

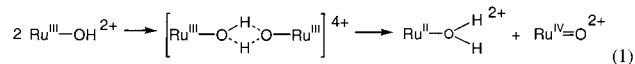
Surface Control of Oxidation by an Adsorbed Ru<sup>IV</sup>–Oxo ComplexLaurie A. Gallagher and Thomas J. Meyer\*<sup>†</sup>Contribution from the Department of Chemistry, CB #3290,  
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**Abstract:** When adsorbed to optically transparent, thin films of TiO<sub>2</sub> nanoparticles on glass, the aqua complex [Ru<sup>II</sup>(tpy)(bpy(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>)(OH<sub>2</sub>)<sup>2+</sup> (bpy(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub> is 2,2′-bipyridyl-4,4′-diphosphonic acid; tpy is 2,2′:6′,2′′-terpyridine) is oxidized by Ce<sup>IV</sup>(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub> in 0.1 M HClO<sub>4</sub> to its Ru<sup>IV</sup>=O<sup>2+</sup> form as shown by UV–visible measurements and analysis of oxidative equivalents by oxidation of hydroquinone to quinone. Kinetic studies on the oxidations of cyclohexene, benzyl alcohol, phenol, and *trans*-stilbene by surface-bound Ru<sup>IV</sup>=O<sup>2+</sup> by UV–visible monitoring reveal direct evidence for initial 2-electron steps to give Ru<sup>II</sup> intermediates in all four cases. These steps are masked in solution where Ru<sup>IV</sup> → Ru<sup>II</sup> reduction is followed by rapid reactions between Ru<sup>II</sup> intermediates and Ru<sup>IV</sup>=O<sup>2+</sup> to give Ru<sup>III</sup>. Reactions between Ru<sup>II</sup> and Ru<sup>IV</sup>=O<sup>2+</sup> on the surface are inhibited by binding to the surface, which restricts translational mobility. Rate constants on the surface and in solution are comparable, pointing to comparable reactivities. The surface experiments give unprecedented insight into oxidation mechanism with important implications for achieving product selectivity in synthesis by limiting oxidation to two electrons.

## Introduction

There is an extensive oxidation chemistry of high oxidation state ruthenium–oxo complexes in solution.<sup>1</sup> We have previously reported the appearance of Ru<sup>III</sup>–OH<sup>2+</sup>/Ru<sup>II</sup>–OH<sup>2+</sup> and Ru<sup>IV</sup>=O<sup>2+</sup>/Ru<sup>III</sup>–OH<sup>2+</sup> couples of [Ru(tpy)(bpy(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>)(OH<sub>2</sub>)<sup>2+</sup> (bpy(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub> is 2,2′-bipyridyl-4,4′-diphosphonic acid; tpy is 2,2′:6′,2′′-terpyridine) adsorbed on optically transparent ITO (In<sub>2</sub>O<sub>3</sub>:Sn) electrodes by phosphonate binding to the surface.<sup>2</sup> One finding was an inhibition toward oxidation of Ru<sup>III</sup>–OH<sup>2+</sup> to Ru<sup>IV</sup>=O<sup>2+</sup> on surfaces dilute in complex. Direct oxidation is slow because of the high potential of the Ru<sup>IV</sup>=OH<sup>3+</sup>/Ru<sup>III</sup>–OH<sup>2+</sup> one-electron couple. Chemical binding to the surface restricts translational mobility and, with it, an alternate mechanism involving cross-surface disproportionation by proton-coupled electron transfer, eq 1. We report here the use



of Ru<sup>IV</sup>=O<sup>2+</sup> adsorbed on optically transparent TiO<sub>2</sub> thin films to obtain results which give unprecedented insight into oxidation mechanisms and which suggest a possible new approach to achieving product selectivity in synthesis by limiting oxidation to two electrons.<sup>3</sup>

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## Experimental Section

**Materials.** High-purity acetonitrile was used as received from Burdick & Jackson. House-distilled water was purified further by using a Barnstead E-Pure deionization system. High-purity (99.9%) benzyl alcohol was obtained from Aldrich and used as received. Cyclohexene was obtained from Aldrich and purified by fractional distillation. Phenol was received from Aldrich and used as received. *trans*-Stilbene was obtained from Aldrich and recrystallized from ethanol. Purity of all substrates was verified by GC-MS prior to use. Ammonium cerium(IV) nitrate, sodium hypochlorite solution (10–13% available chlorine), and perchloric acid (70%) were used as received from Aldrich. All other common reagents were ACS grade and were used without additional purification.

