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# Nonaqueous Catalytic Water Oxidation

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the requirement of both electron and proton transfer at the electrode.<sup>6</sup> With added water, the catalytic water oxidation occurs at the onset for the oxidation of Ru(IV) to Ru(V). Addition of water shifts the  $\text{Ru}^{\text{III}}\text{--OH}_2^{3+}/\text{Ru}^{\text{II}}\text{--OH}_2^{2+}$  couple negatively through an outer-sphere solvation effect, with  $E_{1/2}$  reaching 0.94 V with 8% added water. CVs under the conditions in Figure 1a are stable indefinitely with respect to multiple scans.

The catalytic peak current for water oxidation,  $i_{\text{cat}}$ , at 1.8 V varies linearly with  $[\text{H}_2\text{O}]^{1/2}$  to the limit of miscibility, 0–8% (0–4.4 M) in added water (Figure 1b). It also varies linearly with  $[\text{Ru}^{\text{II}}\text{--OH}_2^{2+}]$  (Figure S6). Similar results were obtained in 1:1 PC/EC mixtures containing 0–12% (0–6.6 M) water (Figure S7), with evidence for saturation at higher concentrations. These observations are consistent with an electrocatalytic mechanism for water oxidation involving rate-limiting O-atom transfer to  $\text{H}_2\text{O}$  (Scheme 1), the rate law in eq 1, and the current expression in eq 2:<sup>7</sup>

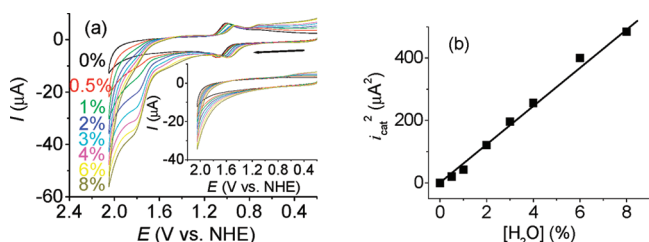
$$\text{rate} = k_{\text{cat}}[\text{Ru}^{\text{V}}=\text{O}^{3+}] = k_0[\text{Ru}^{\text{V}}=\text{O}^{3+}][\text{H}_2\text{O}] \quad (1)$$

$$\begin{aligned} i_{\text{cat}} &= nFA[\text{Ru}](k_{\text{cat}}D_{\text{Ru}})^{1/2} \\ &= nFA[\text{Ru}](k_0D_{\text{Ru}}[\text{H}_2\text{O}])^{1/2} \end{aligned} \quad (2)$$

where  $n = 4$  is the electrochemical stoichiometry,  $F$  is the Faraday constant,  $A$  is the electrode surface area (in  $\text{cm}^2$ ),  $[\text{Ru}]$  is the concentration of catalyst (in  $\text{mol/L}$ ), and  $D_{\text{Ru}} \approx 0.7 \times 10^{-6} \text{ cm}^2/\text{s}$  is the diffusion coefficient for catalyst **1** as determined by scan rate dependent measurements and the Randles–Sevcik equation. The same catalytic currents and value of  $E_{1/2}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})$  were obtained in 6%  $\text{H}_2\text{O}/\text{PC}$  with and without 30 mM  $\text{HNO}_3$  (Figure S8), showing that local pH effects associated with water oxidation ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ) play no role in the electrochemical response.

As expected for a solution couple, a linear relationship between the peak current ( $i_d$ ) for the Ru(III/II) couple and the square root of the scan rate ( $v^{1/2}$ ) exists for  $v = 3\text{--}1000 \text{ mV/s}$  (Figure S9b). The catalytic peak current normalized to the square root of the scan rate ( $i_{\text{p,a}}/v^{1/2}$ ) increases with decreasing scan rate at low scan rates (Figure S9a), consistent with a rate-limiting step prior to electron transfer to the electrode and the mechanism in Scheme 1 with rate-limiting O-atom transfer from  $\text{Ru}^{\text{V}}=\text{O}^{3+}$  to  $\text{H}_2\text{O}$ .

