.73 \pm 0.08) \times 10^4$	$(2.67 \pm 0.04) \times 10^2$
298.0	1.0	0.050	$(2.74 \pm 0.09) \times 10^4$	$(2.45 \pm 0.06) \times 10^2$
298.0	1.0	0.070	$(2.72 \pm 0.12) \times 10^4$	$(2.50 \pm 0.06) \times 10^2$
298.0	1.0	0.100	$(2.22 \pm 0.06) \times 10^4$	$(2.47 \pm 0.11) \times 10^2$
288.0	1.0	0.100	$(1.41 \pm 0.02) \times 10^4$	$(1.97 \pm 0.07) \times 10^2$
308.0	1.0	0.100	$(3.50 \pm 0.09) \times 10^4$	$(3.50 \pm 0.08) \times 10^2$
318.0	1.0	0.100	$(5.69 \pm 0.07) \times 10^4$	$(4.25 \pm 0.07) \times 10^2$
298.0	0.3	0.100	$(1.13 \pm 0.03) \times 10^4$	$(6.70 \pm 0.03) \times 10^1$
298.0	0.5	0.100	$(1.51 \pm 0.02) \times 10^4$	$(1.18 \pm 0.04) \times 10^2$

Kinetics. The kinetics of the reaction were followed at 325 nm (λ_{max} of Ru^{VI}). In the presence of at least a 20-fold excess of $[Fe(H_2O)_6]^{2+}$, two well-separated consecutive steps were observed (Fig. 4b). Both steps followed pseudo-first-order kinetics and the observed rate constants were independent of $[Ru^{VI}]$ (5×10^{-5}–2×10^{-4} mol dm^{-3}), but depended linearly on $[Fe^{2+}]$ (1×10^{-3}–2×10^{-2} mol dm^{-3}). Representative second-order rate constants for the first (k_{Fe}) and the second (k_{Fe}') steps are shown in Table 2.

Both k_{Fe} and k_{Fe}' increased with ionic strength and were independent of acid concentration in the range of pH = 1–3. The activation parameters ($I = 1.0$ mol dm^{-3}, pH = 1.0) for the first step are $\Delta H^\ddagger = 32.5 \pm 1.5$ kJ mol^{-1} and $\Delta S^\ddagger = -52.5 \pm 7$ J mol^{-1} K^{-1}; while for the second step, $\Delta H^\ddagger = 17.3 \pm 1.2$ kJ mol^{-1} and $\Delta S^\ddagger = -140 \pm 13$ J mol^{-1} K^{-1}.

Mechanism. E^0 for the $[Fe(OH_2)_6]^{3+/2+}$ couple is +0.77 V *vs.* NHE,[17] so thermodynamically both Ru^{VI} and Ru^V are capable of oxidizing $[Fe(H_2O)_6]^{2+}$ to $[Fe(H_2O)_6]^{3+}$. Thus the two steps observed are assigned to $Ru^{VI} \longrightarrow Ru^V$ and $Ru^V \longrightarrow Ru^{IV}$:

$$cis\text{-}[Ru^{VI}L(O)_2]^{2+} + [Fe^{II}(OH_2)_6]^{2+} \longrightarrow cis\text{-}[Ru^{V}L(O)_2]^{+} + [Fe^{III}(OH_2)_6]^{3+} \quad (11)$$

$$cis\text{-}[Ru^{V}L(O)_2]^{+} + [Fe^{II}(OH_2)_6]^{2+} + 2H^+ \longrightarrow cis\text{-}[Ru^{IV}L(O)(OH_2)]^{2+} + [Fe^{III}(OH_2)_6]^{3+} \quad (12)$$

Thermodynamically *cis*-$[Ru^{IV}L(O)(OH_2)]^{2+}$ should also be able to oxidize $[Fe(H_2O)_6]^{2+}$ at pH $\lesssim$ 2.5. A third step was indeed observed on a much longer time-scale. The kinetics of this step was not investigated, however, mainly because the spectral changes for this step were too small for rate constants to be determined accurately.

