

Instability of the oxidation catalysts $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ and $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ in alkaline solution

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Received 20 August 2003; received in revised form 31 October 2003; accepted 4 November 2003

Abstract

The Os(III) complexes $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ and $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ (bpy: 2,2'-bipyridine, py: pyridine, tpy: 2,2',2''-terpyridine) are unstable toward self-reduction in alkaline solution. Product analysis performed by using UV-Vis spectroscopy, cyclic voltammetry, HPLC and GC show that ca. 90% of the reduced product that appears is the unmodified polypyridyl complex of Os(II), $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ or $[\text{Os}^{\text{II}}(\text{bpy})_3]^{2+}$. The remaining 10% of the products are accounted for by other Os(II) complexes, including several which appear to have undergone varying degrees of ligand oxidation or substitution. Another product of the reduction of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ in basic solution has been identified as $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ which results from metal reduction and concomitant pyridine ligand loss. No O_2 was detected as a product of the base-catalyzed self-reduction reaction. The Os(III) complexes are stable towards self-reduction and ligand loss in the dark in acetonitrile or aqueous solutions buffered below pH = 6. The rates observed for the self-reduction processes are sufficiently rapid at pH values above 7 that useful catalytic rate data cannot be obtained in basic solution unless the substrate of interest is sufficiently reactive and is present in large excess. Triple mixing, pH jump techniques have successfully been employed to observe reaction rates under strongly alkaline conditions.

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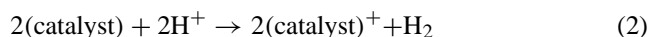
Keywords: Oxidation; Catalysis; Osmium; Polypyridyl; Self-reduction

1. Introduction

Polypyridyl complexes containing high valent group 8 metals have been used as stoichiometric or catalytic oxidants for a wide variety of organic and inorganic substrates. Efforts have been directed toward the design of stable, yet strongly oxidizing, homogeneous catalysts. A potentially important variable in using these reagents as oxidants is pH because ligand loss and ligand oxidative degradation have been noted as primary sources of catalyst deactivation, especially in basic media. The instability arises from self-reduction of the high valent metal center by ligand oxidation as the pH is increased as has been reported for many pyridyl and polypyridyl complexes, including $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ and $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}$ [1–3]. Creutz and Sutin describe the kinetics of decomposition of $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ in basic media as dominated by rate-determining nucleophilic attack by hydroxide on the bound bipyridine ligand. However, Nord and co-workers suggest that the rate-determining

step upon addition of $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}$ to basic solution is hydroxide attack on the metal center. Creutz and Sutin have observed only trace levels of O_2 production, whereas Nord and co-workers observe significant O_2 production with concomitant formation of $>85\%$ $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$.

Oxidation of water to dioxygen is the terminal reaction of Photosystem II. Although much has been learned about this system, little is known about the how O_2 is evolved. There are a few well defined molecules which effect this conversion [4–6] one being the “blue dimer”, *cis,cis*- $[(\text{bpy})_2(\text{H}_2\text{O})\text{Ru}^{\text{III}}\text{ORu}^{\text{III}}(\text{OH}_2)(\text{bpy})_2]^{4+}$, and several of its derivatives. These molecules are important because they have provided insights into possible mechanisms for water oxidation [7–10]. Development of a water oxidation catalyst that can cycle through Eqs. (1) and (2) is of considerable interest for the development of alternative fuel sources.



For typical polypyridyl group 8 complexes, dioxygen formation is rarely reported, however. Base-catalyzed

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self-reduction can occur without dioxygen formation, and the nature of the oxidized products and the mechanism of their formation is, therefore, of some interest. We have investigated and report here the results of a systematic series of studies on the instability of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ and $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ toward self-reduction and ligand loss in basic solution. Although a similar study with $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ has been published [11], we chose to reinvestigate the base-catalyzed self-reduction of this substrate under identical conditions as $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$. The compound $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ was selected to allow for the evaluation of the stability of monodentate, bidentate, or tridentate pyridine moieties towards ligand loss and pH induced intramolecular electron transfer. The goal of this work was to evaluate the availability of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ and other high valent polypyridyl osmium complexes to act as oxidation catalysts in basic solution. It is an important study because it is necessary to define pH regions of catalyst stability if these compounds are to regularly be used as one-electron, outer-sphere oxidants.