From the scan-rate-dependent measurements, a  $k_0$  value of  $\sim 0.3 \text{ M}^{-1} \text{ s}^{-1}$  was obtained from the slope of a plot of  $i_{\text{cat}}/i_d$  versus  $v^{-1/2}$  (Figure S9c) on the basis of eq 3, which was derived by use of the Randles–Sevcik equation to eliminate the dependence on  $[\text{Ru}]$ ,  $A$ , and  $D_{\text{Ru}}$ .<sup>7</sup>

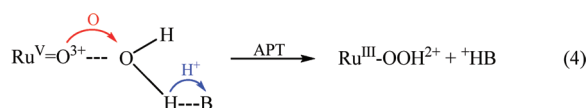


**Figure 1.** (a) CVs of 1 mM **1** in 0.1 M  $t\text{Bu}_4\text{NPF}_6/\text{PC}$  upon addition of increasing amounts of water, as indicated by the percentages in the figure. The inset shows the corresponding backgrounds in the absence of **1**. (b) Plot of  $i_{\text{cat}}^2$  (background subtracted) at 1.85 V (vs NHE) vs  $[\text{H}_2\text{O}]$  (see eq 2). Electrode, GC; scan rate, 100 mV/s.

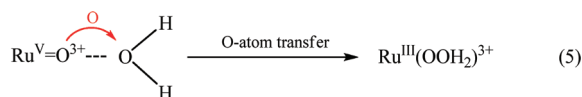
$$\begin{aligned} \frac{i_{\text{cat}}}{i_d} &= 2.242 \left( \frac{k_{\text{cat}}RT}{nFv} \right)^{1/2} \\ &= 2.242 \left( \frac{k_0RT[\text{H}_2\text{O}]}{nFv} \right)^{1/2} \end{aligned} \quad (3)$$

where  $T$  is the temperature (in K) and  $R$  is the gas constant. On the basis of this value of  $k_0$ , there is a rate enhancement of  $\sim 300$  for water oxidation by  $\text{Ru}^{\text{V}}=\text{O}^{3+}$  in 6% (3.3 M)  $\text{H}_2\text{O}/\text{PC}$  ( $k_{\text{cat}} \approx 1 \text{ s}^{-1}$ ) relative to the same catalyst at pH 1 in aqueous solution ( $k_{\text{cat}} \approx 3.1 \times 10^{-3} \text{ s}^{-1}$ ).<sup>2b</sup>

In water, the key O–O bond-forming step involves O-atom attack on  $\text{H}_2\text{O}$  by  $\text{Ru}^{\text{V}}=\text{O}^{3+}$  in concert with proton transfer to a second water molecule or added base in a concerted atom–proton transfer (APT) pathway (eq 4):<sup>8</sup>



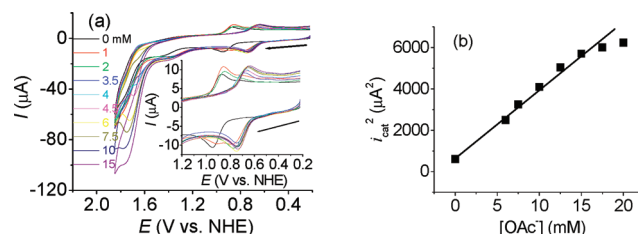
A significant  $\text{H}_2\text{O}/\text{D}_2\text{O}$  kinetic isotope effect (KIE) of up to  $\sim 6.6$  was observed for  $\text{H}_2\text{O}$  as the base.<sup>8</sup> In contrast, the rate law for the reaction in PC points to the involvement of a single water molecule and O-atom transfer to  $\text{H}_2\text{O}$  in the O–O bond-forming step. As shown by CV comparisons for **1** (Figure S10),  $k_{\text{cat,H}_2\text{O}}/k_{\text{cat,D}_2\text{O}} = (i_{\text{cat,H}_2\text{O}}/i_{\text{cat,D}_2\text{O}})^2 \leq 1.4$  in PC. These observations are consistent with a different mechanism in PC, one involving a single water molecule and, presumably, direct O-atom transfer to give a coordinated hydrogen peroxide intermediate (eq 5):



On the basis of initial density functional theory gas-phase calculations, the isomer  $\text{Ru}^{\text{III}}(\text{OOH}_2)^{3+}$  is favored over  $\text{Ru}^{\text{III}}(\text{HOOH})^{3+}$  by  $\sim 8 \text{ kcal/mol}$ .<sup>9</sup> The nonaqueous rate enhancements and change in mechanism may be due to a higher activity for water and decreased acidity for  $\text{Ru}^{\text{III}}(\text{OOH}_2)^{3+}$  in the largely organic solvent environment.<sup>10</sup>

As shown by the data in Figure 2 and Figure S11, there is also evidence for a competing APT pathway with added acetate ion,  $\text{CH}_3\text{COO}^-$  ( $\text{OAc}^-$ ), in 1:1 mol/mol  $\text{LiOAc}/\text{HOAc}$ , with  $\text{OAc}^-$  as the proton-acceptor base and TFE as the solvent.<sup>11</sup> These experiments were conducted with 0.1 M  $\text{LiClO}_4$  as the supporting electrolyte because  $n\text{Bu}_4\text{N}^+$  is susceptible to oxidation under these conditions with added bases.

