Inorg. Chem. **1986**, *25*, 4807–4808 **4807**

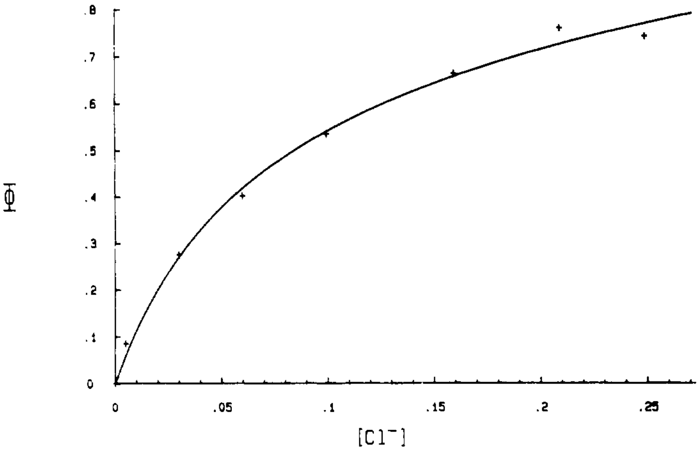

Figure 1. Plot of the disappearance quantum yield for reaction 1 at 505 nm in THF vs. [Cl$^-$]. I = 4.8 × 10^{-8} einstein/min. The curve is a nonlinear least-squares fit of the data points to eq 7.

A plot of Φ vs. [Cl$^-$] is shown in Figure 1.[6,8] The curve in the figure is a nonlinear least-squares fit[9] of the data points to the expression in eq 7. The best fit was obtained for the following values: $K' = 3.7$; $K = 3.4 \times 10^{10}$; $\phi = 0.63$. Because $K = k_5K_{eq}$, we can determine K_{eq} if we have a value for k_5. Although the value for k_5 is unknown (it is the rate constant for a termination step in which a 17-electron species reacts with a 19-electron species, eq 6), we can estimate its maximum value as the diffusion-controlled rate constant ($\approx 10^9$ M^{-1} s^{-1}). Using this value, we find $K_{eq} \geq 3.4 \times 10^1$, which, in turn, yields a maximum value for $\Delta G°$ (eq 3, X$^-$ = Cl$^-$) ≤ -2.1 kcal/mol. A similar analysis using Br$^-$ yields $K = 6.5 \times 10^{10}$ and $\Delta G°$ (eq 3, X$^-$ = Br$^-$) ≤ -2.5 kcal/mol. For I$^-$, we find $K = 2.0 \times 10^{11}$ and thus $\Delta G° \leq -3.1$ kcal/mol.[10] Obviously, if reaction 6 proceeds at less than the diffusion-controlled rate, then $\Delta G°$ will be even more negative. The driving force for the formation of the 19-electron adduct is presumably the formation of the Mo–X bond.[4]

These results demonstrate two important points. First, for the specific case of the disproportionation reaction in eq 1, the 19-electron adducts are reasonable intermediates. Second, in a general sense, these results demonstrate that 19-electron species are not necessarily high-energy species with respect to 17-electron metal radical complexes and a halide ligand. The implication of this last statement is that if reaction pathways involve 17-electron metal radicals (and if Lewis bases are present), then 19-electron species must also be considered as possible reaction intermediates.

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(6) Quantum yields were measured in THF as described previously.[2] Samples for quantum yield measurements were prepared in a dry box by adding an appropriate amount of P(n-Bu)$_4{}^+$Br$^-$ or P(n-Bu)$_4{}^+$Cl$^-$ to a 10-mL volumetric flask containing 22 mg of Cp$_2$Mo$_2$(CO)$_6$. N(n-Bu)$_4{}^+$PF$_6{}^-$ was then added to bring the total ionic strength of the sample up to 0.25 M. Lamp intensities were determined by using Aberchrome 540.[7] All reactions were run at room temperature (298 K).

(7) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 341–343.

(8) (η^5-CH$_3$C$_5$H$_4$)$_2$Mo$_2$(CO)$_6$ was used instead of (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$ because the former complex is more soluble in THF.

(9) Nonlinear Regression, a program written by Brian W. Clare, was used for the least-squares analysis.

(10) The best fits for Br$^-$ and I$^-$ were obtained with the following values (errors are expressed with a 90% confidence interval): Br$^-$, $K = 6.5 \times 10^{10} \pm 1.4 \times 10^{10}$, $K' = 1.6 \times 10 \pm 6 \times 10^{-1}$, $\phi = 0.24 \pm 0.02$; I$^-$, $K = 2.0 \times 10^{11} \pm 0.7 \times 10^{11}$, $K' = 5.3 \times 10 \pm 1.0 \times 10$, $\phi = 0.52 \pm 0.02$.

