Characterisation of the Kinetic Intermediate of the Inner-sphere Electron-transfer Reaction involving Hexa-aquotitanium(III) Cation and Di-μ-acetato-diaquodi-μ-oxalato-diruthenium(II,III) Anion

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A long-lived intermediate (formation constant 8 × 10^2 dm^3 mol^{-1}) is involved in the reduction (25 °C, 1 M LiO_3SCF_3) of di-μ-acetato-diaquodi-μ-oxalato-diruthenium(II,III) anion by hexa-aquotitanium(III) cation; the rate constant for intramolecular electron transfer within the conjugate base of the trinuclear intermediate is 30 s^{-1} (enthalpy of activation, 58 kJ mol^{-1}).

In the reduction of di-μ-acetato-diaquodi-μ-oxalato-diruthenium(II,III) anion by $\{Ti(H_2O)_6\}^{3+}$, electron-transfer (ET) is slow with respect to substitution, so that a long-lived intermediate builds up during the redox process. This is the first report of a long-lived intermediate that undergoes rate-limiting ET in a redox process involving t_{2g} orbitals both as electron-donor and as electron-acceptor orbitals;[1] extensive work and controversy has centred on Ru^{II}–Ru^{III} mixed-valence dimers that involve such orbitals.[2] The oxidant we use is the first compound known in which a non-insulating group is in conjugation with a metal–metal bond in a Ru^{II}–Ru^{III} dimer.

Di-μ-acetato-diaquodi-μ-oxalato-diruthenium(II,III) anion was made by the reaction of tetra-μ-acetato-diruthenium(II,III) chloride[3] with aqueous oxalic acid (H_2ox). Reduction of $\{Ru_2(ox)_2(OAc)_2\}^-$, in 1 M LiO_3SCF_3 at 25 °C [using at least tenfold excess of $\{Ti(H_2O)_6\}^{3+}$, hereafter Ti^{3+}], was studied on a computer-linked Durrum stopped-flow spectrophotometer between 400 and 600 nm. Absorbance–time traces were adequately fitted by a double exponential expression, with one rate constant, k, corresponding to increase of absorbance, and another rate constant, k', corresponding to decay of that absorbance. The extinction coefficient of the intermediate responsible[3] for this absorbance is 2.3 × 10^3 at 440 nm and 2.8 × 10^4 dm^3 mol^{-1} cm^{-1} at 375 nm.

The stoicheiometry of the overall reaction corresponds to reduction of the Ru^{II}–Ru^{III} dimer to Ru^{II} products. The rate of formation of the intermediate is several orders of magnitude greater than that consistent with an outer-sphere reduction,† indicating that an inner-sphere mechanism must be involved. The overall rate law for formation of the intermediate is given in equation (1) and that for the decomposition of the intermediate follows from equation (2). The

$$k = a\,[Ti^{3+}]\,[H^+]^{-1}/(b + [Ti^{3+}])\,(c + [H^+]^{-1}) \qquad (1)$$

$$k' = d + e\,[H^+]^{-1} \qquad (2)$$

values of the rate parameters are: a = 30 s^{-1}; b = 1.2 × 10^{-3} M; c = 66 M; d = 0.45 s^{-1}; and e = 1.6 × 10^{-2} dm^3 mol^{-1} s^{-1}.

Non-linear dependence on $[Ti^{3+}]$ requires a mechanism involving a trinuclear intermediate as shown in equation (3) [X = $(ox)_2(OAc)_2$]. The data are consistent with a formation

$$Ti^{3+} + \{Ru_2^{III,II}(X)\}^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \{Ru_2^{III,II}(X)Ti\}^{2+} \qquad (3)$$

constant (k_1/k_2) of 8 × 10^2 dm^3 mol^{-1} for this intermediate at all acidities studied. The acid dependence of the high-

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† This assumes that the larger rate constant corresponds to the formation of the intermediate, and the smaller one to its decomposition.

titanium-limiting rate indicates that an acid–base reaction of the intermediate is also important (equation 4). At the

$$\{Ru_2^{III,II}(X)Ti\}^{2+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \{Ru_2^{III,II}(X)Ti(OH)\}^{+} + H^{+} \quad (4)$$

low-acid limit of concentration for this high-titanium-limiting rate rapid relaxation is faster than the rate of decomposition of the $Ru_2^{II,II}$ product.[5] We are constrained to assign this process as intramolecular ET through a bridging oxalate group (reaction 5). The value of k_5 at 25 °C is $30\,s^{-1}$. The

$$\{Ru_2^{III,II}(X)Ti(OH)\}^{+} \xrightarrow{k_5} \{Ru_2^{II,II}(X)Ti^{IV}\}^{2+} \quad (5)$$

activation enthalpy associated with k_5 is $58\,kJ\,mol^{-1}$, consistent with our assignment of the rate-limiting process as through-bridge intramolecular ET.

The slower relaxation (k') is independent of concentration of Ti^{III}, and nearly independent of acid concentration. The overall rate for that relaxation is quite similar to that observed[4] for break-up of tetra-acetato-$Ru_2^{II,II}$. The second relaxation in the reaction of present interest is interpreted as decomposition of the product of the ET reaction (reaction 6).

$$\{Ru_2^{II,II}(X)Ti^{IV}\}^{2+} \xrightarrow{k_6} \text{products} \quad (6)$$

The relatively slow rate of ET within the deprotonated intermediate [compared to that in the intermediate involved[6] in reduction of $\{Ru(NH_3)_4C_2O_4\}^{+}$ by Ti^{3+}] probably results from a relatively large energy difference between electron-donor and electron-acceptor orbitals. Visible-region spectra indicate that the LUMO for the dioxalato-oxidant is relatively high in energy, consistent with that rationalization.

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