**Preparations.** The ligand 2,2′-bipyridyl-4,4′-diphosphonic acid was provided by Fabrice Odobel, prepared by a published method.<sup>4</sup>

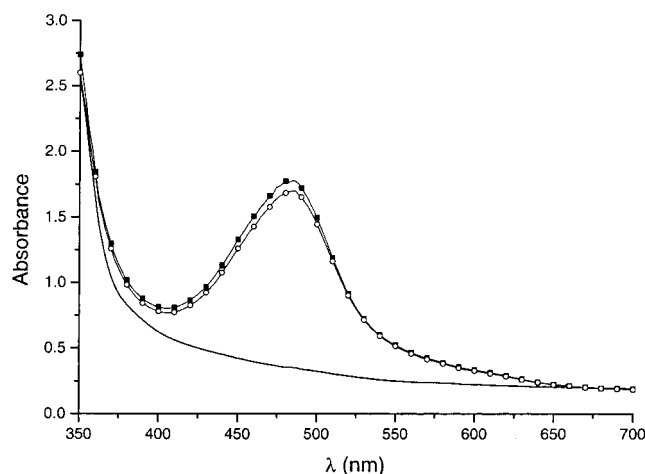
[Ru(tpy)(bpy(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>)(OH<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub>. This salt was prepared by modifying the procedure used to synthesize [Ru(tpy)(bpy)(OH<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub>,<sup>5</sup> and has been slightly modified since first reported.<sup>2</sup> Approximately 10 mg of [Ru(tpy)(bpy(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>)(Cl)](PF<sub>6</sub>) was heated at reflux in approximately 20 mL of 4 M HCl under argon for 16 h. Water and HCl (gas) were removed by rotary evaporation. The product was redissolved in approximately 20 mL of water and a slight excess of AgClO<sub>4</sub> was added to remove any remaining Cl<sup>-</sup>. AgCl(s) was removed by gravity filtration. The resulting solution was used to prepare films.

**Formation and Characterization of Modified Films.** Films of nanoparticle TiO<sub>2</sub> (3–5 μm) on glass<sup>6</sup> were modified by adsorption of [Ru(tpy)(bpy(PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>)(OH<sub>2</sub>)](ClO<sub>4</sub>)<sub>2</sub> from HClO<sub>4</sub> (pH ~2) to give glass|TiO<sub>2</sub>–Ru<sup>II</sup>–OH<sup>2+</sup> surface structures. The extent of surface loading was estimated by UV–visible measurements at λ<sub>max</sub> = 486 nm by assuming the aqueous solution value of ε = 9500 M<sup>-1</sup> cm<sup>-1</sup> for

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**Figure 1.** UV-visible spectra of (■)  $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy}(\text{PO}_3\text{H}_2)_2)(\text{OH}_2)]^{2+}$  and (—)  $[\text{Ru}^{\text{IV}}(\text{tpy})(\text{bpy}(\text{PO}_3\text{H}_2)_2)(\text{O})]^{2+}$  after oxidation of the aqua complex by  $\text{Ce}^{\text{IV}}(\text{NH}_4)_4(\text{NO}_3)_6$  in 0.1 M  $\text{HClO}_4$  and of (○)  $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy}(\text{PO}_3\text{H}_2)_2)(\text{OH}_2)]^{2+}$  after rereduction by  $2 \times 10^{-6}$  M hydroquinone in water.

$[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy}(\text{PO}_3\text{H}_2)_2)(\text{OH}_2)]^{2+}$ .<sup>2</sup> Surface adsorption at 25 °C followed the Langmuir isotherm with  $K = 3 \times 10^5 \text{ M}^{-1}$  for surface binding, with equilibrium coverage achieved in dilute solutions ( $< 1 \times 10^{-5} \text{ M}$ ) after 3 days. The maximum coverage was approximately  $1 \times 10^{-7} \text{ mol/cm}^2$ , which corresponds to  $\sim 1000$  effective monolayers based on the area of the surface and assuming a monolayer coverage of  $\sim 1 \times 10^{-10} \text{ mol/cm}^2$  as estimated from van der Waals radii.<sup>7</sup>

**Kinetic Studies.** UV-visible spectra were collected as a function of time with a Hewlett-Packard 8452A diode array spectrophotometer interfaced with a Gateway computer. Films of  $[\text{Ru}(\text{tpy})(\text{bpy}(\text{PO}_3\text{H}_2)_2)(\text{O})](\text{ClO}_4)_2$  were placed in substrate solutions in acetonitrile at room temperature in standard quartz cuvettes. Solutions were stirred to avoid a contribution to the kinetics from diffusion with a NSG Precision Cells electronic cell stirrer. There was no dependence on stir rate with any of the substrates under the conditions used for kinetics experiments.