2. Experimental

2.1. Materials

High purity acetonitrile (Burdick & Jackson) was used as the solvent for the kinetic studies after distillation from P_2O_5 with use of a Vigreux column. High quality water was prepared by distilling house-deionized water from alkaline potassium permanganate. $(\text{NH}_4)_2\text{OsCl}_6$ was obtained from Englehard Ind. 2,2',2''-Terpyridine was obtained from G.F. Smith and 2,2'-bipyridine was obtained from Aldrich. Sodium phosphate monobasic monohydrate, $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, sodium phosphate dibasic heptahydrate, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, sodium phosphatetribasic dodecahydrate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, and phosphoric acid, H_3PO_4 were obtained from Fisher Scientific and were used without further purification in the preparation of buffer solutions. All other materials were reagent grade and used without additional purification.

2.2. Preparations

2.2.1. $[\text{Os}(\text{bpy})\text{Cl}_4]$ and $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{Cl})](\text{PF}_6)$

These compounds were prepared by slight modification of the procedure of Buckingham et al. [12]. Typically, a 1 g sample of $(\text{NH}_4)_2\text{OsCl}_6$ was dissolved in 50 ml of 3 M HCl and was stirred at 70 °C. To this was added 0.42 g bpy which was dissolved in a minimum of 3 M HCl. The solution was cooled to 0 °C for 2 h. The precipitate was collected by vacuum filtration using a glass frit, washed (3×10 ml each) with 3 M HCl, water, and diethyl ether. The $(\text{bpy}-\text{H}_2)$ $[\text{OsCl}_6]$ was dried in a vacuum oven at 70 °C overnight, and then was converted into $[\text{Os}(\text{bpy})\text{Cl}_4]$ by pyrolysis in a molten salt bath (290 °C for 6 h). A 1 g sample of $[\text{Os}(\text{bpy})\text{Cl}_4]$ was

combined with 0.54 g tpy in 50 ml ethylene glycol and was heated at reflux under Ar for 1 h. After cooling to room temperature, 50 ml water and 5 ml $\text{Na}_2\text{S}_2\text{O}_4$ were added to the stirring solution. A few milliliters of saturated ammonium hexafluorophosphate, NH_4PF_6 , were added and the precipitate was collected on a fritted funnel. The solid was purified by elution from an alumina column using 1:1 (v:v) acetonitrile:toluene as eluant. The first purple/brown band eluted is the desired product. The solvent was removed under vacuum by rotary evaporation. The solid was further purified by dissolving the complex in a small volume of acetonitrile and adding this solution dropwise to a large excess of rapidly stirring ether. The precipitated complex was collected by filtration and washed (3×30 ml) with fresh ether.

2.2.2. $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{Otf})](\text{Otf})_2$ (*Otf* is trifluoromethanesulfonate)

A 0.20 g sample of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{Cl})](\text{PF}_6)$ was combined with 5 g neat triflic acid in a 25 ml roundbottom flask. The solution was stirred at reflux under Ar for 1 h, then cooled to RT. The solid was precipitated by slowly dripping the solution into ca. 300 ml of rapidly stirring ether. The pale brown precipitate was collected on a glass frit and was washed 3×10 ml with fresh ether. The product was dried in a vacuum desiccator overnight.

2.2.3. $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})](\text{PF}_6)_2$

It was prepared through a modification of a literature procedure [13]. A 1.4 ml sample of pyridine was added to 5 ml of an Ar sparged solution of ethylene glycol. To this was added 0.2 g $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{Otf})](\text{Otf})_2$. The solution was heated at reflux under Ar for 5 h. Under an Ar atmosphere, the solution was cooled to room temperature. Twenty milliliters of H_2O and several milliliters of saturated NH_4PF_6 were added. The solution was stirred at 0° for 2 h. The precipitate was collected on a fritted funnel and was washed with a minimum amount of water followed by ether. The solid was purified by elution from an alumina column using 1:1 (v:v) acetonitrile:toluene as eluant. The first brown band eluted is the desired product. The solvent was removed under vacuum by rotary evaporation. The solid was further purified by dissolving the complex in a small volume of acetonitrile and adding this solution dropwise to a large excess of rapidly stirring ether. The precipitated complex was collected by filtration and washed (3×30 ml) with fresh ether and was air dried.

