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Ruthenium(II)-Catalyzed Water Oxidation by a Direct $[Ru^{IV}=O]^{2+}$ Pathway

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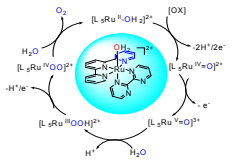
Proposed Mechanisms for Water Oxidation by a Single Ru Center: Formation of O-O Bond

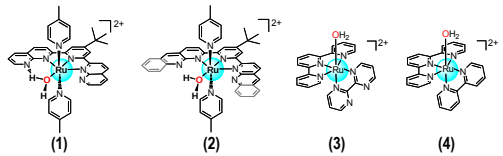
- Formation of a Ru^{V} oxo species, followed by an addition of a water molecule results in a Ru peroxo intermediate proposed by Meyer *et al.* in **2008**.
- Formation of a $Ru^{IV}O–ORu^{IV}$ peroxo dimer via coupling of two Ru^{V}=O centers by Privalov, Llobet and Sun in **2012**.
- Our new findings indicate that the formation of the O–O bond does not have to proceed through the high oxidation state of Ru^{V}, but through $[Ru^{IV}=O]^{2+}$ in neutral and basic solutions by Polyansky *et al. in* **2012**

Overall reaction:

$$2H_2O + [Ru^{II}–OH_2]^{2+} \rightarrow 4H^+ + 4e^- + O_2$$



Mononuclear Ru(II) Water Oxidation Catalysts



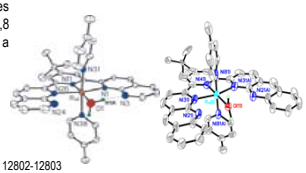
(1) $[Ru^{II}(1)—(OH_2)]^{2+}$ (2) $[Ru^{II}(2)—(OH_2)]^{2+}$ (3) (4) $[Ru^{II}(OH_2)(tpy)(L)]^{2+}$, L = bpm, bpy

- In (**1**) and (**2**) the aqua ligand occupies an equatorial position w.r.t. to the 1,8 nap ligand, H-bonding of H_2O with a single N atom is only seen for (**1**)

$[Ru^{II}(1)—(OH_2)]^{2+}$ (pK_a > 13)

$[Ru^{II}(2)—(OH_2)]^{2+}$ (pK_a > 12)

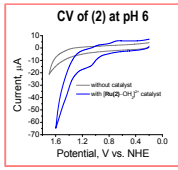
$[Ru^{II}(OH_2)(tpy)(bpm)]^{2+}$ (pK_a 9.7)

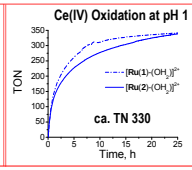


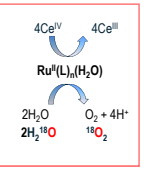
Thummel *et al. J. Am. Chem. Soc.* **2005**, *127*, 12802-12803

Meyer *et al. Inorg. Chem.* **1984**, *23*, 1845-1851

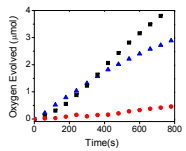
Oxygen Evolution Studies



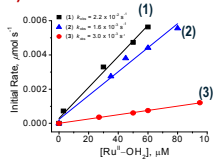


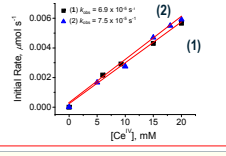


Kinetics of Ce(IV) Oxidation



[Ru(II)] (**1**, **2**) 60 mM, 0.1 M HNO_3 (**3**) in 0.5 M HNO_3
[Ce^{IV}] = 10 mM, Ocean fiber optics





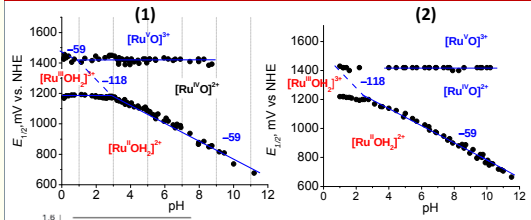
rate = $dO_2/dt = k_{O2}[Ru(II)][Ce^{IV}]$