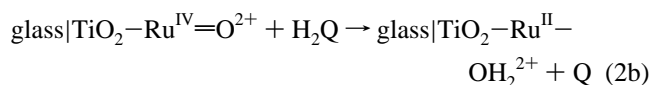
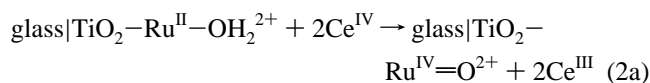
**Product Analysis.** Organic products were analyzed with a Hewlett-Packard 5890 series II gas chromatograph with a  $0.25 \text{ m} \times 0.2 \text{ mm} \times 0.33 \mu\text{m}$  film thickness HP-FFAP column and a Hewlett-Packard 5971A mass selective detector both interfaced with a Hewlett-Packard computer. Product analysis was performed by using multiple films of  $[\text{Ru}(\text{tpy})(\text{bpy}(\text{PO}_3\text{H}_2)_2)(\text{O})](\text{ClO}_4)_2$  in a nitrogen-purged glovebox under red light. When the reaction was complete, the films were rinsed several times with a solvent chosen based on preliminary TLC experiments on the possible products. The solution containing the organic products was concentrated on a vacuum line before GCMS was performed.

## Results and Discussion

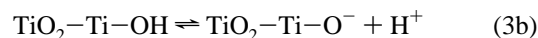
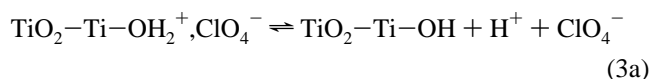
Phosphonate binding to the surface provides a water-stable linkage in acidic solution (in contrast to carboxylate binding).<sup>8</sup> Oxidation of the modified film by  $\text{Ce}^{\text{IV}}(\text{NH}_4)_2(\text{NO}_3)_6$  in 0.1 M  $\text{HClO}_4$  leads to loss of the characteristic MLCT absorption band at 486 nm accompanied by the formation of  $\text{glass}|\text{TiO}_2-\text{Ru}^{\text{IV}}=\text{O}^{2+}$  (Figure 1). The extent of oxidation on the surface was established by adding an aqueous solution of hydroquinone ( $[\text{H}_2\text{Q}] \sim 2 \times 10^{-6} \text{ M}$ ) and monitoring the quinone (Q) product spectrophotometrically. Experiments were carried out in the absence of air and light in order to avoid oxidation by direct

band gap excitation of the semiconductor.<sup>9</sup> The amount of benzoquinone produced was determined by UV-visible spectroscopy with  $\epsilon(248 \text{ nm}) = 143 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\epsilon(290 \text{ nm}) = 2600 \text{ M}^{-1} \text{ cm}^{-1}$  for hydroquinone and  $\epsilon(248 \text{ nm}) = 20700 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\epsilon(290 \text{ nm}) = 357 \text{ M}^{-1} \text{ cm}^{-1}$  for benzoquinone.<sup>1c</sup> Hydroquinone reduction restored the MLCT band of the surface-bound complex at 486 nm (Figure 1). Surface coverages obtained by analysis of quinone produced and by assuming complete oxidation to  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  on the surface were systematically higher (10–15%) than by direct UV-visible measurements, presumably because of a slightly decreased molar absorptivity on the surface. Blank experiments on films with adsorbed  $\text{Ru}^{\text{II}}-\text{OH}_2^{2+}$  in the absence of air and light gave no benzoquinone product.

These results are consistent with surface oxidation and reduction as in eq 2.

