Spontaneous Oxidation of Water to Oxygen by the Mixed-valence μ-Oxo Ruthenium Dimer L₂(H₂O)Ru^{III}–O–Ru^{IV}(OH)L₂ (L = 2,2′-bipyridyl-5,5′-dicarboxylic acid)

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The mixed-valence μ-oxo ruthenium dimer L₂(H₂O)Ru^{III}–O–Ru^{IV}(OH)L₂, where L = 2,2′-bipyridyl-5,5′-dicarboxylic acid, converts spontaneously into L₂(H₂O)Ru^{III}–O–Ru^{III}(H₂O)L₂ under simultaneous oxidation of water to oxygen under conditions where the driving force of the reaction is less than 0.1 eV per transferred electron.

The mixed-valence μ-oxo ruthenium dimer L₂(H₂O)Ru^{III}–O–Ru^{IV}(OH)L₂,† abbreviated hereafter as Ru^{III}–O–Ru^{IV}, was recently identified as a precursor of an active and durable molecular water oxidation catalyst.[2] Oxygen evolution was proposed to proceed through higher oxidation states of Ru, e.g. Ru^{IV}–O–Ru^{IV} and Ru^{V}–O–Ru^{V}.[1,2] We have discovered that in acidic aqueous solutions containing non-complexing anions, such as 1 M CF₃SO₃H or HClO₄, Ru^{III}–O–Ru^{IV} is unstable with respect to reduction to Ru^{III}–O–Ru^{III}. This property distinguishes it from the unsubstituted dimeric complex[2] (bpy)₂(H₂O)Ru^{III}–O–Ru^{IV}(OH)(bpy)₂ (bpy = 2,2′-bipyridine) which is stable under similar conditions. The redox potential of Ru^{III}–O–Ru^{IV} in 1 M CF₃SO₃H [E^0 1.03 V vs. standard calomel electrode (S.C.E.)] is higher than that of the latter dimer with no carboxylic acid groups (E^0 0.79 V vs. S.C.E.), rendering the oxidation of water to oxygen feasible [reaction (1)].

$$4Ru^{III}–O–Ru^{IV} + 2H_2O \rightarrow 4Ru^{III}–O–Ru^{III} + O_2 + 4H^+ \quad (1)$$

The occurrence of reaction (1) was scrutinized in the following experiments. Ru^{III}–O–Ru^{III} was obtained as a solid as previously described.[2] A 6.25 × 10^{-5} M solution in 1 M aqueous CF₃SO₃H displayed the characteristic visible absorption maximum at 650 nm (ε 18 300 dm³ mol⁻¹ cm⁻¹). Addition of stoicheiometric amounts of Co^{III} in CF₃SO₃H resulted in

practically instantaneous oxidation to Ru^{III}–O–Ru^{IV}. This solution exhibits the typical absorption feature of the mixed-valence dimer ($\lambda_{max.}$ 510 nm, ε 17 000 dm³ mol⁻¹ cm⁻¹ in 1 M CF₃SO₃H). Figure 1 shows that the intensity of the 510 nm band decreases with time with simultaneous formation of the 650 nm absorption of the Ru^{III}–O–Ru^{III} dimer. This indicates that spontaneous reduction of the mixed-valence dimer occurs. The conversion into Ru^{III}–O–Ru^{III} is clean, the appearance of an isosbestic point at 562 nm indicating the absence of any significant side reaction. The dashed line in Figure 1 obtained after 60 h exhibits the 650 nm feature of the Ru^{III}–O–Ru^{III} dimer which at this time has been regenerated (88%). A small hump at 450 nm is also visible along with the residual Ru^{III}–O–Ru^{IV} absorption at 510 nm. This is attributed to an impurity, presumably an isomer of Ru–O–Ru whose reduction to the III–III state is slower than that of the principal component. Upon extending the reaction time to several days, the recovery of the initial Ru^{III}–O–Ru^{III} absorption is practically complete (>97%). The oxidation with Co^{III} and spontaneous back-conversion into Ru^{III}–O–Ru^{III} was repeated three times without noticeable degradation of the dimer.