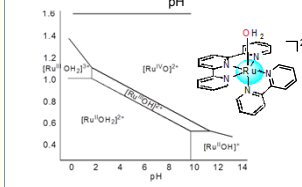
k_{O2} = 2.2 (± 0.1) $M^{-1}s^{-1}$, Complex (**1**)

k_{O2} = 1.6 (± 0.1) $M^{-1}s^{-1}$, Complex (**2**)

O_2 evolution is the first order in [Ru] and [Ce^{IV}] with comparable rates

Pourbaix Diagrams



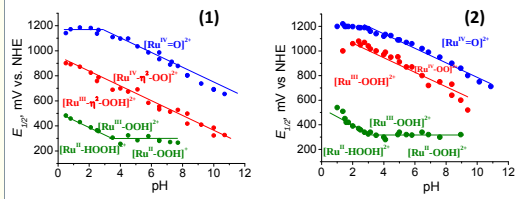


$$E = E^{\circ}_{O/R} + \frac{RT}{nF}\ln\left(\frac{a_O}{a_R}\right) - \frac{m}{n}\cdot 0.0591\cdot pH$$

Slope	Description
0	ET only
59	1 e⁻ 1H⁺ PCET
30	2 e⁻ 1H⁺ PCET
118	1 e⁻ 2H⁺ PCET

- Pourbaix diagrams for (**1**) and (**2**) are quite similar and indicate that the additional *benzo* groups in (**2**) do not alter the electronic properties; the similarities include:
  - i. 2e⁻ / 2H⁺ PCET process is observed for $[Ru^{II}–OH_2]^{2+}$ to $[Ru^{IV}=O]^{2+}$ between pH (3–12)
  - ii. A wave with slope of –118 mV/pH due to a (1e⁻ / 2H⁺) PCET process for $[Ru^{III}–OH_2]^{2+}$ to $[Ru^{IV}=O]^{2+}$ is not observed
  - iii. A pH-independent oxidation process at 1420 mV is due to $[Ru^{V}=O]^{2+}/[Ru^{IV}=O]^{3+}$
  - iv. $[Ru^{III}–OH]^{2+}$ disproportionates to $[Ru^{II}–OH_2]^{2+}$ and $[Ru^{IV}=O]^{2+}$, see Pulse radiolysis section.

Electrochemistry of Oxidation Products: $[Ru^{IV}(OO)]^{2+}$



The applied potential < $E_{1/2}$ (Ru^{V}/Ru^{IV} couple)

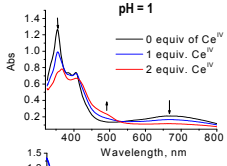
$[Ru^{IV}=O]^{2+} + H_2O \rightarrow [Ru^{III}–OOH]^{2+} + e^- + H^+$

- Cathodic scans identified PCET couples of oxidation products such $[Ru^{III}–OOH]^{2+}$ and $[Ru^{IV}–OO]^{2+}$ with (**1**) and (**2**) indicated by the green and red lines
- ESI-MS labeling experiments and Resonance Raman indicated that the source of O–O in $[Ru^{IV}–OO]^{2+}$ is $H_2{}^{18}O$
- A controlled-potential electrolysis experiment with $[Ru(OH_2)(tpy)(bpm)]^{2+}$ (**3**) at a held potential of 1250 mV (350 mV < Ru^{V}/Ru^{IV}) at pH 6 resulted in a net two-electron oxidation consistent with the formation of the $[Ru^{IV}=O]^{2+}$ species and not the $[Ru^{IV}–OO]^{2+}$ species

Cerium(IV) Oxidation to One- and Two-Electron Species

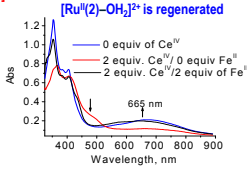
$[Ru^{II}(2)–OH_2]^{2+} - 2e^- \rightarrow [Ru^{IV}(2)=O]^{2+}$

pH = 1

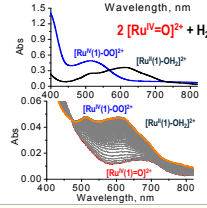


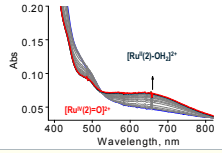
$[Ru^{IV}=O]^{2+}$ + Fe(II)