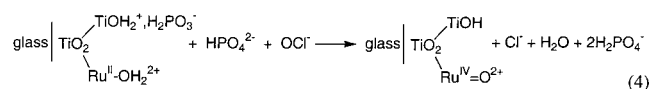


The  $\text{TiO}_2$  films are acidic because of the presence of surface aqua and hydroxyl groups and the acid-base equilibria,



On the basis of potentiometric titrations on anatase P25 powder, the  $\text{p}K_a$  values of the above equilibria are 4.98 and 7.80, respectively.<sup>10</sup>

Because of potential complications from acid-catalyzed reactions after oxidation, such as ring opening of epoxides (see below), films containing  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  were also prepared by using  $\text{NaOCl}$  in a phosphate buffer at pH 7.3 ( $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ ). Under these conditions, the same absorbance changes were observed but of lesser magnitude. This may be due to partial loss of complex from the surface at the higher pH.<sup>8,11</sup> Oxidation under these conditions gives  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  adsorbed on a nonacidic surface, eq 4.<sup>12</sup>



**Oxidation of Cyclohexene.** Based on the results of kinetic studies,  $^{18}\text{O}$  isotopic labeling, and elucidation of intermediates, the first step in the oxidation of cyclohexene by *cis*- $[\text{Ru}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  in  $\text{CH}_3\text{CN}$  has been proposed to occur

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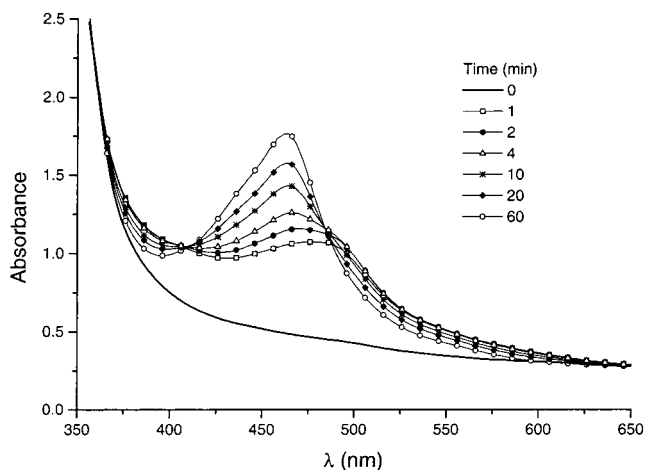
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**Figure 2.** UV-vis spectral changes for the reaction between  $5.0 \times 10^{-3}$  M cyclohexene and  $\text{glass|TiO}_2\text{-Ru}^{\text{IV}}=\text{O}^{2+}$  in  $\text{CH}_3\text{CN}$  at room temperature.

by C-H insertion.<sup>13</sup> This step is followed by oxidation of the



$\text{Ru}^{\text{II}}$  intermediate by  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$ , which occurs rapidly to give an observable  $\text{Ru}^{\text{III}}(\text{enolate})^{2+}$  intermediate. It undergoes further reaction to give the final product, 2-cyclohexen-1-one.<sup>13</sup> At high cyclohexene concentrations, the corresponding alcohol, 2-cyclohexen-1-ol, also appears as a minor product due to oxidation of free olefin by  $\text{Ru}^{\text{III}}$ .<sup>13</sup>

Absorbance changes that occur on  $\text{glass|TiO}_2\text{-Ru}^{\text{IV}}=\text{O}^{2+}$  following addition of cyclohexene reveal a stepwise reaction (Figure 2). In contrast to the reaction in solution, the initial product of reduction of  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  is  $\text{Ru}^{\text{II}}$  rather than  $\text{Ru}^{\text{III}}$ . The  $\text{Ru}^{\text{II}}$  intermediate that forms has a characteristic  $\lambda_{\text{max}}$  at 510 nm. There is no evidence for  $\text{Ru}^{\text{III}}$  as an intermediate oxidation state.

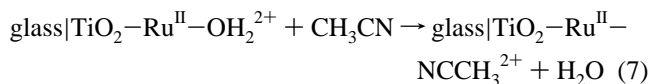
Once formed, the  $\text{Ru}^{\text{II}}$  intermediate undergoes solvolysis to give  $\text{glass|TiO}_2\text{-Ru}^{\text{II}}\text{-NCCH}_3^{2+}$  ( $\lambda_{\text{max}} = 462$  nm). Solvolysis occurs by biexponential kinetics, eq 6a. In eq 6a,  $\Delta A_t$  is the absorbance change at the monitoring wavelength,  $A_t - A_\infty$ , with  $A_t$  the absorbance at time  $t$  and  $A_\infty$  the absorbance at  $t = \infty$ .  $\Delta A_1$  and  $\Delta A_2$  are the contributions to the total absorbance change by the two kinetic components,  $\Delta A = A_0 - A_\infty$ , with  $A_0$  the absorbance at  $t = 0$ . The component rate constants are  $k_1$  and  $k_2$ . The average rate constant,  $\langle k \rangle$ , was calculated from eq 6b.

