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Electrochemistry in Liquid Sulfur Dioxide. 3. Electrochemical Production of New Highly Oxidized 2,2'-Bipyridine Complexes of Ruthenium and Iron

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Abstract: The electrochemical oxidation of Ru(bpy)$_2^{2+}$ and Fe(bpy)$_2^{2+}$ in liquid sulfur dioxide was investigated. Ru(bpy)$_2^{2+}$ shows two oxidation waves corresponding to the 3+ (1.01 V) and 4+ (2.76 V) forms while Fe(bpy)$_2^{2+}$ undergoes three oxidations to the 3+ (0.70 V), 4+ (2.92 V), as well as 5+ ($\approx$ 3.09 V) forms. While the 3+ form is stable for both compounds on a coulometric time scale, the higher oxidation states react with solvent to regenerate the 3+ form. The kinetics of this reaction was studied as a function of temperature by cyclic voltammetry, chronocoulometry, and chronoamperometry.

Introduction

Liquid sulfur dioxide containing a suitable electrolyte (e.g., tetra-n-butylammonium perchlorate, TBAP) has been shown to be a useful solvent for electrochemical studies, especially in the region of very positive potentials where strongly oxidizing species can exist. Thus the limit for background oxidation with 0.1
M TBAP was estimated as \( \approx 3.4 \) V vs. an aqueous saturated calomel electrode (SCE) by comparison of the potentials for oxidation of 9,10-diphenylanthracene (DPA) in \( \text{SO}_2 \) and acetonitrile. We report here the electrochemical oxidation of Ru(bpy)\(^{3+}\) (bpy = 2,2'-bipyridine) to the 3\(^+\) and 4\(^+\) forms and Fe(bpy)\(^{3+}\) to the 3\(^+\), 4\(^+\), and 5\(^+\) forms and data concerning the stability of these states in \( \text{SO}_2 \). The electrochemistry of Ru(bpy)\(^{3+}\), Fe(bpy)\(^{3+}\), and related compounds has been investigated in both protic and aprotic solvents.\(^1,4\) While oxidation to the 3\(^+\) form is frequently observed, to our knowledge no more highly oxidized species have been reported.

**Experimental Section**

Electrochemical studies were carried out in conventional one- and three-compartment cells using previously reported experimental procedures.\(^1,4\) [Ru(bpy)\(_3\)]PF\(_6\) was prepared by refluxing cis-(bpy)RuCl\(_2\)\(_2\)H\(_2\)O, prepared by published procedures,\(^2\) with 1.2 equiv of bpy (Aldrich Chemical Co., Milwaukee, WI) in dimethylformamide under nitrogen. An excess of NH\(_4\)PF\(_6\) was then added to precipitate the PF\(_6\) salt. The resulting orange product was recrystallized from acetone/ether, washed with ether, and air-dried. [Fe(bpy)\(_3\)]PF\(_6\) was prepared by adding 3 equiv of bpy to an aqueous solution of FeSO\(_4\). The PF\(_6\) salt was obtained by adding NH\(_4\)PF\(_6\). The red product was recrystallized from acetone/ether, washed with ether, and dried in vacuo. The supporting electrolyte, tetra-n-butylammonium fluoroborate ([TBA]BF\(_4\), polarographic grade, Southwestern Analytical Chemicals, Austin, TX) and NH\(_4\)PF\(_6\) (Ozark-Mahoning) were added to acetone. NH\(_4\)PF\(_6\) was removed by filtration, and (TBA)PF\(_6\) was precipitated with water. The product was recrystallized first from hot ethanol and then from acetone/ether.