2.2.4. $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)](\text{PF}_6)_2$

It was prepared by modification of a literature preparation [14]. To a 0.5 g sample of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{Otf})](\text{Otf})_2$ was added 10 ml H_2O and a zinc amalgam. The solution was stirred under Ar for 3 h. After the zinc amalgam was separated from the solution through decantation, the addition of several milliliters of saturated NH_4PF_6 solution induced precipitation of the desired complex. The compound was purified by column chromatography using Sephadex SP-C25

cation exchange as the column support and Na_2SO_4 as the eluant. By use of a 0.2 M ionic strength sodium sulfate eluant, a brown band was recovered from the Sephadex column. The solution was reduced in volume to ca. 25 and 2 ml of saturated NH_4PF_6 were added. The solution was cooled at 0 °C overnight and a dark brown product was collected by filtration.

3. Instrumentation

Routine UV-Vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer by using standard quartz cells. The temperature of the reactant solutions was controlled to 25 ± 0.1 °C by using a Peltier temperature controller. Manual mixing of solutions from conventional syringes into standard cuvettes was employed. The pH of solutions was determined by using a Corning 320 pH Meter with a general purpose combination electrode (476530) after calibration with standard buffer solutions. In the kinetic experiments the initial concentrations of $[\text{Os}^{\text{II}}(\text{bpy})_3]^{2+}$, $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$, $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$, and $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ were varied from 8×10^{-7} to 2×10^{-4} M. Rate data in water were collected by following visible spectral changes at a series of pH values. Wavelengths were chosen where large spectral changes were observed or where component absorbances could be isolated. Triple mixing was employed at basic pHs (pH > 6) because of the instability of $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ for extended periods under these conditions. The pH jump experiments minimize complications from decomposition of $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$.

Dioxygen detection was achieved by use of an Orion Model 97-08-00 O_2 electrode interfaced to a Standard pH Meter. HPLC isolation and purity determination of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ was achieved using a HEMA cation exchange column with either 450 nm or 290 nm detection using a Varian Prostar 210 Model pump system with a Varian Prostar 340 Model UV-Vis detector and a flow rate of 0.5 ml/min. ^1H NMR spectra were obtained in CD_3CN , D_2O or CD_3CN using a General Electric QE-300 MHz FT-NMR spectrometer. Chemical shifts are reported as ppm versus TMS at 20 °C. IR spectra were recorded using a Nicolet Magna-IR 560 spectrometer and were made in KBr pellets or made in CD_3CN solution by use of a demountable cell with NaCl plates and teflon spacers or a fused BaF_2 cell with a 1 mm path length. GC measurements were made using a Hewlett-Packard 5890 Series II Model chromatograph or an Agilent (Hewlett-Packard) Model 6890 equipped with flame ionization detection (GC-FID, J&W DB-5 columns (30 M \times 0.32 mm with a 0.25 μm film thickness). He carrier gas, 2.0 ml/min flow rate. APEX ProSep 800XT pre-column injection system (held at 20 °C for injection and then programmed to 300 °C at 300 °C/min, 10:1 split ratio). Gas chromatography–mass spectrometry (GC-MS) was performed using a Hewlett-Packard Model 5973 GC/MS/DS or a Finnigan 700 with column conditions

comparable to the GC-FID. Initial oven temperature of 40 °C, 250 °C final oven temperature (10 °C/min temperature ramp, 15 min hold time), 250 °C injection port temperature, and 300 °C detector temperature. The injection size was 2 μl .