$$\Delta A_t = \Delta A_1 \exp(-k_1 t) + \Delta A_2 \exp(-k_2 t) \quad (6a)$$

$$\langle k \rangle = (k_1 \Delta A_1 + k_2 \Delta A_2) / (\Delta A_1 + \Delta A_2) \quad (6b)$$

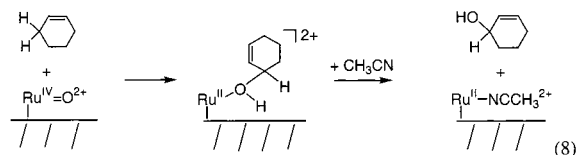
The solvolysis kinetics were independent of monitoring wavelength with  $\langle k_{\text{solv}} \rangle = 1.1(\pm 0.2) \times 10^{-3} \text{ s}^{-1}$ . These observations rule out surface-bound  $\text{Ru}^{\text{II}}\text{-OH}_2^{2+}$ ,  $\text{glass|TiO}_2\text{-Ru}^{\text{II}}\text{-OH}_2^{2+}$ , as the initial intermediate, since its  $\lambda_{\text{max}}$  occurs at 486 nm and it undergoes solvolysis with  $\langle k_{\text{solv}} \rangle = 1.6(\pm 0.1) \times 10^{-3} \text{ s}^{-1}$  by independent measurement, eq 7. The appearance of nonexponential kinetics on the surface is presumably a consequence of there being a distribution of surface sites which differ somewhat in reactivity, in this case toward solvolysis.

(13) (a) Stultz, L. K.; Huynh, M. H. V.; Binstead, R. A.; Curry, M.; Meyer, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 5984. (b) Seok, W. K.; Dobson, J. C.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 5.



When monitored at 484 nm, an isobestic point between the  $\text{Ru}^{\text{II}}$  intermediate and  $\text{Ru}^{\text{II}}\text{-NCCH}_3^{2+}$ , the absorbance-time changes for the initial redox step also followed biexponential kinetics. Treatment of the data by using eq 6b gave  $\langle k_{\text{obs}} \rangle$  and a plot of  $\langle k_{\text{obs}} \rangle$  vs [cyclohexene] from 0.001 to 0.1 M was linear, showing that the surface reaction was first order in olefin. From the slope,  $\langle k \rangle = 0.85 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1}$ , compared to  $k = 0.16 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$  for oxidation of cyclohexene by  $\text{cis-}[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  in  $\text{CH}_3\text{CN}$  at 25 °C.<sup>13a</sup> This comparison shows that  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  reactivity is retained on the surface. The increase in rate constant for the surface-bound reaction is a consequence, in part, of the fact that adsorbed  $[\text{Ru}^{\text{IV}}(\text{tpy})(\text{bpy})(\text{PO}_3\text{H}_2)_2(\text{O})]^{2+}$  is a stronger 2-electron oxidant than  $\text{cis-}[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  in solution by 160 mV.<sup>2,14</sup>

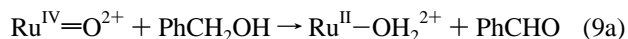
In contrast to the solution reaction, product analysis by GC-MS after oxidation and solvolysis showed that 2-cyclohexen-1-ol was the major product and 2-cyclohexen-1-one a minor product.<sup>15</sup> This observation and the appearance of the  $\text{Ru}^{\text{II}}$  as an intermediate provide direct evidence that the mechanism of oxidation of cyclohexene by  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  is initial C-H insertion followed by solvolysis, eq 8. The ketone probably originates



from oxidation of 2-cyclohexen-1-ol released by solvolysis from the surface. Oxidation of the alcohol by  $\text{cis-}[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  in solution is more rapid than oxidation of the olefin by a factor of  $\sim 14$  with  $k(25 \text{ °C}, \text{CH}_3\text{CN}) = 2.2 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>13</sup>