Oxygen generation was assayed with 15 ml solutions of 5 × 10^{-4} M Ru^{III}–O–Ru^{III} in 1 M CF₃SO₃H contained in 20 ml glass vials. Gas samples were withdrawn from the head space for g.c. analysis (Poropack column, thermal conductivity detector, carrier gas Ar) through a septum connected to the interior of the vial through a stop cock. The stop cock was closed during the reaction preventing air diffusion across the septum.[3] The absence of air leakage was confirmed in blank experiments. Solutions were thoroughly degassed with Ar.

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† The mixed-valence dimer is formulated with one deprotonated water ligand. The pK_a value for the water ligand is 0.6 in the case of the analogous dimer with no carboxylic acid groups.[1]
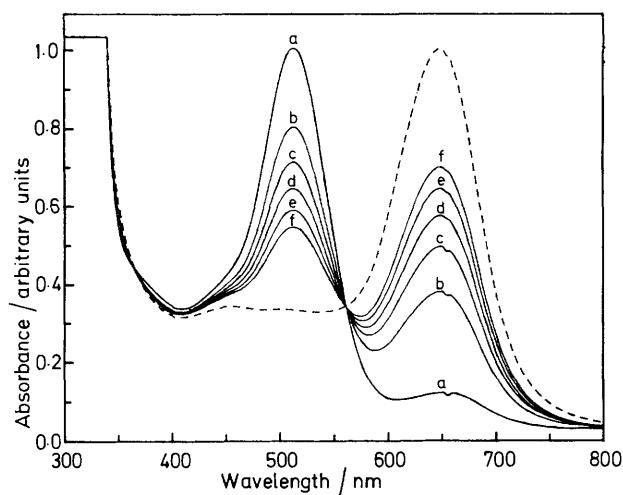
Figure 1. Visible absorption spectra of a 6.25×10^{-5} M solution of Ru^{III}–O–Ru^{III} in 1 M CF$_3$SO$_3$H after oxidation by a stoicheiometric amount of Co^{III} to the mixed-valence dimer Ru^{III}–O–Ru^{IV}. Time interval after oxidation (a) 20 min, (b) 5 h, (c) 10 h, (d) 15 h, (e) 20 h, (f) 25 h; (– – –) 60 h.

Subsequently, a deaerated solution of Co^{III} in CF$_3$SO$_3$H was added to oxidize the Ru^{III}–O–Ru^{III} to the mixed-valence dimer Ru^{III}–O–Ru^{IV}. The quantity of Co^{III} used corresponded to a 5—10% excess with respect to stoicheiometric one-electron oxidation. Back-conversion of Ru^{IV}–O–Ru^{III} into Ru^{III}–O–Ru^{III} was followed spectrophotometrically and the oxygen analysis was simultaneously performed.

Oxygen was unambiguously identified as a reaction product, the stoicheiometry of reaction (1) being obeyed within the accuracy limits of our g.c. analysis, estimated to be 20%. For example, after a reaction time of 24 h, when 50% of the Ru^{III}–O–Ru^{IV} had reconverted into the III–III oxidation state, 32 μl (STP) of O$_2$ were produced. Since up to 5 μl of O$_2$ could arise from the excess of Co^{III} used to oxidize Ru^{III}–O–Ru^{III}, 27 μl O$_2$ are attributed to water oxidation by Ru^{III}–O–Ru^{IV}. From reaction (1) one would expect 22 μl of O$_2$, which agrees with the experimental result within the error limits of the analysis.

Ru^{III}–O–Ru^{IV} was also generated electrochemically by anodic oxidation of Ru^{III}–O–Ru^{III} in 1 M CF$_3$SO$_3$H. Spontaneous back-conversion into Ru^{III}–O–Ru^{III} under simultaneous water oxidation occurred in the same manner as before when Co^{III} was used as an oxidant.

An intriguing aspect of our finding is that Ru^{III}–O–Ru^{IV} oxidizes water to oxygen at surprisingly small thermodynamic driving force. From the standard redox potentials, this is lower than 0.1 eV for each electron transferred. The ratio of reduced to oxidized dimer at equilibrium is given by relation (2), where $K = 108$ is the equilibrium constant for reaction (1), $p_{O_2} \leqslant 0.001$ atm is the partial pressure of O$_2$ under the experimental conditions where oxygen measurements were performed, a_{H^+} ~0.7 is the estimated hydrogen ion activity in 1 M CF$_3$SO$_3$H, and γ is the activity coefficient for the dimeric Ru complex. Assuming that γ(Ru^{III}–O–Ru^{IV}) = γ(Ru^{III}–O–Ru^{III}), r is calculated to be 15, corresponding to 94% conversion of the mixed-valence dimer into the reduced state at equilibrium. Since K has a relatively large error, these predictions are compatible with the experimental results.