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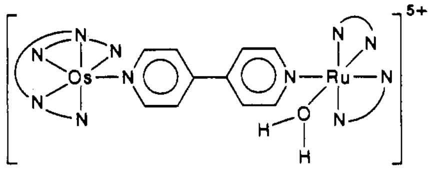
pH-Induced Intramolecular Electron Transfer

Sir:

Oxidation of transition-metal complexes containing aqua ligands characteristically leads to an enhanced acidity and to redox couples whose potentials are pH-dependent, e.g.[1]

$$[(\mathrm{bpy})_2(\mathrm{py})\mathrm{Ru^{II}(OH_2)}]^{2+} \xrightarrow{-e^-} [(\mathrm{bpy})_2(\mathrm{py})\mathrm{Ru^{III}(OH)}]^{2+} + \mathrm{H^+}$$

where py is pyridine and bpy is 2,2′-bipyridine. We demonstrate here that in the ligand-bridged, mixed-valence dimer [(trpy)(bpy)Os^{III}(4,4′-bpy)Ru^{II}(H$_2$O)(bpy)$_2$]$^{5+}$ (trpy is 2,2′:6′,2″-terpyridine and 4,4′-bpy is 4,4′-bipyridine), which contains both an aqua-based, pH-dependent couple and a pH-independent couple, changes in pH can be utilized to induce intramolecular electron transfer across the ligand bridge. The structure of the dimer is



where N atoms connected by arcs are used to illustrate the polypyridyl ligands, and the cis geometry at the Ru site is also shown. Further, in the twice-oxidized Os(III)–Ru(III) dimer, pH-induced intramolecular electron transfer can be used to concentrate the stored redox equivalents at a single site, thus gaining a significantly enhanced oxidative reactivity toward an organic substrate.

The dimer [(trpy)(bpy)Os^{II}(4,4′-bpy)Ru^{II}(H$_2$O)(bpy)$_2$](BF$_4$)$_4$ was prepared by the reaction between [(trpy)(bpy)Os^{II}(4,4′-bpy)]$^{2+}$ and [(bpy)$_2$Ru^{II}(OH$_2$)$_2$]$^{2+}$ in refluxing 1:1 EtOH/0.1 M CF$_3$SO$_3$H(aq) for 4 h.[2] The dimer was precipitated as the PF$_6{}^-$ salt, purified by passing through a Sephadex C-25-120 cation-exchange column by eluting with aqueous NaBF$_4$, and isolated as the BF$_4{}^-$ or PF$_6{}^-$ salt.[3]

In the related monomer [(bpy)$_2$(py)Ru^{II}(OH$_2$)]$^{2+}$, the pH dependences of both the Ru(III/II) and Ru(IV/III) couples have been described.[1] The results of pH-dependent cyclic voltammetric and differential pulse polarographic studies on the dimer are summarized in the $E_{1/2}$ vs. pH or Pourbaix diagram in Figure 1, where $E_{1/2}$ is measured vs. the saturated calomel electrode, SCE. The electrochemical studies provide clear evidence for a pH-independent Os(III/II) couple at $E_{1/2}$ = +0.63 V and the expected pH-dependent Ru(III/II) and Ru(IV/III) couples. In the diagram the oxidation state distributions and proton contents of the various forms of the dimer are shown in the potential–pH regions where they are dominant. Slow electrode kinetics for the Ru^{IV}(O)/Ru^{III}(OH) couple (as observed for related monomers)[1] makes direct observation of this couple in the dimer difficult below pH 8. The potential for the Os^{III}–Ru^{IV}(O)/Os^{III}–Ru^{III}(OH) couple shown by the dashed line was estimated by adding the potential difference between the Os^{II}–Ru^{III}(OH)/Os^{II}–Ru^{II}(OH$_2$) and

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(1) (a) Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436. (b) Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845.

(2) The monomer [(trpy)(bpy)Os^{II}(4,4′-bpy)]$^{2+}$ was prepared by the reaction between [(trpy)(bpy)Os^{III}(TFMS)](TFMS)$_2$ (TFMS is trifluoromethanesulfonate anion) and a 20-fold excess of 4,4′-bpy, which were heated in refluxing ethylene glycol for 30 min. The PF$_6{}^-$ salt was isolated by the addition of aqueous NH$_4$PF$_6$ and then purified by column chromatography on alumina using 1:1 acetonitrile/toluene as eluant. [(trpy)(bpy)Os^{III}(TFMS)](TFMS)$_2$ was isolated from the reaction between [(trpy)(bpy)Os^{II}Cl](PF$_6$) and neat trifluoromethanesulfonic acid (ref 1b) by dropping the reaction mixture into 500 mL of anhydrous diethyl ether, collecting the precipitate, and storing the water-sensitive solid under vacuum. The complex [(bpy)$_2$Ru(OH$_2$)$_2$]$^{2+}$ was prepared in situ by dissolving [(bpy)$_2$Ru(CO$_3$)] (Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211) in the acidic solvent. Rapid loss of carbonate as CO$_2$ occurs upon the addition of acid. (Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.)