All electrochemical measurements were made with a Model 173 potentiostat, employing positive feedback for IR compensation, a Model 175 universal programmer, and a Model 179 digital coulometer (Princeton Applied Research Corp., Princeton, NJ). Current-voltage curves for scan rates less than 500 mV/s were recorded on a Model 2000 X-Y recorder (Houston Instruments, Inc., Austin, TX). Chronocoulometric and cyclic voltammetric data at scan rates greater than 500 mV/s were recorded with a Model 3001 processing digital oscilloscope (Norland Corp., Fort Atkinson, WI). Numerical integration of current transients with the digital oscilloscope yielded the chronocoulometric results. All potentials in this work are reported against an Ag quasi-reference electrode (AgRE) of a type previously described;\(^4\) this has a potential of \(-0.22 \text{ V vs. AgRE}\). Visible absorption spectra were obtained with a Model 1250 optical multichannel analyzer (Princeton Applied Research Corp., Princeton, NJ) with a holographic grating (150 lines/mm) and a xenon lamp source.

**Results**

**Background Limits.** The anodic background limit for \( \text{SO}_2 \), 0.1 M TBAP, at a Pt electrode occurs at \( +2.4 \text{ V vs. AgRE} \) and has been attributed to oxidation of perchlorate ion.\(^5\) Thus the useful working range of the solvent should be extended to more positive potentials if anions more difficult to oxidize than perchlorate are employed. Two such anions are BF\(_4^−\) and PF\(_6^−\). The anodic limit of \( \text{SO}_2 \) containing either (TBA)BF\(_4\) or (TBA)PF\(_6\) as supporting electrolyte is extended by another 0.6 V. This potential limit probably represents the oxidation of \( \text{SO}_2 \) itself, since the same positive limit is obtained whether (TBA)BF\(_4\) or (TBA)PF\(_6\) or tetra-n-butylammonium fluoride is used.

**Oxidation of Ru(bpy)\(^{3+}\).** A typical cyclic voltammogram for the oxidation of Ru(bpy)\(^{3+}\) at a Pt-disk electrode is shown in Figure 1a. The first wave with an anodic peak potential, \( E_{pa} \), of 1.03 V corresponds to a Nernstian one-electron, electrochemically reversible process. The difference between the cathodic and anodic peak potentials, \( \Delta E_p = E_{pa} - E_{pc} \), is 48 mV, which corresponds closely to the expected value for a Nernstian wave at \(-40 \text{ °C (44 mV).} \) Controlled-potential coulometry (CPC) carried out at 1.50 V gave an \( n_{pp} \) value (faradays/mole of reactant consumed) of 0.99; the resultant light blue solution of Ru(bpy)\(^{3+}\) was stable on the time scale of the experiment (\( \sim 5 \) h).

The second oxidation wave shown in Figure 1a, \( E_{pa} = 2.78 \text{ V} \), corresponds to a second, one-electron oxidation. The Ru(bpy)\(^{3+}\) species is not stable at \( \nu = 100 \text{ mV/s} \) as shown by the presence of a second wave at 2.8 V. The second oxidation wave is not clearly resolved in 

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of only a small cathodic wave upon potential reversal. The effect of sweep rate on the CV waves for the Ru(bpy)$_2$$^{3+}$ and the electrogenerated 4+ species is stable on the time scale of the experiment. At these high scan rates the couple exhibits Nernstian behavior and an $E^{0}$ value (taken as the average of the anodic and cathodic peak potentials) of 2.76 V.

At low scan rates such as those of Figure 1a the $t_{pa}$ value of the second (3+ → 4+) wave is larger than that of the first (2+ → 3+). This behavior is characteristic of a catalytic reaction, where the electrogenerated species reacts with a nonelectroactive one to regenerate the starting material (eq 1 and 2). The occurrence of such a catalytic reaction is also clear from controlled-potential coulometric oxidation of a 17 mM Ru(bpy)$_2$$^{3+}$ solution at 2.85 V. After three times the number of coulombs needed for complete oxidation for a one-electron process has passed, the solution remained light blue and its voltammetric behavior was essentially identical with that obtained for the original Ru(bpy)$_2$$^{3+}$ solution. The current during coulometry did not decay to background levels but rather remained constant throughout the experiment. Isolation of the compound after coulometry and dissolution in MeCN gave a green solution. Cyclic voltammetric studies on this solution showed a reversible one-electron reduction wave at 1.29 V vs. SSCE corresponding to the Ru(bpy)$_2$$^{3+}$ couple.