A Bioanalytical Systems (BAS) CV-50W voltammetric analyzer and BAS CV-50W version 1.0 software was used for all cyclic voltammogram measurements and bulk oxidation experiments. In a typical electrolysis experiment (bulk electrochemical oxidation of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ or $[\text{Os}^{\text{II}}(\text{bpy})_3]^{2+}$), a reticulated vitreous carbon electrode in a three-arm electrolysis cell was used. After a given amount of charge was passed, electrolysis was interrupted and the solution subjected to CV analysis using a glassy-carbon working electrode. Electrolysis and cyclic voltammetric experiments were conducted using a platinum-wire auxiliary electrode and a saturated sodium calomel reference electrode (SSCE) for aqueous solutions or Ag/Ag^+ in acetonitrile. Typical CV scan rates are 10 mV/s or 100 mV/s. An ionic strength of 0.1 M was maintained using phosphate buffers in aqueous solutions and tetrabutyl ammonium hexafluoro phosphate (TBAH) in acetonitrile. Buffer solutions for electrochemical measurements were prepared from aqueous perchloric acid, HClO_4 , with LiClO_4 (pH = 1–2), and HClO_4 with $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (pH = 2–12), and NaOH with $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (pH = 12–14). The $E_{0.5}$ values reported in this work were calculated from cyclic voltammetric waveforms as an average of the oxidative and reductive peak potentials, $(E_{p,a} + E_{p,c})/2$. All cyclic voltammograms were obtained after purging with argon, and the solutions were kept in the dark to avoid photolabilization of the pyridine ligands.

4. Results and discussion

$[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ and $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ are stable for extended periods, ca. days, in acetonitrile or aqueous acidic solutions below pH 6. Cyclic voltammetry and UV-Vis measurements before and after bulk electrolysis of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ oxidation to $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ or from $[\text{Os}^{\text{II}}(\text{bpy})_3]^{2+}$ to $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ are identical in acetonitrile and under acidic conditions.

The major products (>90%) of the spontaneous reductions of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ or $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ in basic solution are the corresponding Os(II) complexes, $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ or $[\text{Os}^{\text{II}}(\text{bpy})_3]^{2+}$. However, under basic conditions waves appeared after electrolysis that were not present in the initial solution. After acidification with 1 M HClO_4 or 1 M trifluoromethanesulfonic acid (HOTf), precipitates can be separated from each product solution which are identified as the unmodified Os(II) complexes by UV-Vis spectroscopy, cyclic voltammetry, ^1H NMR and HPLC. HPLC enabled the separation of the unmodified Os(II) complexes from at least two other Os(II)-containing side products.

