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Multiple Pathways for Benzyl Alcohol Oxidation by $Ru^{V}=O^{3+}$ and $Ru^{IV}=O^{2+}$

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Significant rate enhancements are found for benzyl alcohol oxidation by the $Ru^{V}=O^{3+}$ form of the water oxidation catalyst [Ru(Mebimpy)-(bpy)(OH_2)]$^{2+}$ [Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine; bpy = 2,2′-bipyridine] compared to $Ru^{IV}=O^{2+}$ and for the $Ru^{IV}=O^{2+}$ form with added bases due to a new pathway, concerted hydride proton transfer (HPT).

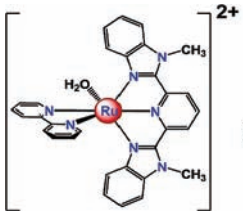
There is an extensive literature of catalytic and mechanistic studies on alcohol oxidation by high-oxidation-state polypyridyl Ru=O.[1−8] Multiple mechanisms have been proposed for these reactions including H-atom transfer,[2,3,9] C−H insertion,[10,11] and $2e^{-}/1H^{+}$ hydride transfer.[3,12] Oxidants used in previous studies such as $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and $[Ru^{IV}$-(tpy)(bpy)$(O)]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) were kinetically slow and were limited to acidic solutions because of the instability of their high-oxidation-state forms toward ligand oxidation.[4,5]

In a recent development, a related family of single-site water oxidation catalysts has been identified that functions both in solution and as phosphonate derivatives on electrode surfaces.[13−17] An example is [Ru(Mebimpy)-(bpy)$(H_2O)]^{2+}$ (**1**). It undergoes oxidative activation by stepwise proton-coupled electron transfer (PCET),

$$Ru^{II}\text{-}OH_2^{2+} \xrightarrow{-e^-/-H^+} Ru^{III}\text{-}OH^{2+} \xrightarrow{-e^-/-H^+} Ru^{IV}=O^{2+},$$

followed by 1 e^{-} oxidation to $Ru^{V}=O^{3+}$. With a family of oxidation catalysts available having properties systematically tunable by ligand variations, it is possible to decrease water oxidation as a background reaction and investigate oxidation of competing substrates based on both $Ru^{IV}=O^{2+}$ and the more powerful oxidant, $Ru^{V}=O^{3+}$.

We report here the results of a preliminary study on the oxidation of benzyl alcohol (BnOH) by the $Ru^{IV}=O^{2+}$ and $Ru^{V}=O^{3+}$ forms of (**1**). The results are notable in demonstrating a significant rate enhancement for $Ru^{V}=O^{3+}$ compared to $Ru^{IV}=O^{2+}$ and in identifying multiple pathways for alcohol oxidation by $Ru^{IV}=O^{2+}$ including a novel base-assisted pathway that appears to involve concerted hydride proton transfer (HPT).[18]



[Ru(Mebimpy)(bpy)$(OH_2)]^{2+}$ **(1)**

Synthesis and characterization of the catalyst were reported elsewhere.[19,20] At pH = 1, $E_{1/2}$ values for the pH-dependent Ru^{III}-OH_2^{3+}/Ru^{II}-OH_2^{2+} and $Ru^{IV}=O^{2+}/Ru^{III}$-OH_2^{3+} couples are 0.82 and 1.30 V versus normal hydrogen electrode (NHE). For the pH-independent $Ru^{V}=O^{3+}/Ru^{IV}=O^{2+}$ couple, $E_{1/2}$ = 1.65 V.[19] For convenience, a plot of $E_{1/2}$ versus pH and a listing of $E_{1/2}$ values are given in Supporting Information, Figure SI 1 and Table SI 1.

For kinetic measurements, cyclic voltammetry experiments were performed at a boron-doped diamond (BDD) electrode. In Figure 1 is shown a series of cyclic voltammograms of (**1**) at pH = 7.4 in a phosphate buffer ($H_2PO_4^{-}/HPO_4^{2-}$) in KNO_3 (I = 0.1 M) with increasing concentrations of added BnOH. Under these conditions, the peak-to-peak separation for the $Ru^{IV}=O^{2+}/Ru^{III}$-OH^{2+} couple at $E_{1/2}$ = 0.95 V is much greater than 60 mV and wave forms are broadened because of kinetically slow PCET oxidation of Ru^{III}-OH^{2+} to $Ru^{IV}=O^{2+}$.[21]

