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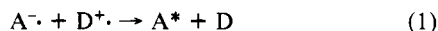
## Electrogenerated Chemiluminescence. 41. Electrogenerated Chemiluminescence and Chemiluminescence of the $\text{Ru}(2,2'\text{-bpy})_3^{2+}\text{-S}_2\text{O}_8^{2-}$ System in Acetonitrile–Water Solutions

Henry S. White and Allen J. Bard\*

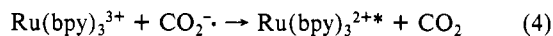
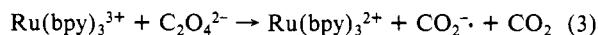
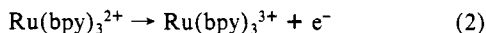
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**Abstract:** The electrogenerated chemiluminescence (ecl) produced in acetonitrile–water solutions (1:1 by volume) by the reaction of electrogenerated  $\text{Ru}(\text{bpy})_3^+$  with the strongly oxidizing intermediate,  $\text{SO}_4^{\cdot-}$ , generated during reduction of  $\text{S}_2\text{O}_8^{2-}$  is described. The orange luminescence ( $\lambda_{\text{max}} = 625 \text{ nm}$ ) corresponds to emission from  $\text{Ru}(\text{bpy})_3^{2+*}$ . The relative ecl intensity is a function of  $\text{S}_2\text{O}_8^{2-}$  concentration, and for a 1 mM  $\text{Ru}(\text{bpy})_3^{2+}$  solution the maximum ecl intensity was obtained at 15–20 mM  $\text{S}_2\text{O}_8^{2-}$ . Slightly higher concentrations ( $>30 \text{ mM S}_2\text{O}_8^{2-}$ ) effectively quench light emission because of the  $\text{Ru}(\text{bpy})_3^{2+*}\text{-S}_2\text{O}_8^{2-}$  reaction. The ecl efficiency (photons produced/electrons consumed) was  $\sim 5\%$  and was insensitive to dissolved  $\text{O}_2$ . A chemiluminescence based on reduction with Mg metal is also described.

A large number of reactions have been discovered in which excited states are generated by energetic electron transfers.<sup>1</sup> These usually involve the reaction of strong reductants ( $\text{A}^{\cdot-}$ ) and strong oxidants ( $\text{D}^{\cdot+}$ ) generated (usually electrochemically) in an aprotic solvent such as acetonitrile (MeCN). These reactions usually

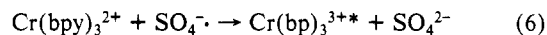
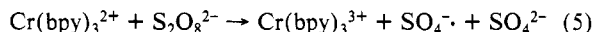


must be carried out under rigorously water- and oxygen-free conditions, since the precursors  $\text{A}^{\cdot-}$  and  $\text{D}^{\cdot+}$  react readily with these species. Recently, electrogenerated chemiluminescence (ecl) and chemiluminescence (cl) resulting from the production of strong oxidants or strong reductants by a bond-cleavage reaction have been investigated.<sup>2</sup> For example, the metal-to-ligand charge-transfer (MLCT) excited state of  $\text{Ru}(\text{bpy})_3^{3+}$  ( $\text{bpy} = 2,2'$ -bipyridine) can be generated by the oxidation of  $\text{Ru}(\text{bpy})_3^{2+}$  in the presence of oxalate. In this case the oxidation of  $\text{C}_2\text{O}_4^{2-}$  leads to a strong reductant,  $\text{CO}_2^{\cdot-}$ , and the reaction sequence<sup>2c</sup>



Thus by "oxidative reduction" both precursors to the electron-transfer ecl reaction were generated.

We were interested in investigating whether ecl could be generated by an analogous "reductive oxidation" (i.e., generation of a strong oxidant on reduction followed by bond cleavage). Balzani and co-workers<sup>3</sup> recently produced the luminescent metal-centered (MC) excited state of  $\text{Cr}(\text{bpy})_3^{3+}$  by oxidation of  $\text{Cr}(\text{bpy})_3^{2+}$  with peroxydisulfate or  $\text{Ti}^{3+}$ .



