

## Probing Key Reaction Steps in Ce(IV)-driven Water Oxidation Catalyzed by a Mononuclear Ruthenium Complex

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**Keywords:** Oxidation reaction; Oxygen evolution; Reaction intermediates; Artificial photosynthesis

Water splitting is a promising way to solve energy and environmental problems. Water oxidation (WO) corresponds to the half reaction of water splitting, considered as the bottleneck reaction, because it requires removal of four protons and four electrons ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ). It is thus important to clarify the mechanism of WO to develop efficient catalysts for this reaction. In this context, we previously reported that a mononuclear ruthenium complex ( $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ ) serves as a molecular catalyst in the WO driven by  $\text{Ce}^{4+}$  (Ceric Ammonium Nitrate; CAN) as an oxidizing reagent.<sup>1,2</sup>

In this study, we have succeeded in isolating a high valent ruthenium(IV) oxo intermediate  $[\text{Ru}^{\text{IV}}(\text{O})(\text{tpy})(\text{bpy})]^{2+}$  ( $\text{Ru}^{\text{IV}}=\text{O}$ ), as judged by elemental analysis, EDX, ESI-TOF-MS, IR, EPR and Raman spectroscopy. Square wave voltammograms of  $\text{Ru}^{\text{IV}}=\text{O}$  and CAN recorded in acetonitrile solution indicate that the outer-sphere electron transfer (ET) from  $\text{Ru}^{\text{IV}}=\text{O}$  to  $\text{Ce}^{4+}$  is thermodynamically unfavorable, implying that the oxidation of  $\text{Ru}^{\text{IV}}=\text{O}$  by CAN is likely to proceed via the inner-sphere ET path (Figure 1).

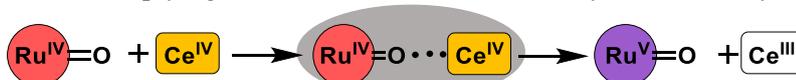


Figure 1. Inner-sphere electron transfer between  $\text{Ru}^{\text{IV}}=\text{O}$  and CAN.

Figure 2 shows the UV-Vis spectral change for the reaction between  $\text{Ru}^{\text{IV}}=\text{O}$  (0.05 mM) and CAN (0.05 mM) at 21°C. The Eyring plot, developed by measuring the temperature dependence of the observed first-order rate constant, afforded the activation parameters of  $\Delta H^\ddagger = 75 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -40 \text{ J K}^{-1} \text{ mol}^{-1}$ . The negative  $\Delta S^\ddagger$  value is consistent with promotion of an inner-sphere ET, assignable to the adduct formation of  $\text{Ru}^{\text{IV}}=\text{O}$  and CAN presumably having a  $\text{Ru}^{\text{IV}}\text{-O-Ce}^{\text{IV}}$  core. We will also discuss the mechanism of WO based on the inner-sphere ET from  $\text{Ru}^{\text{IV}}=\text{O}$  to CAN in detail.

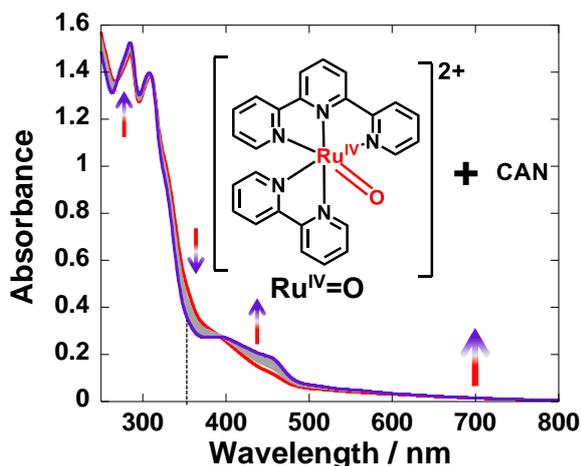


Figure 2. UV-Vis spectral change during the reaction of  $\text{Ru}^{\text{IV}}=\text{O}$  with CAN in acetonitrile.

1) M. Yoshida, S. Masaoka, J. Abe, K. Sakai, *Chem. Asian J.*, **2010**, *5*, 2369.

2) A. Kimoto, K. Yamauchi, M. Yoshida, S. Masaoka, K. Sakai, *Chem. Commun.* **2012**, *48*, 239.