The data in Figure 2 and Figure S11 indicate the following:



**Figure 2.** (a) CVs of 1 mM **1** in 0.1 M  $\text{LiClO}_4/\text{TFE}$  with 6% (3.3 M) added  $\text{H}_2\text{O}$  and increasing amounts of  $\text{OAc}^-$  in 1:1 mol/mol  $\text{LiOAc}/\text{HOAc}$ , as indicated by the concentrations in the figure. The inset shows a magnified view of the Ru(III/II) couple. (b) Plot of  $i_{\text{cat}}^2$  (background subtracted) vs  $[\text{OAc}^-]$ . Catalytic currents for  $[\text{OAc}^-] < 6 \text{ mM}$  were omitted because separate waves for direct and APT oxidation were observed (see the text). Electrode, GC; scan rate, 100 mV/s. Also see Figure S11.

(1) With no added  $\text{OAc}^-$ , the CV of **1** in 6% (v/v)  $\text{H}_2\text{O}/\text{TFE}$  is similar to that in  $\text{H}_2\text{O}/\text{PC}$ , with  $E_{1/2}(\text{Ru}^{\text{III}}-\text{OH}_2^{3+}/\text{Ru}^{\text{II}}-\text{OH}_2^{2+}) = 0.92$  V,  $E_{1/2}(\text{Ru}^{\text{IV}}=\text{O}^{2+}/\text{Ru}^{\text{III}}-\text{OOH}_2^{3+}) = 1.38$  V, and  $E_{\text{p,a}} = 1.8$  V for catalytic water oxidation. The diffusion coefficient increases to  $D_{\text{Ru}} \approx 1.3 \times 10^{-6}$   $\text{cm}^2/\text{s}$ , and the rate constant for water oxidation increases slightly to  $k_0 \approx 0.35$   $\text{M}^{-1} \text{s}^{-1}$  with a KIE of  $\leq 1.3$ .

(2) Upon addition of 1 mM  $\text{OAc}^-$ , a second  $\text{Ru}(\text{III}/\text{II})$  wave appears at  $E_{1/2} = 0.75$  V. It shifts slightly to  $E_{1/2} = 0.70$  V at 3.5 mM  $\text{OAc}^-$ . There is no further shift at higher concentrations of added  $\text{OAc}^-$ , but this couple dominates as  $\text{OAc}^-$  is further increased. The shift to lower potential with added  $\text{OAc}^-$  is consistent with the appearance of the pH-dependent  $\text{Ru}^{\text{III}}-\text{OH}_2^{3+}/\text{Ru}^{\text{II}}-\text{OH}_2^{2+}$  couple and its reported  $E^\circ$ -pH diagram.<sup>3</sup>

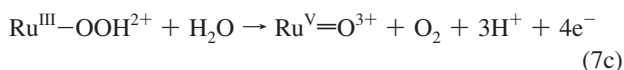
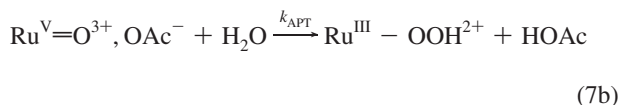
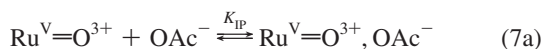
(3) At 3.5–4.5 mM  $\text{OAc}^-$ , two separate water oxidation waves appear, with a new wave appearing at 1.7 V that points to the appearance of an APT pathway with added  $\text{OAc}^-$  as the proton-acceptor base. The waves merge past  $[\text{OAc}^-] = 6$  mM, and the currents level off at  $[\text{OAc}^-] \geq 15$  mM. As shown by the plot of  $i_{\text{cat}}^2$  versus  $[\text{OAc}^-]$  in the inset in Figure 2b,  $i_{\text{cat}}^2$  increases linearly with  $[\text{OAc}^-]$  from 6 to 15 mM. This observation is consistent with the rate law given by eqs 6:

$$\text{rate} = (k_0 + k_{\text{B}}[\text{OAc}^-])[\text{Ru}^{\text{V}}=\text{O}^{3+}][\text{H}_2\text{O}] \quad (6a)$$

$$k_{\text{cat}} = (k_0 + k_{\text{B}}[\text{OAc}^-])[\text{H}_2\text{O}] \quad (6b)$$

A  $k_{\text{B}}$  value of  $\sim 260$   $\text{M}^{-2} \text{s}^{-1}$  was obtained from the scan-rate-dependent data in Figure S12 by use of eq 3. For comparison,  $k_{\text{B}} \approx 10$   $\text{M}^{-1} \text{s}^{-1}$  in water with  $\text{OAc}^-$  as the added base.<sup>8</sup>