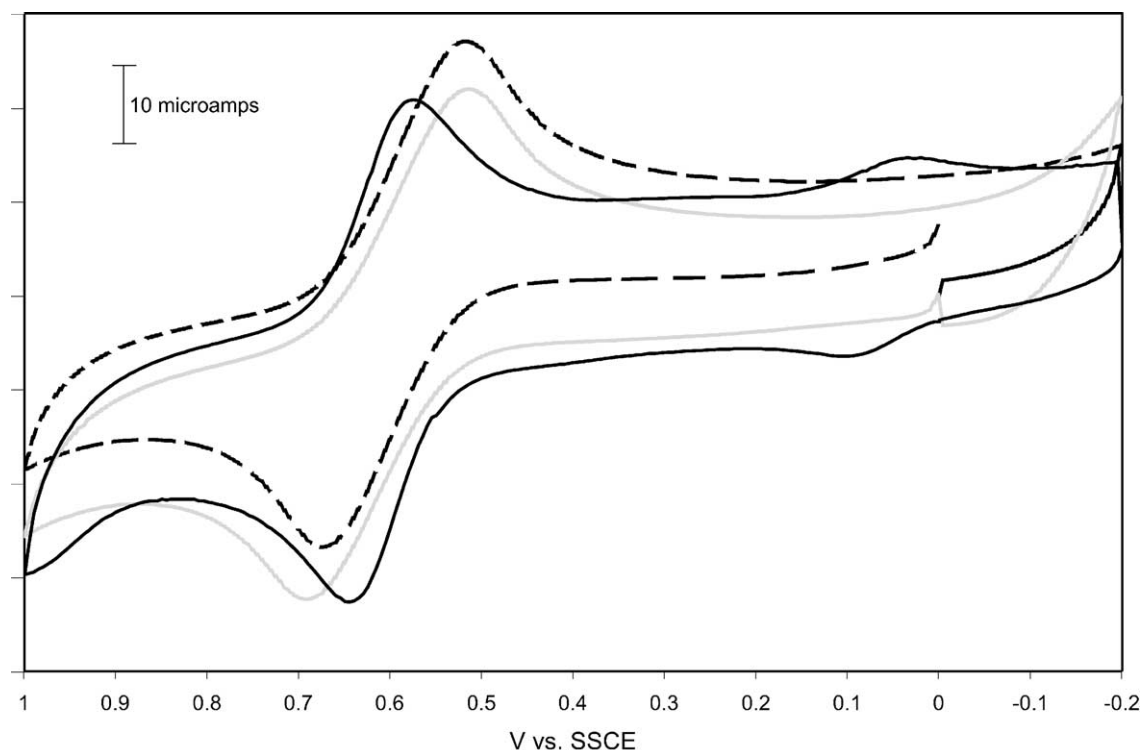


Fig. 1. Cyclic voltammograms at glassy-carbon electrode of deoxygenated (—) 10^{-5} mol $[\text{Os}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ at pH = 4.5, before electrolysis; (—) $[\text{Os}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ at pH = 4.5, 1 h after electrolysis at 650 mV (80 min, $n = 0.97e^-$); and (---) $[\text{Os}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ at pH = 7.71, 1 h after electrolysis and base addition. The potential scan rate was 0.1 V/s.

In a typical electrolysis experiment 10^{-5} to 10^{-6} mol of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ was dissolved in ca. 6 ml of solution and electrolyzed at ≥ 650 mV using a reticulated vitreous carbon electrode in a three-arm electrolysis cell. After a given amount of charge was passed, electrolysis was interrupted and the solution subjected to analysis by CV using a glassy-carbon electrode placed in the working electrode compartment. In Fig. 1 is shown a cyclic voltammogram of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ which was dissolved at pH = 4.5. The originally greenish solution was oxidized to a pinkish/purple $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ by exhaustive electrolysis at 650 mV versus SSCE ($n = 0.97e^-$). A CV of the $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ solution at pH = 4.5 is nearly identical to the CV before electrolysis and shows only the waves for the $\text{Os}^{\text{II/III}}$ couple. This solution is stable for several hours in the dark as shown by CV and UV-Vis analysis. However, after 1 h at pH = 7.71 (generated by base addition to the original solution), the wave for the $\text{Os}^{\text{II/III}}$ couple for $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ is still present, but there is also a new wave attributed to the $\text{Os}^{\text{II/III}}$ couple for $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$. At slower scan rates (≤ 20 mV/s), a wave for the $\text{Os}^{\text{III/IV}}$ couple is also present (not shown).

Fig. 2 shows UV-Vis spectral changes observed for the base-catalyzed self-reduction of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ at pH = 7.71 at 25.0 °C. $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ was generated from $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ at pH = 4.5 by electrolysis

at 650 mV versus SSCE. Electrolysis was followed by base addition and the total scan time = 10 h after base addition. These data reveal an increased absorbance with time in the region from 400 to 600 nm and a decreased absorbance at 260 nm (as shown in the inset). The resulting spectrum is consistent with polypyridyl $\text{Os}(\text{II})$ species, however, the molar extinction coefficients (calculated from $A = \epsilon bc$) are not equal to that of pure $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$. These data combined with the CV data of the same solution (Fig. 1) reveal that other $\text{Os}(\text{II})$ species are present in the alkaline solution.