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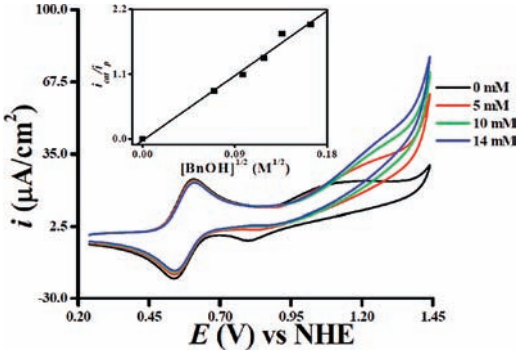

Figure 1. Cyclic voltammograms (vs NHE) of 1 mM (**1**) in a 30 mM phosphate buffer ($H_2PO_4^-/HPO_4^{2-}$) at pH = 7.4 (I = 0.1 M; KNO_3, 21 ± 2 °C) at 10 mV s^{-1}, showing the influence of added BnOH on the oxidative wave for the $Ru^{IV}{=}O^{2+}/Ru^{III}$-$OH^{2+}$ couple at $E_{1/2}$ = 0.95 V at this pH (Figure SI (**1**) in the Supporting Information). The electrode was BDD (0.07 cm^2). In the inset is shown a plot of i_{cat}/i_p at 1.24 V vs $[BnOH]^{1/2}$, see the text.

At a scan rate of 10 mV s^{-1}, $E_{p,a}$ for the $Ru^{IV}{=}O^{2+}/Ru^{III}$-$OH^{2+}$ couple appears at ~1.24 V with and without added BnOH. As shown in the inset in Figure 1, with added BnOH, the current ratio (i_{cat}/i_p) at 1.24 V increases linearly with $[BnOH]^{1/2}$ (i_p and i_{cat} are the peak currents without and with added alcohol). This potential was chosen for analysis because it is the peak potential for the oxidative component of the $Ru^{IV}{=}O^{2+}/Ru^{III}$-$OH^{2+}$ wave and it is well separated from the $Ru^{V}{=}O^{3+}/Ru^{IV}{=}O^{2+}$ couple at $E_{1/2}$ = 1.65 V. The latter dominates catalysis at higher potentials; see below. The ratio i_{cat}/i_p varies linearly with $1/\nu^{1/2}$ (ν is the scan rate) over the range 10−200 mV s^{-1}. i_{cat} increases linearly with a change in the complex concentration from 0.13 to 1.0 mM.

Catalytic rate constants, k_{cat}, were determined from the peak current ratio by use of eq 1.[22] In eq 1, R, T, n, F, and ν are the gas constant, temperature, number of electrons transferred (n = 2 for BnOH oxidation to benzaldehyde; see below), Faraday constant, and scan rate, respectively. Current measurements under argon and in air gave the same results in this and other studies reported here.

$$\frac{i_{cat}}{i_p} = \frac{(RT)^{1/2}}{0.446(nF\nu)^{1/2}} k_{cat}{}^{1/2} = \frac{(RT)^{1/2}}{0.446(nF\nu)^{1/2}} k^{1/2}(\mathrm{BnOH})^{1/2} \quad (1)$$

The scan rate and concentration dependences of i_{cat}/i_p are consistent with eq 1 with $k_{cat} = k_{Ru^{IV}}[BnOH]$ and the rate law in eq 2a. Kinetic measurements were also performed in 0.1 M KNO_3 (pH = 7) at 21 ± 2 °C and at pH = 2.5 and 3.0 with added HNO_3 with no evidence for a pH dependence over the pH range 2.5−7. The average rate constant from the three sets of measurements gave $k_{Ru^{IV}} = 16 \pm 1\ M^{-1}\ s^{-1}$. For comparison, $k_{Ru^{IV}} = 2.43 \pm 0.03\ M^{-1}\ s^{-1}$ for oxidation of BnOH by *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ under similar conditions.[4]

$$\text{rate} = k_{cat}[Ru^{IV}{=}O^{2+}] = k_{Ru^{IV}}[Ru^{IV}{=}O^{2+}][BnOH] \quad (2a)$$

$$\text{rate} = k_{cat}[Ru^{V}{=}O^{3+}] = k_{Ru^{V}}[Ru^{V}{=}O^{3+}][BnOH] \quad (2b)$$

In order to verify benzaldehyde as a major product, a controlled potential electrolysis experiment was conducted.