Production of the electronic excited-state complex in this set of reactions occurs via an electron-transfer reaction involving a strong oxidant ( $\text{SO}_4^{\cdot-}$ ) produced as an intermediate in a precursor reaction. Because  $\text{S}_2\text{O}_8^{2-}$  does not react appreciably with water or oxygen, this two-step sequence appears particularly promising for aqueous ecl or cl systems, where the decomposition of water generally prohibits the direct production by electrolysis of the two reactants needed to generate an excited-state species via eq 1. For example, while the efficiency of production of  $\text{Ru}(\text{bpy})_3^{2+*}$  by the electron-transfer reaction of electrogenerated  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{Ru}(\text{bpy})_3^+$  approaches unity in MeCN, in aqueous solution  $\text{Ru}(\text{bpy})_3^+$  reacts with the solvent and  $3+/\text{+}$  annihilation ecl has not been observed.<sup>4a</sup> However, ecl can be generated upon oxidation of aqueous solutions with the  $\text{Ru}(\text{bpy})_3^{3+}\text{-oxalate}$  system.<sup>2c</sup>

We report here very intense ecl and cl which results from reduction of partially aqueous solutions containing  $\text{Ru}(\text{bpy})_3^{2+}$

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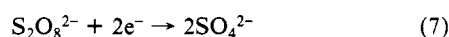
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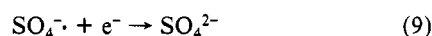
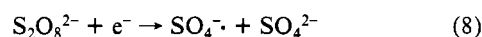
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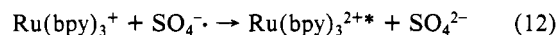
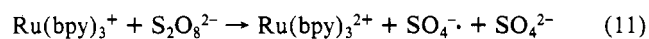
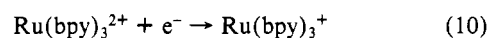
and  $\text{S}_2\text{O}_8^{2-}$ . From the thermodynamic potential,  $E^\circ$ , of the overall



two-electron reduction (1.75 V vs. SCE<sup>6</sup>) and measurements at semiconductor electrodes, Memming<sup>5</sup> estimated the potential for the first and second steps in aqueous solutions as  $\leq 0.35$  and  $\geq 3.15$  V vs. SCE (eq 8 and 9), respectively. Thus the intermediate,



$\text{SO}_4^{\cdot-}$ , formed during  $\text{S}_2\text{O}_8^{2-}$  reduction is sufficiently energetic to generate the lowest excited state of many transition-metal complexes by oxidation of the reduced form. Reduction of  $\text{Ru}(\text{bpy})_3^{2+}$  should generate a species capable of reducing  $\text{S}_2\text{O}_8^{2-}$ , since the potential of the  $\text{Ru}(\text{bpy})_3^{2+/+}$  couple ( $E^\circ \approx -1.5$  V vs. SCE)<sup>7,8</sup> is much more negative than that required for the reduction of  $\text{S}_2\text{O}_8^{2-}$ . We demonstrate in this work that, in a sequence analogous to eq 3 and 4, it is possible to generate the MLCT excited-state  $\text{Ru}(\text{bpy})_3^{2+}$  via oxidation of  $\text{Ru}(\text{bpy})_3^+$  by  $\text{SO}_4^{\cdot-}$  by the sequence



Because  $\text{Ru}(\text{bpy})_3^{2+*}$  is quenched by  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Ru}(\text{bpy})_3^+$  is unstable in aqueous solutions, the conditions for production of ecl must be chosen to take account of these reactions. However, by careful choice of the solvent system and reactant concentrations ecl and cl can be produced at relatively high efficiencies.