$[Ru^{II}(2)–OH_2]^{2+}$ is regenerated

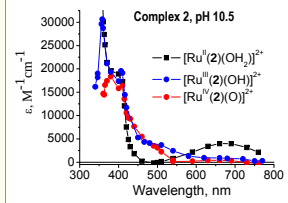


$2\,[Ru^{IV}=O]^{2+} + H_2O \rightarrow [Ru^{IV}–OO]^{2+} + [Ru^{II}–OH_2]^{2+}$





Pulse Radiolysis: Transient Oxidation Intermediates



H_2O ⟿ $OH^{\bullet}$, e^-_{aq}, $H^{\bullet}$, H_2, H_2O_2

$N_2O + e^-_{aq} + H^+, H_2O \rightarrow N_2 + OH^- + OH^{\bullet}$

$OH^{\bullet} + CO_3^{2-} \rightarrow CO_3^{\bullet-}$ ($E_{1/2}$ = 1.59 V, NHE)

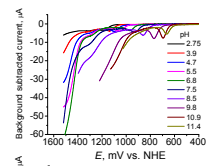
$CO_3^{\bullet-} + [Ru^{II}–OH_2]^{2+} \rightarrow HCO_3^- + [Ru^{III}–OH]^{2+}$

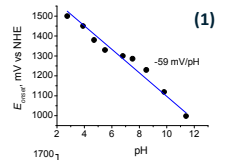
$2\,[Ru^{III}–OH]^{2+} \rightarrow [Ru^{II}–OH_2]^{2+} + [Ru^{IV}=O]^{2+}$ k_{disp}

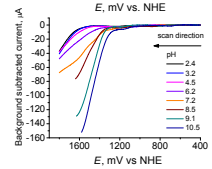
$2CO_3^{\bullet-} + [Ru^{II}–OH_2]^{2+} \rightarrow 2HCO_3^- + [Ru^{IV}=O]^{2+}$

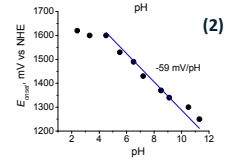
- One- and two-electron oxidized species can be produced cleanly at pH 10 with carbonate radicals (1.59 V vs NHE)
- $[Ru^{III}–OH]^{2+}$ observed by PR disproportionates to $[Ru^{II}–OH_2]^{2+}$ and $[Ru^{IV}=O]^{2+}$ with comparable k_{disp} (6.5 x 10^3 ± 0.5 $M^{-1}s^{-1}$ (**1**), 8.3 x 10^3 ± 0.05 $M^{-1}s^{-1}$ (**2**))

Catalytic Current Dependence on pH





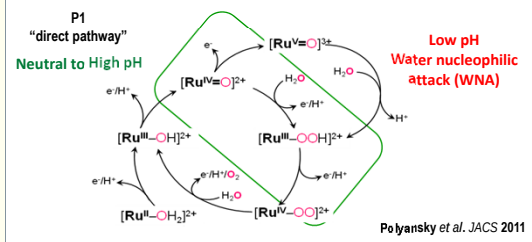




0.5 mM $[Ru^{II}(OH_2)]^{2+}$, 10 mM Britton-Robinson buffer, 0.1 M $CF_3SO_3^-$, low pH was buffered with 0.1 M HNO_3

- Background subtracted CVs of $[Ru^{II}(OH_2)(tpy)(bpm)]^{2+}$ (**3**) and $[Ru^{II}(OH_2)(tpy)(bpy)]^{2+}$ (**4**) between pH 5-11 show that the onset potentials of catalytic oxidation have negligible pH-dependency with a constant magnitude near or above the Ru^{V}/Ru^{IV} couple.

Proposed Water Oxidation Mechanism for (1) and (2)



- In neutral and high pH, (**1**) and (**2**) proceed by a "**direct pathway**" that involves the reaction of $[Ru^{IV}=O]^{2+}$ with water via a PCET process and avoids the formation of $[Ru^{V}=O]^{3+}$ **"non-PCET pathway"**
- Evidence for this mechanism:
  - 1) pH-dependent onset catalytic potentials that are indicative of PCET driven catalysis
  - 2) The electrochemical generation of O–O containing products (for e.g. $[Ru^{IV}–OO]^{2+}$ and $[Ru^{III}–OOH]^{2+}$) at an applied potential below $E_{1/2}$(Ru^{V}/Ru^{IV})

Acknowledgement

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