Communications to the Editor

Mechanisms of Surface Electron Transfer. Proton-Coupled Electron Transfer

Scott A. Trammell, John C. Wimbish, Fabrice Odobel,† Laurie A. Gallagher, Poonam M. Narula, and Thomas J. Meyer*

Department of Chemistry
University of North Carolina at Chapel Hill, CB# 3290
Chapel Hill, North Carolina 27599-3290

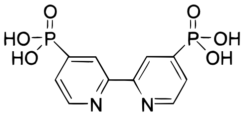
Received June 23, 1998

Electron-transfer reactions involving pH-dependent redox couples such as quinone/hydroquinone[1,2] or $Ru^{IV}(tpy)(bpy)O^{2+}/Ru^{III}(tpy)(bpy)OH^{2+}/Ru^{II}(tpy)(bpy)OH_2^{2+}$ (tpy is 2,2′,2″-terpyridine; bpy is 2,2′-bipyridine)[3,4] typically undergo slow heterogeneous charge-transfer kinetics. Kinetic barriers are created from the requirement that electron transfer occur without change in proton content since this occurs at potentials greater than the thermodynamic potential for the couple. For example, oxidation of $Ru^{II}(tpy)(bpy)(H_2O)^{2+}$ to $Ru^{III}(tpy)(bpy)(H_2O)^{3+}$ occurs at $E^{\circ\prime} = 0.80$ V vs SSCE independent of pH below 1.7, while the potential for the pH-dependent couple in eq 1 at pH 7 is 0.49 V.

$$Ru^{III}(tpy)(bpy)(OH)^{2+} + H^+ + e^- \rightarrow Ru^{II}(tpy)(bpy)(OH_2)^{2+} \quad (1)$$

This increases the potential at which Ru^{II} is oxidized to Ru^{III} by 0.31 V for a mechanism involving initial outer-sphere oxidation of $Ru^{II}(tpy)(bpy)(H_2O)^{2+}$ to $Ru^{III}(tpy)(bpy)(H_2O)^{3+}$. For oxidation at the thermodynamic potential, more complex mechanisms may intervene. For example, oxidation of $Ru{-}OH^{2+}$ to $Ru{=}O^{2+}$ can occur via disproportionation (eq 2). Mechanistically, disproportionation[5,6] occurs by proton-coupled electron transfer as evidenced by a k_{H_2O}/k_{D_2O} isotope effect of 12.[7] Stable monolayers or submonolayers of redox active molecules have been reported to form on oxide substrates in aqueous solution by phosphonate binding.[8,9] We report here the preparation of surface structures based on $Ru^{II}(tpy)(4,4'\text{-}(PO_3H_2)_2bpy)(H_2O)^{2+}$ ($4,4'\text{-}(PO_3H_2)_2bpy$ is 2,2′-bipyridyl-4,4′-diphosphonic acid)[10] and kinetic evidence that surface oxidation of $Ru^{III}{-}OH^{2+}$ to $Ru^{IV}{=}O^{2+}$ involves proton-coupled electron transfer.

$$2Ru^{III}(tpy)(bpy)(OH)^{2+} \rightarrow Ru^{II}(tpy)(bpy)(OH_2)^{2+} + Ru^{IV}(tpy)(bpy)(O)^{2+} \quad (\Delta G^\circ = 0.09\ \text{eV}) \quad (2)$$



Stable surface coatings of $[Ru(tpy)(4,4'\text{-}(PO_3H_2)_2bpy)(H_2O)](ClO_4)_2$ on ITO were prepared by exposing electrodes to various concentrations (0.1×10^{-5} to 2×10^{-4} M) of metal complex in water at pH 3. The monolayers were relatively stable for several hours at pH 1 with ~10% of the electroactive coverage lost in the first hour of exposure. At pH 7, the complex desorbs from the surface with a half-time of ~30 min. At pH > 10, it desorbs within 10 min. Electrochemical measurements were conducted before significant desorption had occurred. Surface coverages follow the Langmuir isotherm relation with coverage reaching saturation in a solution 2.2×10^{-4} M in complex with a final coverage of $\Gamma = 0.8 \times 10^{-10}$ mol/cm². From the Langmuir analysis, $K = 1.2 \times 10^5$ M⁻¹ for surface adsorption.

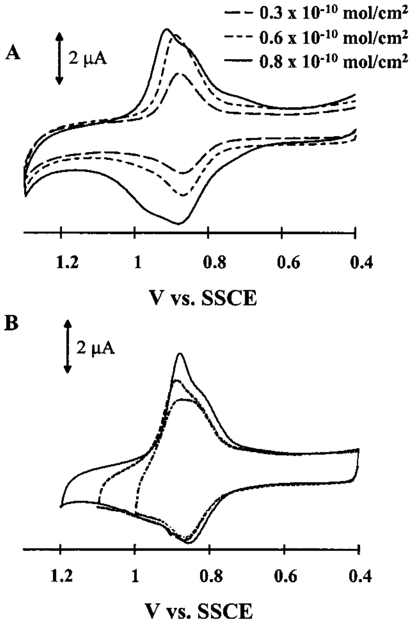


Figure 1. (A) Cyclic voltammograms of $[Ru(tpy)(4,4'\text{-}(PO_3H_2)_2bpy)(H_2O)](ClO_4)_2$ on ITO in 0.1 M $HClO_4$ at a scan rate of 10 mV/s at $\Gamma = 0.3 \times 10^{-10}$, 0.6×10^{-10}, and at saturation, 0.8×10^{-10} mol/cm². (B) As in part A with $\Gamma = 0.8 \times 10^{-10}$ mol/cm² showing the return Ru(IV→III) wave as a function of switching potential.