To gain additional information about the kinetics of this catalytic reaction, we employed double-potential-step chronocoulometry. If the reaction obeys pseudo-first-order kinetics, i.e., $Z$ in eq 2 is present in large excess, then a chemical rate constant can be determined from the ratio $Q_0/Q_0^*$ (where $Q_0$ and $Q_0^*$ are the number of coulombs for oxidation and reduction, respectively) as a function of time for the forward step, $t_f$. Representative results, shown in Figure 3, show good agreement to the catalytic mechanism. Rate constants obtained from such studies are listed in Table I. An Arrhenius plot (in k vs. 1/T) is linear (Figure 4) and yields an activation energy of 12.8 kcal/mol. We believe that the solvent is the species that is oxidized in reaction 2 ($Z$ = SO$_2$) because the rate constant was independent of supporting electrolyte concentration over a range of 0.1–0.3 M and the 4+/3+ reaction occurs near the solvent limit. This implies that the oxidation of SO$_2$ is kinetically slow at the Pt electrode surface (i.e., occurs with a significant overpotential) but is catalyzed by the Ru(bpy)$_2$$^{3+}$/4+ couple. Similar reactions have been observed with other highly oxidized species such as those derived from oxidation of Fe(bpy)$_3$$^{3+}$ as discussed below.

**Oxidation of Fe(bpy)$_3$$^{2+}$.** A typical CV observed for the oxidation of Fe(bpy)$_3$$^{2+}$ in SO$_2$ is shown in Figure 1b. The first wave (E$_{pa}$ = 0.76 V) corresponds to a reversible one-electron oxidation. Controlled-potential coulometry at 1.0 V gave $n_{app}$ = 0.97. The dark blue solution of Fe(bpy)$_3$$^{3+}$ was stable for at least 4 h at temperatures up to −15 °C. Two other oxidation waves are observed at 2.88 and 3.14 V in both the Fe(bpy)$_3$$^{2+}$ and the electrogenerated Fe(bpy)$_3$$^{3+}$ solutions. At higher scan rates (30 V/s) the wave at 2.88 V corresponds to the Nernstian one-electron reaction (3), whereas the wave at 3.14 V corresponds to the quasi-reversible, one-electron reaction (4). At lower scan rates instability of both the 4+ and 5+ forms is observed, again probably caused by a catalytic reaction with SO$_2$. The kinetics of this reaction were studied by CV and chronoamperometry.

**Table 1.** Catalytic Rate Constants for M(bpy)$_x$$^{x+}$ Species

<table>
<thead>
<tr>
<th>M(bpy)$_x$$^{x+}$</th>
<th>temp, °C</th>
<th>rate const, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(bpy)$_2$$^{3+}$</td>
<td>-60</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>-54</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>-50</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>-45</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>-40</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>-35</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>-30</td>
<td>33</td>
</tr>
<tr>
<td>Fe(bpy)$_3$$^{3+}$</td>
<td>-35</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>-30</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>-26</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>-22</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>-15</td>
<td>1.6</td>
</tr>
</tbody>
</table>

a Average of CV and chronoamperometric results.

M at room temperature. The effect of sweep rate on the CV waves for the Ru(bpy)$_2$$^{3+}$ couple is shown in Figure 2. For v ≥ 5 V/s at −40 °C the electrogenerated 4+ species is stable on the time scale of the experiment. At these high scan rates the couple exhibits Nernstian behavior and an $E^{0}$ value (taken as the average of the anodic and cathodic peak potentials) of 2.76 V.