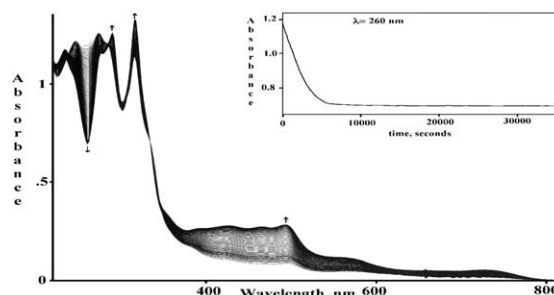


Fig. 2. UV-Vis spectral changes observed for the base-catalyzed self-reduction of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ at pH = 7.71 at 25.0 °C. $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ was generated from $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ at pH = 4.5 by electrolysis at 650 mV vs. SSCE. Electrolysis was followed by base addition and the total scan time = 10 h after base addition. Inset shows decrease in absorbance at $\lambda = 260$ nm.

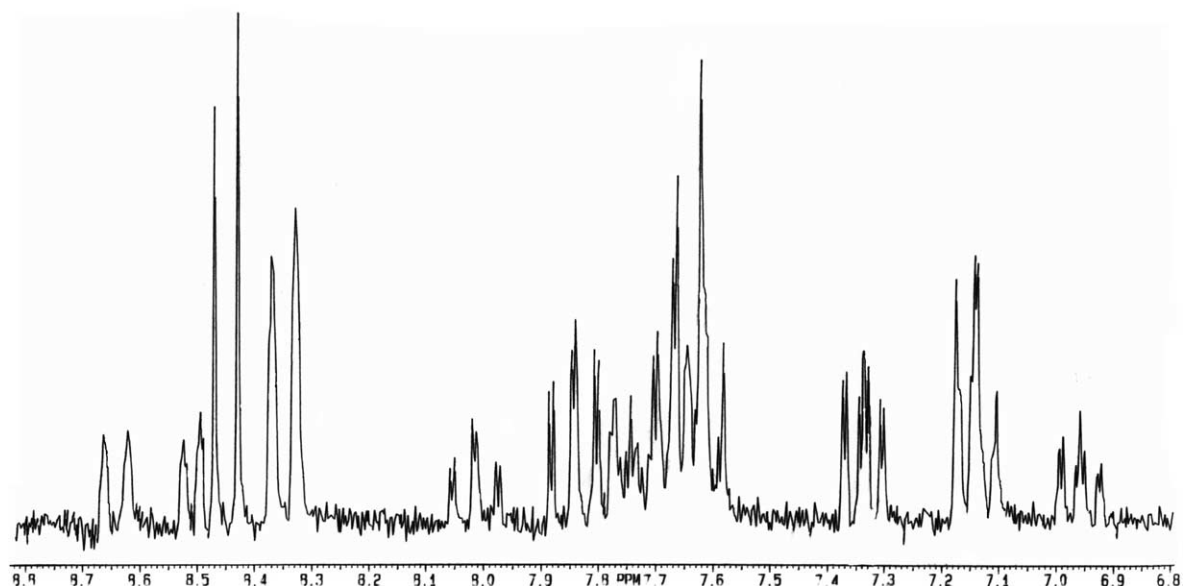


Fig. 3. ^1H NMR of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ in CD_3CN after isolation following self-reduction reaction.

After acidification with 1 M HClO_4 , HPLC enabled the separation of the unmodified Os(II) complex from at least two other Os(II)-containing side products in this case. The aromatic region of a ^1H NMR in CD_3CN of the isolated, unmodified $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ is shown in Fig. 3. One of the side products was isolated using a Sephadex SP-C25 cation exchange column. This compound was identified as $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ by UV-Vis measurements, consistent with the CV identification, and results from pyridine labilization, solvent ligation, and metal center reduction. No O_2 production was detected as a product of the base-catalyzed self-reduction.