**Oxidation of Benzyl Alcohol.** Use of a similar protocol, but with benzyl alcohol as the reductant, also results in the appearance of a  $\text{Ru}^{\text{II}}$  intermediate with  $\lambda_{\text{max}} \sim 486$  nm, also without the intervention of  $\text{Ru}^{\text{III}}$ . In the reduction of  $\text{cis-}[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  by benzyl alcohol in solution under comparable conditions,  $\text{cis-}[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{py})(\text{OH})]^{2+}$  appears as an intermediate.<sup>1h</sup> A kinetics study with benzyl alcohol from 0.001 to 0.1 M in  $\text{CH}_3\text{CN}$  showed that the surface reaction is first order in alcohol. From the slope of a plot of  $k_{\text{obs}}$  vs [benzyl alcohol],  $k = 3.0(\pm 0.5) \text{ M}^{-1} \text{ s}^{-1}$ .<sup>16</sup> For the equivalent reaction in  $\text{CH}_3\text{CN}$  with  $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  as the oxidant,  $k = 1.54(\pm 0.08) \text{ M}^{-1} \text{ s}^{-1}$ .<sup>1h</sup> Rate constants for the surface reaction were the same when  $\text{glass|TiO}_2\text{-Ru}^{\text{II}}\text{-OH}_2^{2+}$  was oxidized at pH 7.3 as when oxidized at pH 1. This shows that the reaction on the surface is unaffected by changing the local surface environment from  $-\text{Ti}-\text{OH}_2^+, \text{ClO}_4^-$  to  $-\text{TiOH}$ , eq 4. Product analysis by GC-MS gave benzaldehyde as the sole product.

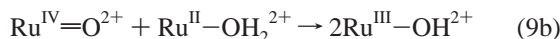
For the solution reaction, an initial two-electron step followed by rapid comproportionation was proposed.<sup>1h</sup>



(14) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436.

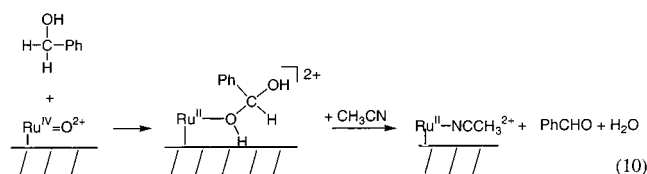
(15) Quantitation of the product distribution by GC-MS has proven difficult because of the small amounts of products produced in the surface experiments.

(16) The kinetics in this case are exponential. The form of the kinetics in these reactions may be symptomatic of the key microscopic (rate determining) steps that occur in the mechanism.

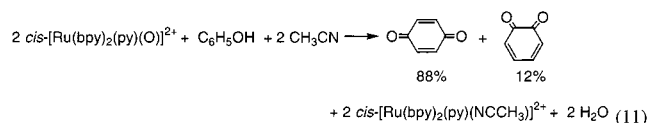


Two-electron transfer is observed on the surface without complication from comproportionation, eq 9b, because of the loss in translational mobility due to surface binding.

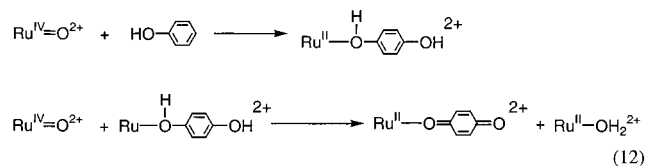
There is additional information in these data. The mechanism originally proposed for benzyl alcohol oxidation was hydride transfer with formation of  $\text{Ru}-\text{OH}_2^{2+}$  (eq 9a).<sup>1b</sup> However, the intermediate that forms on the surface undergoes solvolysis with  $\langle k_{\text{solV}} \rangle = 5.4 \times 10^{-4} \text{ s}^{-1}$  in acetonitrile. This is significantly slower than solvolysis of  $\text{glass}[\text{TiO}_2-\text{Ru}^{\text{II}}-\text{OH}_2^{2+}]$ , with  $\langle k_{\text{solV}} \rangle = 1.6 \times 10^{-3} \text{ s}^{-1}$ . The observations made here are consistent with the recent suggestion of a mechanism in which the initial step is C-H insertion to give a bound aldehyde hydrate,<sup>17</sup> followed by solvolysis and dehydration of the hydrate, eq 10.



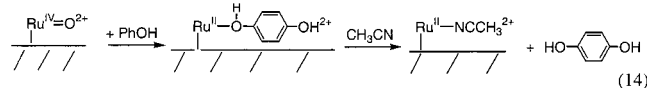
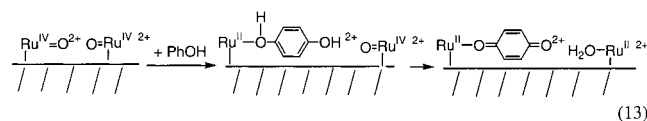
**Oxidation of Phenol.** Oxidation of phenol by  $\text{cis}-[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  in acetonitrile occurs by the net reaction in eq 11.<sup>1g</sup>