The variation of $E_{1/2}$ with pH for the $Ru^{III/II}$ surface couple overlays the dependence of the solution couple.[11] $E_{1/2}$ decreases with pH by ~60 mV/pH unit from pH 1 ($E_{1/2} = 0.86$ V vs SSCE) to 10.8 (0.28 V) consistent with eq 1. Beyond pH 10.8 the couple is pH independent, consistent with eq 3.[12]

$$Ru^{III}(tpy)(bpy)(OH)^{2+} + e^- \rightarrow Ru^{II}(tpy)(bpy)(OH)^{2+} \quad (3)$$

The electrode response is dependent on the extent of surface coverage. As shown in Figure 1A, only the $Ru^{III/II}$ wave appears

---

[†] Laboratoire de Synthèse Organique, Faculté des Sciences et des Techniques de Nantes.

(1) Vetter, K. J. *Elektrochem.* **1952**, *56*, 797.

(2) Laviron, E. *J. Electroanal. Chem.* **1984**, *164*, 213.

(3) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845−1851.

(4) McHatton, R. C.; Anson, F. C. *Inorg. Chem.* **1984**, *23*, 3935−3942.

(5) Binstead, R. A.; Moyer, B. A.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3.

(6) Binstead, R. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 3287.

(7) Farrer, B.; Thorp, H. University of North Carolina at Chapel Hill, Department of Chemistry, 1998, unpublished work.

(8) Péchy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphry-Baker, R.; Grätzel, M. *Chem. Commun.* **1995**, 65−66.

(9) Hupp, J. T.; Yan, S. G. *J. Phys. Chem.* **1996**, *100*, 6867.

(10) Penicaud, V.; Ododel, F.; Bujoli, B. Submitted to Tetrahedron Lett..

(11) Similar electrochemistry for the $Ru^{III/II}$ couple on SnO_2:Sb electrodes has been reported for $[Ru(tpy)(4,4'\text{-}(CO_2H)_2bpy)(H_2O)](ClO_4)_2$ at pHs less than 4; however, the complex was not stable on the surface of the electrode. Meyer, T. J.; Meyer, G. J.; Pfennig, B. W.; Schoonover, J. R.; Timpson, C. J.; Wall, J. F.; Kobusch, C.; Chen, X.; Peek, B. M.; Wall, C. G.; Ou, W.; Erickson, B. W.; Bignozzi, C. A. *Inorg. Chem.* **1994**, *33*, 3952−3964.

(12) There may be changes in H⁺ composition for phosphonic acid groups not surface bond in this pH range, but the effects on the $Ru^{III/II}$ couple are slight.

10.1021/ja9821854 CCC: $15.00

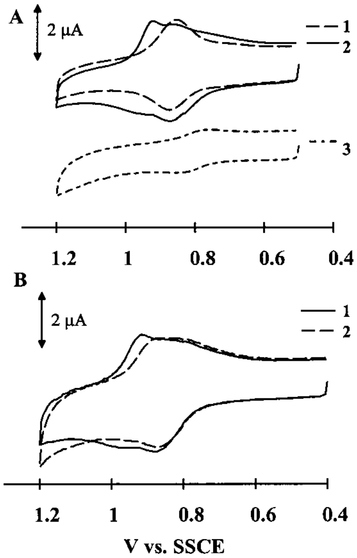


Figure 2. (A) As in Figure 1: **1**, $\Gamma \sim 0.3 \times 10^{-10}$ mol/cm^2; **2**, **1** with 2.4×10^{-6} M $Ru^{II}(tpy)(bpy)(H_2O)^{2+}$ added to the external solution; **3**, a blank ITO with 2.4×10^{-6} M $Ru^{II}(tpy)(bpy)(H_2O)^{2+}$ in the external solution. (B) As in part A with $\Gamma \sim 0.3 \times 10^{-10}$ mol/cm^2 and 2.4×10^{-6} M $Ru^{II}(tpy)(bpy)(H_2O)^{2+}$ in the external solution: **1**, in H_2O; **2**, in 50% D_2O.

at $\Gamma \cong 0.3 \times 10^{-10}$ or 0.6×10^{-10} mol/cm^2, which is less than "monolayer" coverage. The $Ru^{IV/III}$ couple does appear on fully loaded surfaces, $\Gamma = 0.8 \times 10^{-10}$ mol/cm^2. Evidence for a kinetic inhibition for this couple is demonstrated by the switching potential experiments in Figure 1B. These results show that the current for Ru(IV → III) reduction depends on the time held past the $Ru^{IV/III}$ wave. Slow electron transfer is also implied by the fact that the $Ru^{IV/III}$ couple appears only at scan rates of ≤ 20 mV/s. Significantly, as shown in Figure 2A, the $Ru^{IV/III}$ wave does appear even on dilute surfaces if $[Ru(tpy)(bpy)(H_2O)]^{2+}$ is added to the external solution.