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Table 1. Rate Constants for BnOH Oxidation by $Ru^{IV}{=}O^{2+}$ and $Ru^{V}{=}O^{3+}$ at 21 ± 2 °C, I = 0.1 M (KNO_3)

base (B)	pK_a (HB)	$k_B \times 10^{-2}$ ($M^{-2}\ s^{-1}$)
OAc^-	4.7	2.4 ± 0.9
HPO_4^{2-}	7.2	5.8 ± 0.4
PO_4^{3-}	12.3	77 ± 9
$k_{Ru^{IV}}$		16 ± 1 $M^{-1}\ s^{-1}$
$k_{Ru^{V}}$		3230 ± 50 $M^{-1}\ s^{-1}$

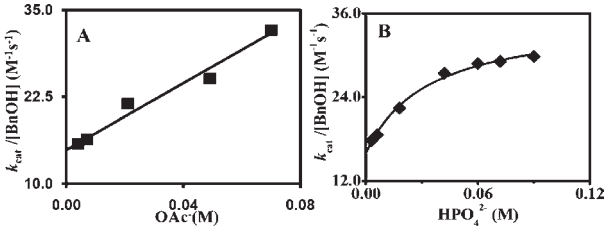

Figure 2. Plots of $k_{cat}/[BnOH]$ vs $[OAc^-]$ at pH = 5.1 (A) and vs $[HPO_4^{2-}]$ at pH = 7.4 (B) for oxidation of BnOH by $Ru^{IV}{=}O^{2+}$ at 21 ± 2 °C with I = 0.1 M (KNO_3).

In this experiment, [BnOH] = 97 mM and $[Ru\text{-}OH_2]^{2+}$ = 2 mM with electrolysis at a *nano*-indium−tin oxide electrode[23] (~5 μm, 0.72 cm^2) at 1.34 V vs NHE in a pH = 7.4 $H_2PO_4^-/HPO_4^{2-}$ buffer (I = 0.1 M). Electrolysis was continued for 580 min with stirring, with a steady-state current density of 140 μA cm^{-2} reached after 2000 s. Following extraction by chloroform, ^1H NMR showed the presence of benzaldehyde (95%) and a small amount of benzoic acid (5%) in the chloroform layer. The total faradaic efficiency was 76%.

In 0.1 M HNO_3, greatly enhanced catalytic currents were observed when oxidative scans were extended to the $Ru^{V}{=}O^{3+}/Ru^{IV}{=}O^{2+}$ wave at $E_{1/2}$ = 1.65 V. i_{cat}/i_p, measured at $E_{p,a}$ = 1.74 V for this couple, varied with $[BnOH]^{1/2}$ over the range 0.1−0.6 mM. Analysis of the data with the rate law in eq 2b gave $k_{Ru^{V}} = (3.2 \pm 0.1) \times 10^3\ M^{-1}\ s^{-1}$ (Table 1). A comparison of the rate constant data in Table 1 shows a rate enhancement of ~200 for BnOH oxidation by $Ru^{V}{=}O^{3+}$ compared to $Ru^{IV}{=}O^{2+}$. With isopropyl alcohol as the added alcohol, $k_{Ru^{V}} = 320 \pm 20\ M^{-1}\ s^{-1}$.

Oxidation of BnOH by $Ru^{IV}{=}O^{2+}$ below pH = 2.5 could not be studied because of the greatly enhanced reactivity of $Ru^{V}{=}O^{3+}$ due to the closely spaced $E_{1/2}$ values for the $Ru^{V}{=}O^{3+}/Ru^{IV}{=}O^{2+}$ and $Ru^{IV}{=}O^{2+}/Ru^{III}$-$OH^{2+}$ couples (Figure SI 1). Studies of BnOH oxidation by $Ru^{V}{=}O^{3+}$ were restricted to pH = 1 because of competitive water oxidation at higher pHs.[13]

Oxidation of BnOH by $Ru^{IV}{=}O^{2+}$ is buffer-base-dependent. In Figure 2 are shown plots of $k_{cat}/[BnOH]$ at fixed pH (5.1 for acetic acid/acetate HOAc/OAc^-; 7.4 for $H_2PO_4^-/HPO_4^{2-}$) for the added buffer bases OAc^- and HPO_4^{2-}. As shown in Figure 2A, $k_{cat}/[BnOH]$ increased linearly with $[OAc^-]$. Extrapolation to $[OAc^-] = 0$ gave $k = 15\ M^{-1}\ s^{-1}$, consistent with $k_{Ru^{IV}} = 16\ M^{-1}\ s^{-1}$ in the absence of added buffer. These observations are consistent with the rate law in eq 3 and an additional term for BnOH oxidation first order in $[OAc^-]$. From the slope of the plot in Figure 2A, $k_B = k_{OAc^-} = 240 \pm 94\ M^{-2}\ s^{-1}$ (Table 1).