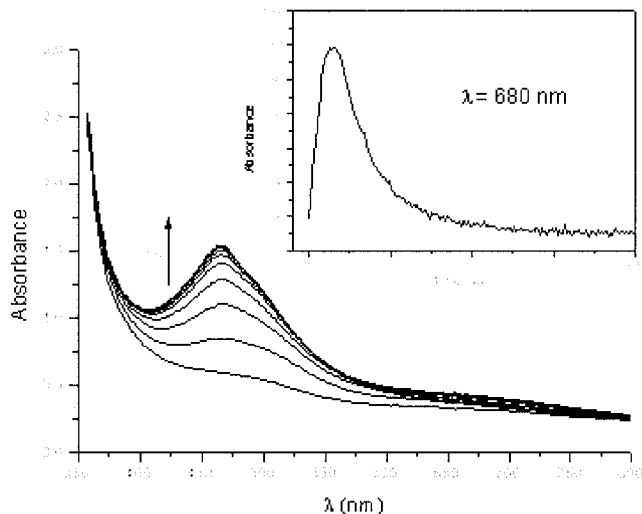
With  $\text{glass}[\text{TiO}_2-\text{Ru}^{\text{IV}}=\text{O}^{2+}]$ , rapid reduction of  $\text{Ru}^{\text{IV}}$  occurs to give a  $\text{Ru}^{\text{II}}$  intermediate with a characteristic  $\lambda_{\text{max}}$  at 680 nm, Figure 3. The absorbance change at 680 nm is small and appears to represent a small fraction of the total reaction. A related observation was made in the oxidation of phenol by  $\text{cis}-[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  in acetonitrile, which gave an intermediate with  $\lambda_{\text{max}} = 675 \text{ nm}$ . It subsequently underwent solvolysis to give  $\text{Ru}-\text{NCCH}_3^{2+}$  with  $k = 3.8 \times 10^2 \text{ s}^{-1}$ .<sup>1g</sup> The intermediate was proposed to be the bound 4-electron quinone product formed by the stepwise reactions, shown in eq 12 for *p*-benzoquinone.



The appearance of the low-energy absorption band for the surface-bound intermediate points to a quinone intermediate on the surface as well, and at least a minor contribution to the mechanism in eq 13. In this mechanism, initial C-H insertion is followed by a second, cross-surface oxidation. It is in competition with two-electron transfer on the surface as shown in eq 14.



(17) Lebeau, E. L.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2174.

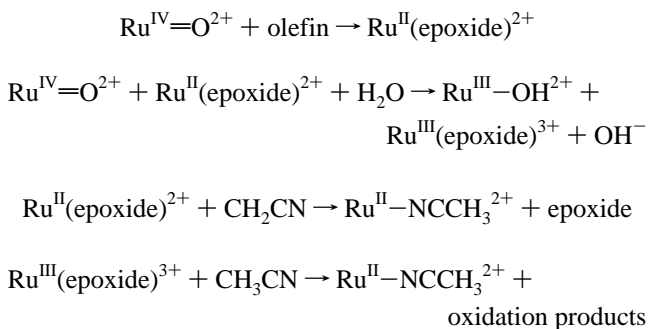


**Figure 3.** UV-vis spectral changes observed for the reaction between  $1.0 \times 10^{-3} \text{ M}$  phenol and  $\text{glass}[\text{TiO}_2-\text{Ru}^{\text{IV}}=\text{O}^{2+}]$  in  $\text{CH}_3\text{CN}$  at room temperature. The insert shows an absorbance vs time trace at 680 nm.

If this suggestion is correct, the amount of benzoquinone intermediate ( $\lambda_{\text{max}} = 680 \text{ nm}$ ) should decrease as the initial surface coverage of  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  is decreased. Experimentally, the absorbance change at 680 nm decreased by a factor of 10 when  $\Gamma$  was decreased from  $\sim 1 \times 10^{-7}$  to  $\sim 5 \times 10^{-8} \text{ mol/cm}^2$ . This observation is reminiscent of the surface coverage dependence of the disproportionation of  $\text{ITO}-\text{Ru}^{\text{III}}-\text{OH}^{2+}$  by cross-surface, proton-coupled electron transfer, eq 1<sup>2</sup>.

Quantitative product analysis in this case is difficult because of the small scale of the reaction, but there is evidence for *o*-benzoquinone ( $\lambda_{\text{max}} = 390 \text{ nm}$ ) on fully loaded surfaces. Hydroquinone is presumably the dominant or sole product on surfaces dilute in  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  with solvolysis at the two-electron stage competing with further oxidation, eq 14.