(3) Anal. Calcd for [(trpy)(bpy)Os(4,4′-bpy)Ru(H$_2$O)(bpy)$_2$](PF$_6$)$_4$·3H$_2$O: C, 36.67; H, 2.86; N, 8.56. Found: C, 36.63; H, 2.88; N, 8.44.

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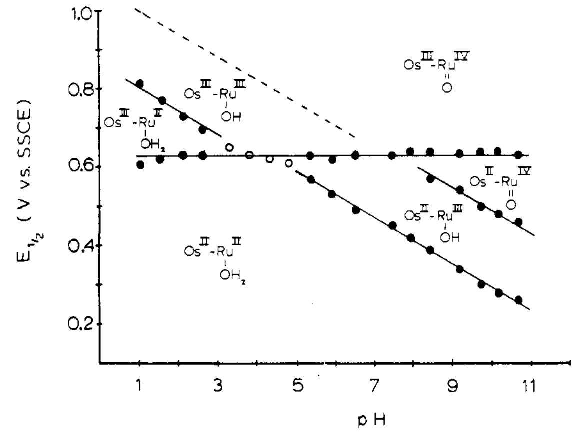


Figure 1. $E_{1/2}$ vs. pH diagram for the dimer $[(trpy)(bpy)Os(4,4'\text{-}bpy)Ru(H_2O)(bpy)_2]^{4+}$. The oxidation state and pH contents of the dimer are indicated in those potential domains in which they are dominant. The dashed line for the Os^{III}–$Ru^{IV}(O)/Os^{III}$–$Ru^{III}(OH)$ couple was calculated as described in the text. For the data shown as open circles, only a single electrochemical wave was observed because of the close proximity of the adjacent couples.

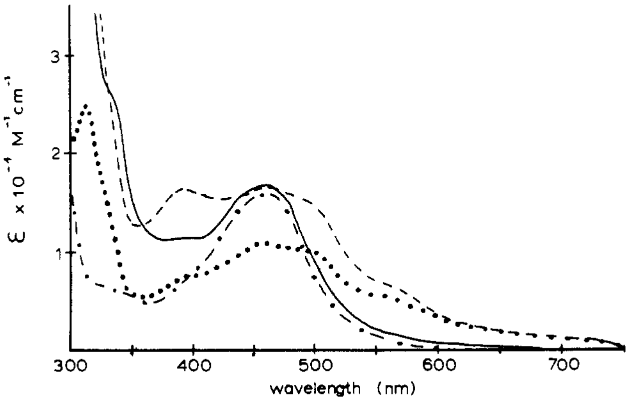


Figure 2. Visible spectra of $[(trpy)(bpy)Os^{III}(4,4'\text{-}bpy)Ru^{II}(H_2O)(bpy)_2]^{5+}$ at pH 1.1 (—), $[(trpy)(bpy)Os^{II}(4,4'\text{-}bpy)Ru^{III}(OH)(bpy)_2]^{4+}$ at pH 8.9 (---), $[(trpy)(bpy)Os^{II}(4,4'\text{-}bpy)]^{2+}$ at pH 1.1 (···), and $[(bpy)_2Ru^{II}(H_2O)(4,4'\text{-}bpy)]^{2+}$ at pH 1.1 (-·-).

Os^{II}–$Ru^{IV}(O)/Os^{II}$–$Ru^{III}(OH)$ couples (0.19 V) to the potential of the Os^{III}–$Ru^{III}(OH)/Os^{III}$–$Ru^{II}(OH_2)$ couple below pH 8.