These observations are consistent with a kinetic inhibition for surface oxidation of $Ru^{III}{-}OH^{2+}$ to $Ru^{IV}{=}O^{2+}$ and a mechanism involving bimolecular reactions. Direct one-electron oxidation of $Ru^{III}{-}OH^{2+}$ to $Ru^{IV}{=}OH^{3+}$ is slow or inaccessible because of the high potential for the $Ru^{IV}{=}OH^{3+}/Ru^{III}{-}OH^{2+}$ couple. Disproportionation in eq 2, followed by $Ru^{II}{-}OH_2^{2+} \rightarrow Ru^{III}{-}OH_2^{3+}$ oxidation provides a viable mechanism for surface oxidation.[6,13,14] High surface loadings are required for a mechanism involving proton-coupled electron transfer within an association complex of the reactants (eq 4).[6,15]

$$(tpy)(bpy)Ru^{III}{-}OH^{2+},\ HO{-}Ru^{III}(bpy)(tpy)^{2+} \rightarrow (tpy)(bpy)Ru^{IV}{=}O^{2+},\ H_2O{-}Ru^{II}(bpy)(tpy)^{2+} \quad (4)$$

Catalysis of the surface couple by $Ru(tpy)(bpy)(H_2O)^{2+}$ also occurs by proton-coupled electron transfer. In $H_2O/HDO/D_2O$ mixtures with the mole fraction of $D(\chi_D)$ varied from 0 to 0.2, the ratio of peak currents for the Ru(III→IV) wave, $i_{p,a}(H_2O)/i_{p,a}(\chi_D)$ varies linearly with χ_D with a slope of 10.9 and a value at $\chi_D = 1$ of 11.9, within experimental error of the solution k_{H_2O}/k_{D_2O} value. The effect of D_2O on the uncatalyzed surface reaction is even more profound. With $\chi_D = 0.05$ in 0.1 M $HClO_4$ and full surface coverage there is no discernible Ru(III → IV) wave. From data obtained from $\chi_D = 0$ to $\chi_D = 0.025$ and assuming that k varies linearly with χ_D, k_{H_2O}/k_{D_2O} must be very large possibly greater than 60. Plots of $i_{p,a}(H_2O)/i_{p,a}(\chi_D)$ vs χ_D are available as Supporting Information.

Proton-coupled electron transfer can also explain the apparent bilayer wave shape for the Ru(IV→III) reduction in Figure 1B.[16] Reduction by direct electron transfer, $Ru^{IV}{=}O^{2+} + e^- \rightarrow Ru^{III}{-}O^+$, is slow since $E_{1/2} < 0.33$.[3] The presence of even a small amount of Ru^{II} on the surface apparently "triggers" the reduction of Ru^{IV} by the reverse of eq 2 for the surface couple. This is followed by rapid reduction of $Ru^{III}{-}OH^{2+}$ to $Ru^{II}{-}OH^+$ and a potential−current waveform that is highly dependent on the surface and the details of the voltammetric sweep.

The observation of different isotope effects for the surface and solution catalyzed reactions is of fundamental importance. Proton-coupled electron transfer requires specific orientations between reactants for nuclear tunneling of the proton to occur. On the surface, there is a spatial distribution of translationally fixed nondiffusional redox sites and restricted orientations. This apparently increases the average tunneling distance, increasing the isotope effect.

We are currently studying these and related effects and the use of these electrodes in electrocatalysis.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-9503738, the Department of Energy subcontracted by Lockheed Martin at Oak Ridge National Laboratory under Grant No. 19X-SX092C, and the Army Research Office under Grant No. DAAH04-95-1-0144.

Supporting Information Available: Preparation and characterization of the metal complexes $[Ru(tpy)(4,4'\text{-}(PO_3Et_2)_2bpy)(Cl)](PF_6)$ and $Ru(tpy)(4,4'\text{-}(PO_3H_2)_2bpy)(H_2O)^{2+}$, electrochemical procedures, and plots of $i_{p,a}(H_2O)/i_{p,a}(\chi_D)$ vs χ_D (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9821854

---

(13) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436−444.

(14) Lebeau, E.; Meyer, T. J. Manuscript in preparation.

(15) At pH 1, there is a mixture of Ru(III) aqua and hydroxo complexes present.

(16) Similar wave shapes for the Ru(IV→III) reduction have been seen in thin films of $[Ru(bpy)_2(PVP)_{10}(H_2O)]^{2+}$. Clarke, A. P.; Vos, J. G.; Bandey, H. L.; Hillman, A. R. *J. Phys. Chem.* **1995**, *99*, 15973−15980.