**Oxidation of *trans*-Stilbene.** In a final study, the oxidation of *trans*-stilbene by surface-bound  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  was investigated. A detailed report has appeared on the oxidation of *trans*-stilbene by  $\text{cis}-[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})(\text{O})]^{2+}$  in acetonitrile in which the following steps were proposed.<sup>1b</sup>

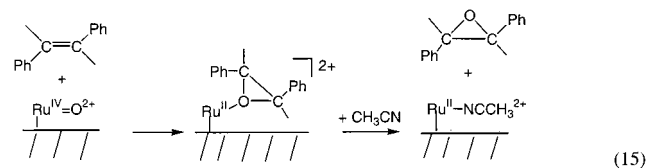


Disproportionation of  $\text{Ru}^{\text{III}}-\text{OH}^{2+}$  into  $\text{Ru}^{\text{IV}}=\text{O}^{2+}$  and  $\text{Ru}^{\text{II}}-\text{OH}_2^{2+}$  further complicated the kinetics and obscured the interpretation of absorbance-time data. Application of global analysis led to the conclusion that a minimum of four distinct kinetic processes were occurring simultaneously.

The surface reaction is far simpler. Under anaerobic conditions, reduction of  $\text{Ru}^{\text{IV}}$  is accompanied by absorbance increases at  $\lambda_{\text{max}} \sim 380$  and  $490 \text{ nm}$  with subsequent solvolysis to give  $\text{glass}[\text{TiO}_2-\text{Ru}^{\text{II}}-\text{NCCH}_3^{2+}]$  with  $\lambda_{\text{max}} = 460 \text{ nm}$ . The appearance of the higher energy feature is reminiscent of  $\text{Ru}^{\text{III}}$ ,<sup>1b</sup> but the appearance kinetics were the same at both wavelengths with

$\langle k \rangle \sim 1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ . There was a slight wavelength dependence in the subsequent solvolysis kinetics with  $\langle k \rangle_{380} = 1.3 \times 10^{-3} \text{ s}^{-1}$  and  $\langle k \rangle_{490} = 1.9 \times 10^{-3} \text{ s}^{-1}$ .

These observations are consistent with a mechanism on the surface in which concerted 2-electron oxidation of *trans*-stilbene occurs by O-atom transfer to give a bound epoxide intermediate. It has a characteristic  $\lambda_{\text{max}}$  at 490 nm, and undergoes solvolysis with  $\langle k \rangle = 1.9 \times 10^{-3} \text{ s}^{-1}$  to give the surface-bound nitrile complex.



Initial attempts to identify organic products by GCMS were unsuccessful. A concern was that any epoxide product generated on the acidic oxide surface could undergo acid-catalyzed ring opening to the diol,<sup>18</sup> which would adsorb strongly to the TiO<sub>2</sub> surface.<sup>19</sup> By using glass|TiO<sub>2</sub>-Ru<sup>IV</sup>=O<sup>2+</sup> generated at pH 7.3, eq 3, as the oxidant, small amounts of *trans*-stilbene oxide were

(18) On, D. T.; Kapoor, M. P.; Kaliaguine, S. *Chem. Commun.* **1996**, 1161.

(19) Connor, P. A.; Dobson, K. D.; McQuillan, A. J. *Langmuir* **1995**, *11*, 4193.

detected along with trace benzaldehyde. Under aerobic conditions, the absorbance–time changes are more complex. This chemistry is currently under investigation.

### Conclusions

The results of the experiments described here demonstrate the value of surface adsorption of the oxidant combined with spectrophotometric monitoring to elucidate the mechanistic details of oxidation reactions at a level of detail not available in solution. The comparability in rate constants demonstrates that solution reactivity is maintained on the surface. This approach relies on the loss of translational mobility of the oxidant by chemical binding to the surface and the optical transparency of the underlying oxide film. Reactions with cyclohexene, benzyl alcohol, phenol, and *trans*-stilbene all involve an initial 2-electron step and formation of adsorbed Ru<sup>II</sup> intermediates. Surface binding of the oxidant prevents oxidation past the two-electron stage. This changes the dominant product of oxidation of cyclohexene from ketone to alcohol and the oxidation of *trans*-stilbene to simple epoxidation. As shown by the cyclohexene result, there may be important implications in these results for the control of product selectivity in synthesis by limiting oxidation to two electrons.

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