Figure 1 shows that the oxidation-state distribution in the dimer is dependent on pH, suggesting that it should be possible to induce intramolecular electron transfer between the ligand-bridged metal sites by variations in the pH.[4] In Figure 2 are shown visible spectra of the once-oxidized, mixed-valence dimer at pH 1.1 and 8.9, as well as spectra for the related monomers $[(bpy)_2(4,4'\text{-}bpy)Ru(OH_2)]^{2+}$ and $[(trpy)(bpy)Os(4,4'\text{-}bpy)]^{2+}$. The spectra are dominated by Ru(II),Os(II) → π^*(bpy or trpy) metal to ligand charge-transfer transitions. The spectral shifts with pH clearly show that a pH jump from 1.1 to 8.9 induces net intramolecular electron transfer

$$[(trpy)(bpy)Os^{III}(4,4'\text{-}bpy)Ru^{II}(H_2O)(bpy)_2]^{5+} \rightarrow [(trpy)(bpy)Os^{II}(4,4''\text{-}bpy)Ru^{III}(OH)(bpy)_2]^{4+} + H^+$$

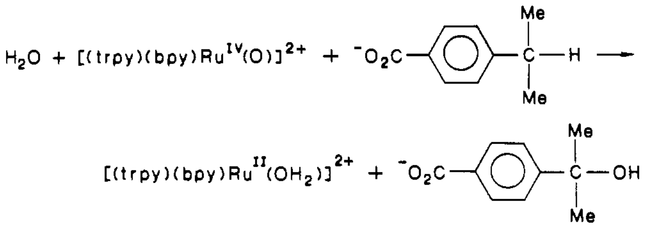
which is reversible if the pH is returned to 1. This is a significant result since it shows that long-range electron transfer between redox sites can be induced by local changes in the pH. In a related experiment, it was recently shown that long-range electron transfer across a redox-active polymeric film could be induced by pH changes in the external solution.[5] The results of both experiments suggest approaches to coupling electron-transfer processes to other, pH-dependent chemical processes.

A pH-induced intramolecular electron transfer above pH 7 also occurs in the twice-oxidized dimer

$$OH^- + [(trpy)(bpy)Os^{III}(4,4'\text{-}bpy)Ru^{III}(OH)(bpy)_2]^{5+} \rightleftharpoons [(trpy)(bpy)Os^{II}(4,4'\text{-}bpy)Ru^{IV}(O)(bpy)_2]^{4+} + H_2O$$

which has the effect of concentrating both oxidative equivalents at the ruthenium site. Above pH 7 the twice-oxidized dimer contains a chemically reactive $Ru^{IV}{=}O$ site for which studies on related monomers have shown an extensive stoichiometric and catalytic oxidation chemistry including oxidation of primary and secondary alcohols, cyclic ketones, and aldehydes,[6] epoxidation of olefins,[7] and allylic oxidation of olefins and aromatic hydrocarbons.[6,8]

Upon addition of *p*-isopropylbenzoate anion to the Os^{III}–Ru^{III} dimer at pH 5 at room temperature ($\mu = 0.1$), the mixed-valence dimer appears slowly followed by the even slower appearance of the Os^{II}–Ru^{II} dimer. Under pseudo-first-order conditions in the benzoate anion its oxidation by the Os^{III}–Ru^{III} dimer to give the Os^{II}–Ru^{III} dimer occurs with $k = (6.2 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1}. However, at pH 10, where the dimer is in the reactive Os^{II}–$Ru^{IV}(O)$ form, $k = 5.0 \pm 1.0$ M^{-1} s^{-1}. Oxidation of the same substrate by $[(trpy)(bpy)Ru^{IV}(O)]^{2+}$ and $[(trpy)(bpy)Ru^{III}(OH)]^{2+}$ occurs with $k_{IV} = 12.2 \pm 1.2$ M^{-1} s^{-1} and $k_{III} < 1 \times 10^{-4}$ M^{-1} s^{-1}.[8] For the Ru(IV) monomer the net reaction is



The enhanced reactivity of the oxo form of the dimer demonstrates that pH-induced electron transfer can be used to concentrate the "stored" redox equivalents in the twice-oxidized dimer at a single site, producing a considerable gain in chemical reactivity on demand by variations in pH.

Acknowledgments are made to the Army Research Office—Durham for support of this research under Grant No. DAAG29-85-K-0121.

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[5] Vining, W. J.; Surridge, N. A.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 2281.

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Heterolytic and Homolytic O-O Bond Cleavage Reactions of (Acylperoxo)manganese(III) Porphyrins

Sir:

Mechanistic studies of transition-metal-mediated reactions of peroxides have attracted attention for over a century.[1] Fenton's reagent, the prototype iron(II)–hydrogen peroxide system, has been inferred from detailed product studies to proceed by a one-electron homolysis of the O–O bond in acidic aqueous media to afford hydroxyl radicals,[2] whereas a heterolytic pathway to produce a reactive ferryl species $[Fe^{IV}{=}O]$ was indicated in

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[1] (a) Bray, W. C.; Gorin, M. H. *J. Am. Chem. Soc.* **1932**, *54*, 2124. (b) Cahill, A. E.; Taube, H. *J. Am. Chem. Soc.* **1952**, *74*, 2312.

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