In all cases where the electrolysis of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ to $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ was performed under acidic

conditions, the number of electron equivalents passed never exceeded one. However, a series of experiments were performed in which the $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ was electrolyzed to $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ under basic conditions and each resulted in greater than one equivalents of electrons. In one such experiment at $\text{pH} = 7.82$, 5 ml of a 5.85×10^{-6} M solution of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ was electrolyzed at 750 mV for 2 h using a reticulated vitreous carbon electrode in a three-arm electrolysis cell. A total of 1.28 C, or 2.25 equivalents of electrons, were passed in this time period. Fig. 4 shows the cyclic voltammograms of the solution before and after electrolysis. In addition, a CV of an independently prepared sample of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ at the same pH is shown. Before electrolysis, only the $\text{Os}^{\text{II/III}}$ wave of

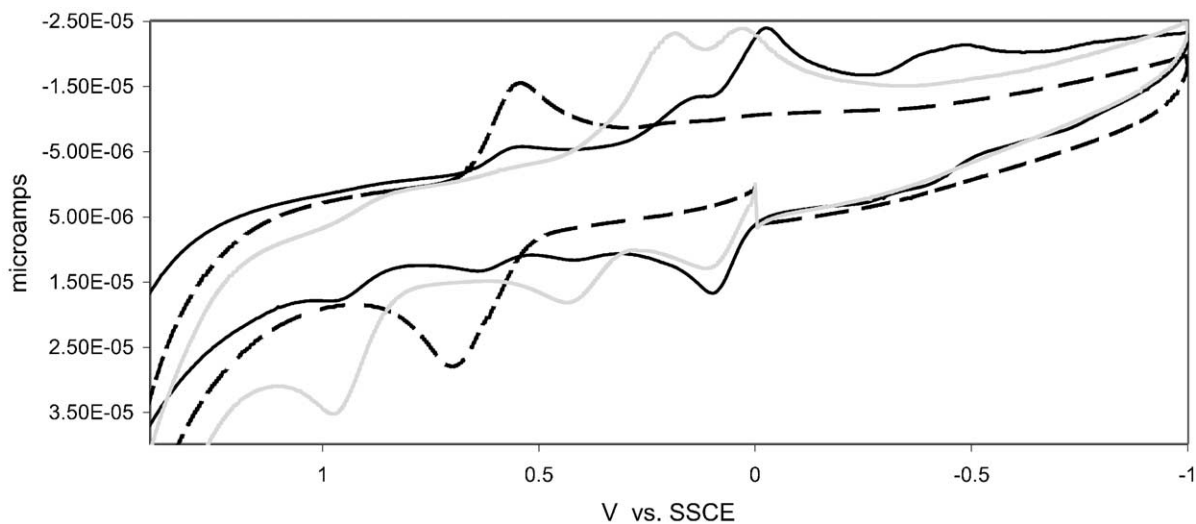
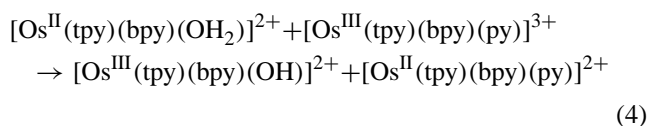
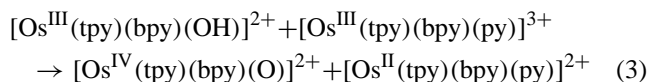


Fig. 4. Cyclic voltammograms at glassy-carbon electrode of deoxygenated 10^{-5} mol $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ at $\text{pH} = 7.82$ before electrolysis (—) and after electrolysis (---) at 750 mV with 2.25 equivalents of e^- passed. Also shown is the CV of an authentically prepared sample of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ at $\text{pH} = 7.82$ (—). The potential scan rate was 0.1 V/s.

the $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ complex is observed. After electrolysis, that wave remains, but there are additional waves clearly present that correspond to the $\text{Os}^{\text{II/III}}$ and $\text{Os}^{\text{III/IV}}$ waves of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$. Literature reports [15] have suggested that the complex $[\text{Os}^{\text{IV}}(\text{tpy})(\text{bpy})(\text{O})]^{2+}$ will lose a bpy ligand once oxidized to the Os^{V} form, $[\text{Os}^{\text{V}}(\text{tpy})(\text{bpy})(\text{O})]^{2+}$. This accounts for the irreversibility of the $\text{Os}^{\text{IV/V}}$ wave at ca. 0.95 V. The waves at $E_{0.5} = -173$ and -315 mV are the $\text{Os}^{\text{II/III}}$ and $\text{Os}^{\text{III/IV}}$ couples of the complex $[\text{Os}^{\text{II}}(\text{tpy})(\text{OH}_2)_3]^{2+}$. Aside from these voltammetric, UV-Vis, and HPLC observations, no further attempts were made to isolate or characterize the various products.