The appearance of a new wave for the  $\text{Ru}-\text{OH}_2^{3+}/\text{Ru}^{2+}$  couple with added  $\text{OAc}^-$  is consistent with formation of an ion pair between **1** and  $\text{OAc}^-$  and oxidation of the ion pair at 0.70 V. At even higher concentrations of added  $[\text{OAc}^-]$ , there is clear evidence for saturation kinetics, the ion-pair mechanism shown in eqs 7, and the rate law given by eqs 8, including a dependence on water concentration (Figure S13).<sup>12</sup> From a plot of  $[(i_{\text{cat,B}}/i_{\text{cat,o}})^2 - 1]^{-1}$  versus  $1/[\text{OAc}^-]$  at fixed  $[\text{H}_2\text{O}]$  (Figure S14), the values  $k_{\text{APT}} = 12 \pm 2$   $\text{M}^{-1} \text{s}^{-1}$  and  $K_{\text{IP}} = 19 \pm 3$   $\text{M}^{-1}$  were obtained.



$$\text{rate} = \left( \frac{k_0 + k_{\text{APT}}K_{\text{IP}}[\text{OAc}^-]}{1 + K_{\text{IP}}[\text{OAc}^-]} \right) [\text{Ru}^{\text{V}}=\text{O}^{3+}][\text{H}_2\text{O}] \quad (8a)$$

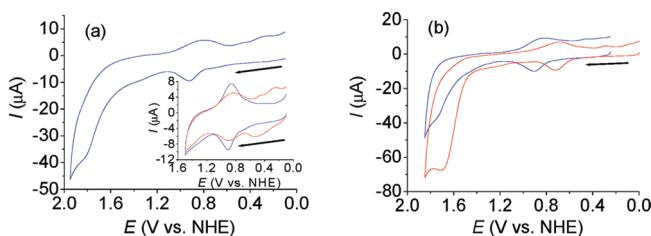
$$\frac{k_{\text{cat}}}{[\text{H}_2\text{O}]} = \frac{k_0 + k_{\text{APT}}K_{\text{IP}}[\text{OAc}^-]}{1 + K_{\text{IP}}[\text{OAc}^-]} \quad (8b)$$

$$\left( \frac{k_{\text{cat}}}{k_0[\text{H}_2\text{O}]} - 1 \right)^{-1} = \left[ \left( \frac{i_{\text{cat,B}}}{i_{\text{cat,o}}} \right)^2 - 1 \right]^{-1} = \frac{k_0}{k_{\text{APT}}} + \frac{k_0}{k_{\text{APT}}K_{\text{IP}}} \left( \frac{1}{[\text{OAc}^-]} \right) \quad (8c)$$

In Figure 3a is shown a CV of  $\text{FTO}|\text{1-PO}_3\text{H}_2$  in 0.1 M  $\text{LiClO}_4/\text{PC}$  with 6%  $\text{H}_2\text{O}$ , 30 mM in  $\text{HNO}_3$ , at 100 mV/s. The pattern of surface

waves in PC is similar to those observed for the solution analogue with  $E^\circ = 0.89$  V for the  $\text{Ru}^{\text{III}}-\text{OH}_2^{3+}/\text{Ru}^{\text{II}}-\text{OH}_2^{2+}$  couple, but there is additional mechanistic information. New waves appear at  $E_{1/2} = 0.50$  and 0.35 V following an oxidative excursion to the water oxidation wave at 1.85 V. We tentatively assign these waves to the peroxidic couples  $\text{Ru}^{\text{IV}}(\text{OO})^{2+}/\text{Ru}^{\text{III}}(\text{OOH}_2)^{3+}$  and  $\text{Ru}^{\text{III}}(\text{OOH}_2)^{3+}/\text{Ru}^{\text{II}}(\text{OOH}_2)^{2+}$ . CV evidence for peroxidic couples in water has been reported previously.<sup>3</sup> The appearance of the peroxidic waves indicates that under these conditions, further oxidation of  $\text{Ru}^{\text{IV}}(\text{OO})^{2+}$  and  $\text{O}_2$  loss are in competition with reduction of the intermediate on the electrode surface (see Scheme 1).

As shown by the data in Figure 3b, the APT pathway also appears for surface electrocatalytic water oxidation in 0.1 M  $\text{LiClO}_4/\text{TFE}$  with 6%  $\text{H}_2\text{O}$  and added  $\text{OAc}^-$ . The shift in the  $E_{1/2}$  values for the  $\text{Ru}(\text{III}/\text{II})$  couple in going from added  $\text{HNO}_3$  to  $\text{OAc}^-$  is consistent with the pH dependence of the  $\text{Ru}(\text{III}/\text{II})$  couple as noted above.