$$\text{rate} = k_{cat}[Ru^{IV}{=}O^{2+}] = \{k_{Ru^{IV}} + k_{OAc^-}[OAc^-]\}[Ru^{IV}{=}O^{2+}][BnOH] \quad (3)$$

With added HPO_4^{2-}, there is evidence for saturation kinetics at high $[HPO_4^{2-}]$ (Figure 2B and the mechanism in eq 4 with preliminary ion-pair formation, eq 4a, followed by

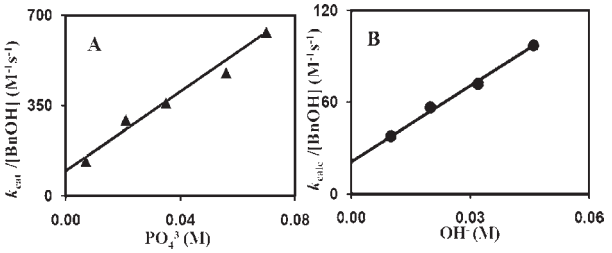

Figure 3. (A) Plot of k_{cat}/[BnOH] vs $[PO_4^{3-}]$ at pH = 12.7 and (B) plot of k_{calc}/[BnOH] vs $[OH^-]$ for BnOH oxidation by $Ru^{IV}{=}O^{2+}$ over the pH range 12−12.7 at 21 ± 2 °C with I = 0.1 M (KNO_3); see the text.

oxidation, eq 4b). The rate law is given in eq 5. The experimental points in Figure 2B were fit to the rate law in eq 5 with $k_{Ru^{IV}}$ = 16 M^{-1} s^{-1}, K_{IP} = 30 M^{-1}, k_{red} = 20 M^{-1} s^{-1}, and $k_{HPO_4^{2-}} = k_{red}K_{IP}$ = 576 ± 44 M^{-2} s^{-1} (Table 1).

$$Ru^{IV}{=}O^{2+} + HPO_4^{2-} \rightleftharpoons Ru^{IV}{=}O^{2+}, HPO_4^{2-} : \quad K_{IP} \tag{4a}$$

$$Ru^{IV}{=}O^{2+}, HPO_4^{2-} + BnOH \rightarrow Ru^{II}\text{-}OH^+ + PhCHO + H_2PO_4^- : \quad k_{red} \tag{4b}$$

$$Ru^{II}\text{-}OH^+ + H^+ \rightleftharpoons RuOH_2^{2+} : \quad \text{rapid}$$

$$\text{rate} = \{k_{Ru^{IV}} + (K_{IP}k_{red}[HPO_4^{2-}])/(1 + K_{IP}[HPO_4^{2-}])\}[Ru^{IV}{=}O^{2+}][BnOH] \tag{5a}$$

$$k_{cat} = \{k_{Ru^{IV}} + (K_{IP}k_{red}[HPO_4^{2-}])/(1 + K_{IP}[HPO_4^{2-}])\}[BnOH] \tag{5b}$$

An additional rate enhancement was observed at pH = 12.7 with added HPO_4^{2-}/PO_4^{3-} buffer. As shown in Figure 3A, k_{cat}/[BnOH] increased linearly with $[PO_4^{3-}]$, consistent with the rate law in eq 6 and a term first order in PO_4^{3-}. From the slope of the plot, $k_{PO_4^{3-}}$ = 7700 ± 900 M^{-2} s^{-1} (Table 1).

$$\text{rate} = \{k_0 + k_{HPO_4^{2-}}[HPO_4^{2-}] + k_{PO_4^{3-}}[PO_4^{3-}]\}[Ru^{IV}{=}O^{2+}][BnOH] \tag{6}$$

$$\text{rate} = \{k_{Ru^{IV}} + k_{OH^-}[OH^-] + k_{HPO_4^{2-}}[HPO_4^{2-}] + k_{PO_4^{3-}}[PO_4^{3-}]\}[Ru^{IV}{=}O^{2+}][BnOH] \tag{7}$$

The intercept of the plot in Figure 3A is 97 M^{-1} s^{-1}, considerably higher than the value $k_{Ru^{IV}}$ = 16 M^{-1} s^{-1}. This suggested a possible role for OH^- as a proton acceptor base. To explore this possibility, experiments were conducted in the pH range 12−12.7 by varying the $[HPO_4^{2-}]$/$[PO_4^{3-}]$ ratio with 10 mM total added buffer (I = 0.1 M). k_{calc} values were obtained at zero buffer base concentration at each pH by subtracting contributions from the PO_4^{3-} pathway from k_{cat} values obtained experimentally by using eq 6 and the known value of $k_{PO_4^{3-}}$. Under these conditions, the $k_{HPO_4^{2-}}$-$[HPO_4^{2-}]$ term was negligible. As shown in Figure 3B, k_{calc}/[BnOH] increases linearly with $[OH^-]$ over the pH range 12−12.7, consistent with an additional pathway first order in $[OH^-]$. The complete rate law is given in eq 7. From the slope of the plot in Figure 3B, k_{OH^-} = 1650 ± 540 M^{-2} s^{-1} (Table 1).