$$r = \frac{[\text{Ru}^{III}\text{–O–Ru}^{III}]}{[\text{Ru}^{III}\text{–O–Ru}^{IV}]} = \left(\frac{K}{p_{O_2}}\right)^{\frac{1}{4}} \frac{\gamma(\text{Ru}^{III}\text{–O–Ru}^{IV})}{a_{H^+}\,\gamma(\text{Ru}^{III}\text{–O–Ru}^{III})} \quad (2)$$
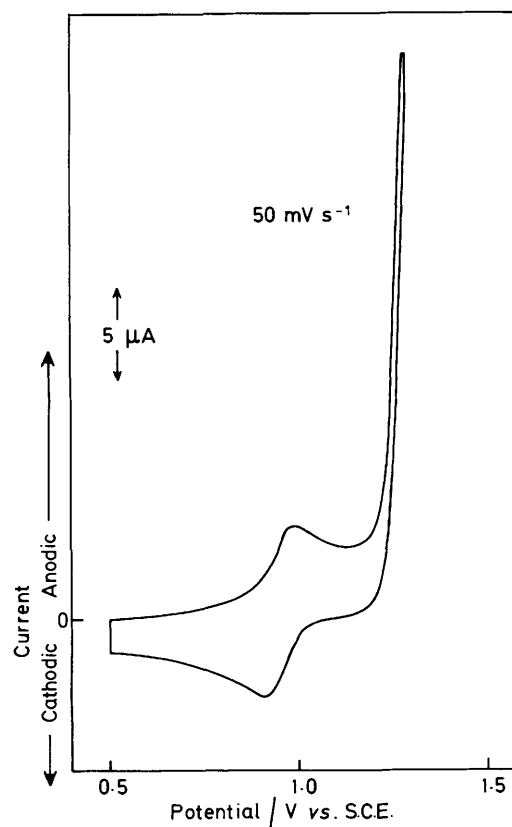

Figure 2. Cyclic voltammogram obtained from a 10^{-4} solution of Ru^{III}–O–Ru^{III} in 0.1 M CF$_3$SO$_3$H. The mid-point potential for the one-electron oxidation is at 0.96 V vs. S.C.E. which is 60 mV less positive than in 1 M CF$_3$SO$_3$H. The catalytic wave for water oxidation starts at 1.15 V. Working electrode: In-doped SnO$_2$ (0.6 cm^2 area); background current < 1 μA throughout the potential range.

Kinetic analysis of the water oxidation process was attempted by studying the effects of pH and initial Ru^{III}–O–Ru^{IV} concentration on the reaction dynamics. A matrix representation was used to interpret the temporal variations of the extinctions at 450, 510, 550, 590, 650, and 690 nm, and the Runge–Kutta method was employed for numerical integration of the rate law. Several mechanisms were considered. Outer sphere one-electron oxidation of water to OH radicals by Ru^{III}–O–Ru^{IV} was excluded on thermodynamic grounds since the free energy barrier for this reaction is at least 1.4 eV. Most likely, the oxygen evolution reaction is initiated by the dismutation of Ru^{III}–O–Ru^{IV} [reaction (3)]. The redox potential for the one-electron oxidation of Ru^{III}–O–Ru^{IV} is not known. However, electrochemical experiments with solutions of the dimeric Ru complex show the onset of the catalytic wave for water oxidation to be ca. 0.2 V positive of the $E°$ value for the Ru^{III}–O–Ru^{IV}/Ru^{III}–O–Ru^{III} couple. A cyclic voltammogram illustrating this behaviour is shown in Figure 2. This gives 1.2 V vs. S.C.E. as a lower bound for E^0 (Ru^{IV}–O–Ru^{IV}/Ru^{IV}–O–Ru^{III}) and $K = 4 \times 10^{-4}$ as the upper limit for the equilibrium constant for reaction (3). Because of its thermodynamically uphill character, reaction (3) contributed to the slow rate of the oxygen generating process. It is followed by a rearrangement of the Ru^{IV}–O–Ru^{IV} complex to a peroxide structure [reaction (4)],[1,2] which is oxidized further to O$_2$ by the excess Ru^{III}–O–Ru^{IV} complex according to the overall equation (5).