$Ru^{VI} \longrightarrow Ru^V$. Since $[Fe(H_2O)_6]^{2+}$ is a labile reductant, this step could be either outer-sphere or inner-sphere. A clue to the mechanism may be obtained by comparing the observed rate constant (k_{Fe}) with the theoretical rate constant (k_{cal}) for outer-sphere electron-transfer calculated using the Marcus cross-relation [eqns. (5) and (6)], using the value of 2×10^4 dm^3 mol^{-1} s^{-1} for the $[Ru^{VI}L(O)_2]^{2+}/[Ru^VL(O)_2]^+$ couple. If the self-exchange rate for $[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}$ is taken as 4 dm^3 mol^{-1} s^{-1},[16] then k_{cal} is found to be 2.3×10^4 dm^3 mol^{-1} s^{-1}, in excellent agreement with the observed value of 2.7×10^4 dm^3 mol^{-1} s^{-1} for k_{Fe}. However, it has been noted that the value of 4 dm^3 mol^{-1} s^{-1} for the self-exchange rate of $[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}$ is often too large to fit experimental results of many reactions.[16,18,19] If a 'working' self-exchange rate of 5×10^{-3} dm^3 mol^{-1} s^{-1} for $[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}$ is used, then k_{cal} is 8.3×10^2 dm^3 mol^{-1} s^{-1}, which is smaller than k_{Fe} by a factor of ≈30. However, this is only slightly beyond the factor of 25 within which outer-sphere electron transfer can be predicted using the Marcus cross-relation.[16,20] We conclude that this electron-transfer reaction is likely to be outer-sphere.

$Ru^V \longrightarrow Ru^{IV}$. The second-order rate constant for this step, k_{Fe}', is independent of acid concentration at pH = 1–3, suggesting that the mechanism is different from that of the reduction by $[Ni(tacn)_2]^{2+}$. The direct reduction of *cis*-$[Ru^VL(O)_2]^+$ to *cis*-$[Ru^{IV}L(O)_2]$ can be ruled out since *cis*-$[Ru^{IV}L(O)_2]$ would be too electron rich and highly unstable. The protonated form, *cis*-$[Ru^{IV}L(O)(OH)]^+$, would be much more stable and when $[Ni(tacn)_2]^{2+}$ is the reducing agent, the kinetic data are consistent with initial protonation of *cis*-$[Ru^VL(O)_2]^+$ prior to electron transfer. In the case of $[Fe(H_2O)_6]^{2+}$, this pathway is apparently not followed, since the rate constant is independent of acidity. We propose the following inner-sphere mechanism:

$$cis\text{-}[Ru^{V}L(O)_2]^{+} + Fe^{2+} \overset{K_I}{\rightleftharpoons} cis\text{-}[Ru^{V}L(O)(OFe^{II})]^{3+} \quad (13)$$

$$cis\text{-}[Ru^{V}L(O)(OFe^{II})]^{3+} \xrightarrow{k_{et}'} cis\text{-}[Ru^{IV}L(O)(OFe^{III})]^{3+} \quad (14)$$

$$cis\text{-}[Ru^{IV}L(O)(OFe^{III})]^{3+} + 2H^+ \xrightarrow{\text{fast}} cis\text{-}[Ru^{IV}L(O)(OH_2)]^{2+} + Fe^{3+} \quad (15)$$

This leads to the following rate law:

$$d[Ru^{IV}]/dt = K_Ik_{et}'[Fe^{2+}][Ru^V]/(1 + K_I[Fe^{2+}]) \quad (16)$$

Under conditions that $K_I[Fe^{2+}] \ll 1$, eqn. (16) reduces to:

$$d[Ru^{IV}]/dt = K_Ik_{et}'[Fe^{2+}][Ru^V] \quad (17)$$

Hence,

$$k_{Fe}' = K_Ik_{et}' \quad (18)$$

According to this mechanism the immediate Ru^{IV} product of the electron transfer reaction [eqn. (14)] is stabilized by an electrophilic Fe^{III} center, hence this $Ru^V \longrightarrow Ru^{IV}$ step should occur at a reasonable rate. The formation of an intermediate prior to electron transfer is also consistent with a lower $\Delta H^\ddagger$ for this step than for the $Ru^{VI} \longrightarrow Ru^V$ step. An inner-sphere mechanism has also been proposed for the reduction of *trans*-$[Ru(tmc)(O)_2]^{2+}$ by $[Fe(H_2O)_6]^{2+}$ based on a $\Delta H^\ddagger$ of almost zero.[5]

Conclusion

Our studies show that *cis*-$[Ru^{VI}L(O)_2]^{2+}$ can act as a facile outer-sphere one-electron oxidant. *cis*-$[Ru^VL(O)_2]^+$ can also act as a facile one-electron oxidant in the presence of protons or *via* inner-sphere pathways. We are currently making use of this information to study the mechanisms of the oxidation of organic substrates by these ruthenium oxo species.

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