A reasonable interpretation for the OH^- pathway is that initial proton loss occurs followed by rapid oxidation of the anion, BnO^- (eq 8). The rate law for this mechanism is given in eq 9 with K_h the hydrolysis constant for the equilibrium: $PhCH_2O^- + H_2O \rightleftharpoons PhCH_2OH + OH^-$ (K_w/K_a = 0.1) with pK_a = 15 for benzyl alcohol. With this interpretation, k_{BnO^-} = 1.7 × 10^4 M^{-2} s^{-1}.

$$PhCH_2OH + OH^- \rightleftharpoons PhCH_2O^- + H_2O : \quad K_h^{-1} \tag{8a}$$

$$PhCH_2O^- + Ru^{IV}{=}O^{2+} \rightarrow Ru^{II}\text{-}OH^+ + PhCHO : \quad k_{BnO^-} \tag{8b}$$

$$\text{rate} = \{k_{Ru^{IV}} + k_{BnO^-}K_h^{-1}[OH^-]\}[Ru^{IV}{=}O^{2+}][PhCH_2OH] \tag{9}$$

The results reported here are notable in expanding the known reactivity of Ru=O complexes toward alcohol oxidation. Although detailed mechanistic studies, including supporting density functional theory calculations and C−H/C−D kinetic isotope effects, are currently under investigation, important features have already been revealed:

(i) $Ru^V{=}O^{3+}$, as $[Ru^V(Mebimpy)(bpy)(O)]^{3+}$, is a facile oxidant, ∼200 times more reactive than $Ru^{IV}{=}O^{2+}$ toward BnOH oxidation.

(ii) There is no O_2 dependence for BnOH oxidation by either $Ru^{IV}{=}O^{2+}$ or $Ru^V{=}O^{3+}$. This is in contrast to the $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ oxidations of isopropyl alcohol and benzyl alcohol, both of which exhibit O_2 dependences.[5,9] The absence of O_2 dependence is consistent with $2e^-$ pathways and net hydride transfer or C−H insertion, although the microscopic details remain to be elucidated.[3]

(iii) Deprotonation to $PhCH_2O^-$ results in a rate enhancement of ∼10^3 compared to $PhCH_2OH$ by a mechanism that appears to involve hydride ($2e^-$/$1H^+$) transfer.[18]

(iv) The pathway first order in added base (OAc^-, HPO_4^{2-}, and PO_4^{3-}) is a new pathway that does not involve prior deprotonation and $PhCH_2O^-$ oxidation because $k_B > k_{BnO^-}K_h^{-1}[OH^-]$ for all three bases.

The appearance of the new base-catalyzed pathway is notable. It points to a pathway for alcohol dehydrogenation by concerted HPT:[18]

$$Ru^{IV}{=}O^{2+} + PO_4^{3-} \rightleftharpoons Ru^{IV}{=}O^{2+}, PO_4^{3-} : \quad K_{IP} \tag{10a}$$

$$Ru^{IV}{=}O^{2+}, PO_4^{3-} + PhCH_2OH \rightarrow Ru^{IV}{=}O^{2+}, PO_4^{3-}, PhCH_2OH \tag{10b}$$

$$Ru^{IV}{=}O^{2+}, PO_4^{3-}, PhCH_2OH \rightarrow \{Ru^{IV}{=}O^{2+}\text{---}HCH(Ph)OH\text{---}OPO_3^{3-}\} \rightarrow Ru^{II}\text{-}OH^+ + PhCHO + HOPO_3^{2-} \tag{10c}$$

This pathway avoids the protonated aldehyde $PhCHOH^+$ as a high-energy intermediate and is qualitatively consistent with the dependence of k_B on the strength of the acceptor base ($-RT \ln K_a$) in Table 1. It is different from typical concerted transfer hydrogenation mechanisms, such as those described by Knowles and Noyori,[24−26] but is related to multicomponent or bifunctional hydrogenation mechanisms.[27]

(i) The acceleration with PO_4^{3-} is especially notable, with a rate acceleration of ∼40 in 0.1 M PO_4^{3-} compared to water, which may be of relevance in electrocatalysis.

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Supporting Information Available: Additional supporting electrochemical results and discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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