$$2Ru^{III}\text{-}O\text{-}Ru^{IV} \rightleftarrows Ru^{III}\text{-}O\text{-}Ru^{III} + Ru^{IV}\text{-}O\text{-}Ru^{IV} \quad (3)$$

$$
\begin{array}{c}
L_2Ru^{IV}\text{-}O\text{-}Ru^{IV}L_2 \rightarrow L_2Ru^{III}\text{-}O\text{-}Ru^{III}L_2 + 2H^+ \\
\underset{OH}{|} \underset{OH}{|} \underset{O}{|}\!-\!\underset{O}{|} \\
\phantom{L_2Ru^{IV}O}(O_2{}^{2-})
\end{array}
\quad (4)
$$

$$
\begin{array}{c}
Ru^{III}\text{-}O\text{-}Ru^{III} + 2Ru^{III}\text{-}O\text{-}Ru^{IV} \rightarrow 3Ru^{III}\text{-}O\text{-}Ru^{III} + O_2 \\
\underset{O}{|}\!-\!\underset{O}{|}
\end{array}
\quad (5)
$$
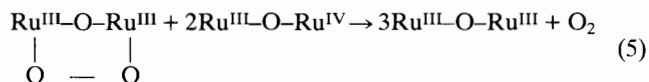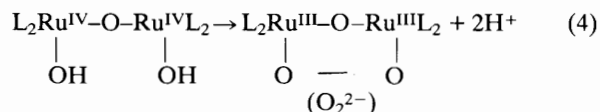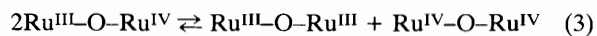
Taqui Khan *et al.* have postulated similar peroxo type intermediates in the water oxidation catalysis by a dimeric oxygen bridged Ru–ethylenediaminetetra-acetic acid (EDTA) complex.[4] Although this sequence of reactions appears plausible to rationalize the observed water oxidation by $Ru^{III}\text{-}O\text{-}Ru^{IV}$, an alternative mechanism cannot be excluded. This would involve dismutation of $Ru^{IV}\text{-}O\text{-}Ru^{IV}$ formed *via* reaction (3) yielding higher oxidation states of the dimeric ruthenium complex,[1] such as $Ru^V\text{-}O\text{-}Ru^V$, which could release O_2 under reformation of $Ru^{III}\text{-}O\text{-}Ru^{III}$. Unfortunately, our kinetic simulation did not resolve this ambiguity since the fit of the numerically integrated rate laws to the experimental data was comparable for both models. Future refinement of the analysis depends on the removal of the isomer impurity from the $Ru^{III}\text{-}O\text{-}Ru^{III}$ preparation whose presence obscures subtleties in the temporal changes of the absorption spectra.

The present study ascertains that the mixed-valence μ-oxo ruthenium dimer $Ru^{III}\text{-}O\text{-}Ru^{IV}$ oxidizes water to oxygen at very low thermodynamic driving force. The unique feature of this complex is that the catalytically active state is accessible at very low overvoltage. This behaviour is unprecedented in homogeneous water oxidation catalysis. Our finding should help to model the processes occurring on the surface of catalysts such as colloidal RuO_2,[5,6] and represents significant progress in the development of artificial analogues of the green plant water splitting enzyme.

References

1 J. A. Gilbert, D. S. Eggleston, W. R. Murphy, D. A. Gesewitz, S. W. Gersten, D. J. Houston, and T. J. Meyer, *J. Am. Chem. Soc.*, 1985, **107**, 3855.
2 F. P. Rotzinger, S. Munavalli, P. Comte, J. K. Hurst, M. Grätzel, F. J. Pern, and A. J. Frank, *J. Am. Chem. Soc.*, 1987, **109**, 6619.
3 D. Duonghong, N. Serpone, and M. Grätzel, *Helv. Chim. Acta*, 1984, **67**, 1014.
4 M. M. Taqui Khan, R. C. Bhardwaj, and C. M. Jadhar, *J. Chem. Soc., Chem. Commun.*, 1985, 1690.
5 R. Humphry-Baker, J. Lilie, and M. Grätzel, *J. Am. Chem. Soc.*, 1982, **104**, 422, and references cited therein.
6 A. Mills, *J. Chem. Soc., Chem. Commun.*, 1984, 1436.