**Figure 3.** (a) CV of  $\text{FTO}|\text{1-PO}_3\text{H}_2$  in 0.1 M  $\text{LiClO}_4/\text{PC}$  with 6% (3.3 M)  $\text{H}_2\text{O}$ , 30 mM in  $\text{HNO}_3$ . The inset shows CVs of  $\text{FTO}|\text{1-PO}_3\text{H}_2$  before (blue line) and after (red line) a potential scan through the catalytic oxidation wave at 1.85 V. (b) CVs of  $\text{FTO}|\text{1-PO}_3\text{H}_2$  in 0.1 M  $\text{LiClO}_4/\text{TFE}$  with 6% (3.3 M)  $\text{H}_2\text{O}$ , with 30 mM  $\text{HNO}_3$  (blue line) or 15 mM in  $\text{OAc}^-$  in 1:1 mol/mol  $\text{LiOAc}/\text{HOAc}$  (red line). Scan rate, 100 mV/s.

Electrocatalytic water oxidation was investigated at  $\text{ITO}|\text{nanoITO}|\text{1-PO}_3\text{H}_2$  with 0.2 mM **1-PO}\_3\text{H}\_2 in the external solution in 15%  $\text{H}_2\text{O}$ , 1:1 PC/EC mixtures at an applied potential of 1.85 V (vs NHE) (Figure S15). Steady-state catalytic current densities of 70  $\mu\text{A}/\text{cm}^2$  were obtained during the electrolysis over extended periods. Under these conditions, the surface mechanism is presumably that shown in Scheme 1 but with  $\text{Ru}^{\text{III}}(\text{OOH}_2)^{3+}$  as an intermediate rather than  $\text{Ru}^{\text{III}}-\text{OOH}_2^{2+}$ . Further oxidation of  $\text{Ru}^{\text{III}}(\text{OOH}_2)^{3+}$  with proton loss to give  $\text{Ru}^{\text{IV}}(\text{OO})^{2+}$  followed by the remainder of the cycle results in oxygen evolution. In the electrocatalytic experiments, released protons (as  $\text{H}_3\text{O}^+$ ) in the 15%  $\text{H}_2\text{O}$ , 1:1 PC/EC mixture are reduced at the auxiliary electrode ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ). After 12 h of electrolysis at 1.85 V,  $\sim 12.0$   $\mu\text{mol}$  of  $\text{O}_2$  was detected by an oxygen electrode (Ocean Optics NeoFox, HIOXY), corresponding to  $\sim 400$  turnovers and a Faradaic efficiency of 70%. Electrolysis at  $\text{ITO}|\text{nanoITO}|\text{1-PO}_3\text{H}_2$  with 0.2 mM **1-PO}\_3\text{H}\_2 in 0.1 M  $\text{LiClO}_4/\text{TFE}$  with 15%  $\text{H}_2\text{O}$  and 15 mM  $\text{OAc}^-$  at 1.75 V occurred with a catalytic current density of 120  $\mu\text{A}/\text{cm}^2$  and a Faradaic efficiency of 65% over an electrolysis period of 12 h.****

The results of this study are significant in demonstrating not only that catalytic water oxidation can occur in nonaqueous environments but also that it occurs with greatly enhanced rates and by a new pathway involving direct O-atom addition to  $\text{H}_2\text{O}$ . There may be important implications in these results for alternate solar-fuel strategies in nonaqueous environments.

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**Supporting Information Available:** Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) The selection of appropriate bases in nonaqueous solvents is limited by solubility and oxidative stability: (1) Lithium acetate ( $\text{CH}_3\text{CO}_2\text{Li}$ ) is difficult to dissolve in PC. (2) Lithium phosphate ( $\text{LiH}_2\text{PO}_4$ ,  $\text{Li}_2\text{HPO}_4$ , or  $\text{Li}_3\text{PO}_4$ ) is not soluble in PC or TFE. (3) Organic bases such as phthalate, histidine, citrate, or 4-(2-hydroxyethyl)-1-piperazineethanesulfonate (HEPES) are oxidized at the electrode or by  $\text{Ru}^{\text{V}}=\text{O}^{3+}/\text{Ru}^{\text{V}}=\text{O}^{2+}$ .
- (12) There is evidence for a direct reaction between  $\text{Ru}^{\text{V}}=\text{O}^{3+}$  and  $\text{OAc}^-$  with no added water; this is currently under investigation.

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