Experiments were conducted at a series of more basic pH values producing similar results when $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ was electrolyzed under basic conditions. A greater number of electron equivalents were passed in a given time period as the solutions were buffered at more basic pH values. One explanation is that the rate of pyridine substitution by hydroxide is increased as the pH is increased. At pH = 7, there is a driving force of approximately 200 mV for the disproportionation reaction shown in Eq. (3). The reaction between $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ and $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ has a driving force of approximately 500 mV and results in the electron transfer reaction shown in equation 4. It is likely that much of the unmodified $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ results from a combination of these two reactions.



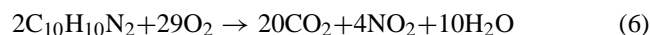
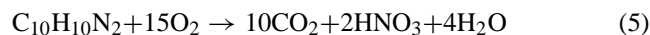
Dioxygen production was not observed as a product of exhaustive, prolonged oxidative electrolysis of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$ in 0.1 M NaOH.

It is clear, however, that the pyridine ligand must be replaced by OH^- to initiate the reactions in 3 and 4. A first-order dependence of the rate of substitution on hydroxide was determined to ca. pH = 11 by a series of triple mixing pH jump experiments (using the initial rate method). Beyond pH = 11, the rate of substitution and self-reduction became too fast to be observed by conventional diode array UV-Vis techniques.

Proton loss from an aqua or hydroxy ligand upon oxidation prevents build-up of charge on the complex from multiple electron loss at the metal and also allows the basic coordination environment for the metal in the different oxidation states to remain the same throughout a catalytic cycle. Because of the increased capacity for π -donation from the lone pairs of the hydroxy or oxo ligands, the higher oxidation states of the metal are stabilized as compared to with the pyridine ligand.

Gillard and Irving [16] and Sutin and co-workers [17] have presented evidence that bpy and phen type ligands

are susceptible to attack by hydroxide, particularly when the metal is in an oxidized form. Once an initial oxidation has been performed on a polypyridyl ligand, it is activated towards further oxidation. The mechanism is reported to involve nucleophilic addition of water or hydroxide to a carbon atom of the activated aromatic amine ligand. High valent metals activate the aromatic amine moiety and OH^- can act as a nucleophile. Although it would require extreme conditions, a fully oxidized bpy ligand could account for up to 60 electron equivalents, Eq. (5), or 58 e^- per bpy, Eq. (6).



We could not identify individual ligand oxidation products, but believe (anecdotally) that it initiates the reactivity observed. $[\text{Os}^{\text{IV}}(\text{tpy})(\text{bpy})(\text{O})]^{2+}$ and $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{OH})]^{2+}$ would be reduced to the observed $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ species by oxidizing a ligand moiety.

5. Conclusions

Spontaneous reduction of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$ and $[\text{Os}^{\text{III}}(\text{bpy})_3]^{3+}$ in water is promoted by basic conditions. At high pH, a fairly simple, first-order dependence of the reduction rate on $[\text{OH}^-]$ is found. Given the absence of O_2 formation in the base-catalyzed self-reduction of $[\text{Os}^{\text{III}}(\text{tpy})(\text{bpy})(\text{py})]^{3+}$, the concurrent formation of several Os-containing compounds, and the >90% yield of $[\text{Os}^{\text{II}}(\text{tpy})(\text{bpy})(\text{py})]^{2+}$, we conclude that the initial redox chemistry observed here is ligand-based. The apparent ligand decomposition reactions observed in this work (and elsewhere) suggest that polypyridine ligands are not always merely “spectator” ligands, especially under alkaline conditions, however useful catalytic rate data can be obtained in basic solution if the substrate of interest is sufficiently reactive and is present in large excess.

Acknowledgements

Acknowledgment is made to the Central Michigan University Faculty Research and Creative Endeavors Committee for support of this research.

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