At low scan rates such as those of Figure 1a the $t_{pa}$ value of the second (3+ → 4+) wave is larger than that of the first (2+ → 3+). This behavior is characteristic of a catalytic reaction, where the electrogenerated species reacts with a nonelectroactive one to regenerate the starting material (eq 1 and 2). The occurrence of such a catalytic reaction is also clear from controlled-potential coulometric oxidation of a 17 mM Ru(bpy)$_2$$^{3+}$ solution at 2.85 V. After three times the number of coulombs needed for complete oxidation for a one-electron process has passed, the solution remained light blue and its voltammetric behavior was essentially identical with that obtained for the original Ru(bpy)$_2$$^{3+}$ solution. The current during coulometry did not decay to background levels but rather remained constant throughout the experiment. Isolation of the compound after coulometry and dissolution in MeCN gave a green solution. Cyclic voltammetric studies on this solution showed a reversible one-electron reduction wave at 1.29 V vs. SSCE corresponding to the Ru(bpy)$_2$$^{3+}$/4+ couple.

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\[
\text{Fe(bpy)$_3$$^{3+}$} \Rightarrow \text{Fe(bpy)$_3$$^{4+}$} + e^-
\]  

(3)

\[
\text{Fe(bpy)$_3$$^{4+}$} \Rightarrow \text{Fe(bpy)$_3$$^{5+}$} + e^-
\]  

(4)
closely spaced waves corresponding to the 1+, 0, and 1- species. vs. AgRE. The wave shows no cathodic reversal current for scan rates up to 20 V/s, suggesting instability of the oxidized product. The actual thermodynamic potential for the bpy+/bpy couple lies constant to be determined. From eq 9.

The oxidation of the free ligand, bpy, in SO2 occurs at +2.1 vs. AgRE. The wave shows no cathodic reversal current for scan rates up to 20 V/s, suggesting instability of the oxidized product. The actual thermodynamic potential for the bpy+/bpy couple lies to more positive values, since a fast following irreversible reaction causes a negative shift of Ep(a). Coordination of the bpy with the metal center probably makes its oxidation more difficult, consistent with the location of the expected Cottrell behavior. From this short time data (5–100 ms), a value for the combined constant ADV2C (where A is the area, D is the diffusion coefficient, and C is the bulk concentration) can be calculated from the slope of the i vs. r1/2 line. With this value the expected current response at longer times in the absence of kinetic perturbation, i(diff), can be calculated. A comparison of the measured catalytic current, i(a), to idiff allows a rate constant to be determined. The rate constants from cyclic voltammetric data were obtained in a similar fashion by comparing the ratio of the expected anodic peak current in the absence of kinetically perturbed reaction and to 

\[ \frac{i(a)}{i(diff)} \]

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The potentials for these reductions are relatively insensitive to the metal center. This is analogous to the reduced forms of Ru(bpy)32+ (2), liquid SO2, with path length 1 cm: (a) 9.87 \times 10^{-3} M Ru(bpy)32+ (1), liquid SO2 (2); (b) 8.90 \times 10^{-3} M Fe(bpy)32+ (1) liquid SO2 (2).

3+/4+ waves at 2.8 V vs. AgRE. Note that the waves for both the Fe(bpy)32+/3+ and Ru(bpy)32+/3+ couples occur at essentially the same potentials (in contrast to the situation for the 2+/3+ waves), consistent with the concept that this represents oxidation of a bpy. Additional evidence for this model is obtained from a joint consideration of the spectroscopic and electrochemical data, as proposed by Creutz, Sutin, and co-workers for reduction of bpy as proposed.

Figure 5. Plot of normalized anodic peak current, \( i(p) / v^{1/2} \), vs. scan rate, \( v \), for Fe(bpy)32+/3+. The solid line is theoretical results for \( k = 1.6 \) s\(^{-1}\). Points represent experimental data at -40°C, 0.13 M (TBA)PF\(_6\).

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New 2,2'-Bipyridine Complexes of Ruthenium and Iron

Figure 7. Absorption spectra of Ru(bpy)$_3^{3+}$ and Fe(bpy)$_3^{3+}$ in liquid SO$_2$, with path length 1 cm: (a) $2.24 \times 10^{-3}$ M Ru(bpy)$_3^{3+}$; (b) $3.90 \times 10^{-3}$ M Fe(bpy)$_3^{3+}$.

Complex solution spectrum, the shorter wavelength portions of both the Ru(bpy)$_3^{2+}$ and the Fe(bpy)$_3^{2+}$ spectrum are distorted by the SO$_2$ absorption edge. The absorption band for Ru(bpy)$_3^{3+}$ and Fe(bpy)$_3^{3+}$ has been assigned to a $\pi \rightarrow \tau_p$ transition, i.e., a ligand to metal charge transfer. The redox potential for the 4+/3+

$\text{[M}^{\text{III}}(\text{bpy})_3^{3+} + \text{hv} = [\text{M}^{\text{III}}(\text{bpy})_3(\text{bpy}^*)]^{3+}$ (5)

$\text{[M}^{\text{III}}(\text{bpy})_3^{3+} + \text{e}^- = [\text{M}^{\text{II}}(\text{bpy})_3]^{2+} E^{3+/2+}$ (6)

$\text{[M}^{\text{II}}(\text{bpy})_3(bpy^*)]^{3+} + \text{e}^- = [\text{M}^{\text{II}}(\text{bpy})_3]^{2+} E^{0+}$ (7)

$\text{[M}^{\text{III}}(\text{bpy})_3(bpy^*)]^{4+} + \text{e}^- = [\text{M}^{\text{II}}(\text{bpy})_3]^{3+} E^{0+}$ (8)

reaction 7 can be estimated ($E^0 = E^{3+/2+} + \text{hv}$). If it is assumed that the oxidation potential of bpy is not significantly affected by the charge on the metal center and if distortions between the ground and excited states are small, then the potential for oxidation of the 3+ species (eq 8) is given by

$E^{4+/3+} = E^0 = E^{3+/2+} + \text{hv}$ (9)

The values of $E^{4+/3+}$ calculated from $E^{3+/2+}$ and the absorption spectrum of the 3+ species shown in Table II agree well with the experimental values of $E^{4+/3+}$. The closely spaced 5+/4+ wave for the iron compound is also in agreement with this idea; a third oxidation wave is expected but would merge into the background oxidation of the solvent.

Conclusion

The large anodic window of SO$_2$ with (TBA)BF$_4$ or (TBA)PF$_6$ supporting electrolyte, equivalent to potentials up to $\sim+4$ V vs. SCE, allows the electrochemical generation of transition-metal complexes in high oxidation states. Although catalytic reactions of these with SO$_2$ occur, the systems appear sufficiently stable, especially at lower temperatures, for characterization, e.g., by spectroscopic techniques, and studies such as these are under way. Preliminary studies involving complexes of first-, second-, and third-row transition metals have provided further examples of the utility of this solvent system for the production of highly oxidized materials. These results will be reported elsewhere.

Acknowledgment. The support of this research by the National Science Foundation (Grant No. CHE 7903729) is gratefully acknowledged. We are indebted to Drs. Norman Sutin and Carol Creutz (Brookhaven National Laboratory) for helpful suggestions and discussions concerning this work.

Registry No. Ru(bpy)$_3^{3+}$, 15158-62-0; Fe(bpy)$_3^{3+}$, 15025-74-8; Ru(bpy)$_3^{4+}$, 18661-01-6; Fe(bpy)$_3^{4+}$, 18661-69-3; Fe(bpy)$_3^{5+}$, 83207-86-7; Ru(bpy)$_3^{5+}$, 83207-87-8; Fe(bpy)$_3^{6+}$, 83207-88-9; SO$_2$, 7446-09-5.