### Experimental Section

Electrochemical measurements were performed in a conventional three-compartment cell with a Pt-wire counter electrode and an aqueous sodium-saturated calomel reference electrode (SSCE). The working electrode was either a Teflon shrouded Pt disk (geometric area,  $0.28 \text{ cm}^2$ ) or a glassy carbon (GC) disk ( $0.17 \text{ cm}^2$ ) polished with  $0.5\text{-}\mu\text{m}$  diamond paste. The ecl and electrochemical studies employed an IBM Model 225 electrochemical system; the measurement techniques and methodology have been previously described.<sup>2a,8</sup> Relative ecl intensity measurements were made with a Hamamatsu R928 photomultiplier tube or an EG&G Model 550-1 radiometer/photometer equipped with a Model 550-3 pulse integrator. An Oriel 7240 grating monochromator with a  $1.0\text{-}\mu\text{m}$  blazed grating was used in obtaining emission spectra.  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  was prepared as previously reported.<sup>12</sup> Ammonium peroxydisulfate (Allied Chemical or MCB) was recrystallized from ethanol-water at room temperature. Sodium peroxydisulfate (Central Scientific Co), sodium borate (Merck), and Mg (W. C. Curtin and Co.) were used as received. Tetramethylammonium perchlorate (TMAP) (Southwestern Chemicals) was recrystallized twice from acetone-ether. MeCN (MCB, spectrograde) was dried over molecular sieves. Triply distilled water was used throughout.

$\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$  solutions were prepared under red light prior to measurements to prevent any changes in the concentration due to the photoreaction between  $\text{Ru}(\text{bpy})_3^{2+*}$  and  $\text{S}_2\text{O}_8^{2-}$  (see below). All experiments were performed under similar darkroom conditions.

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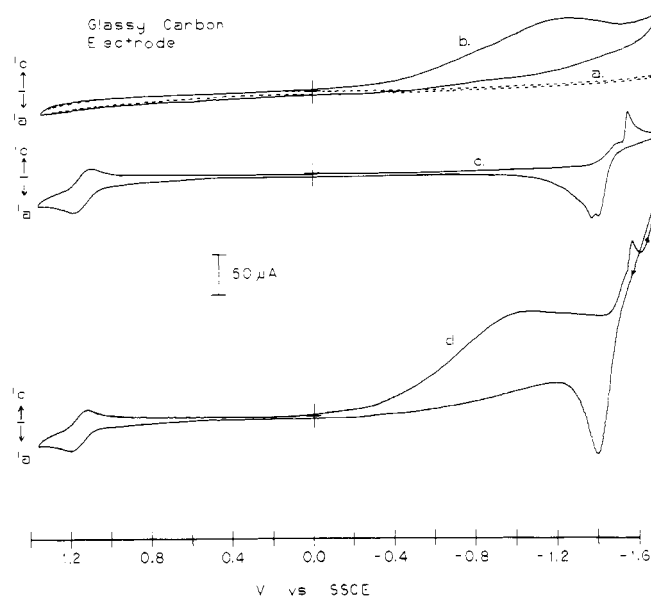
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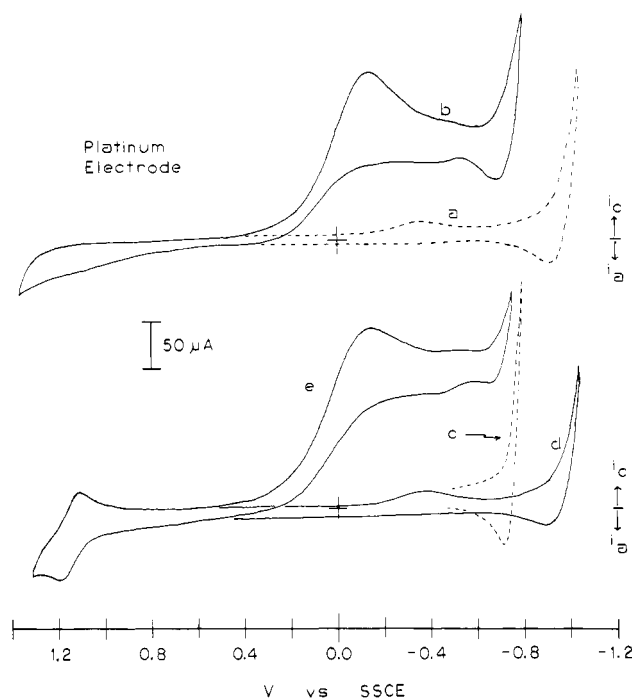
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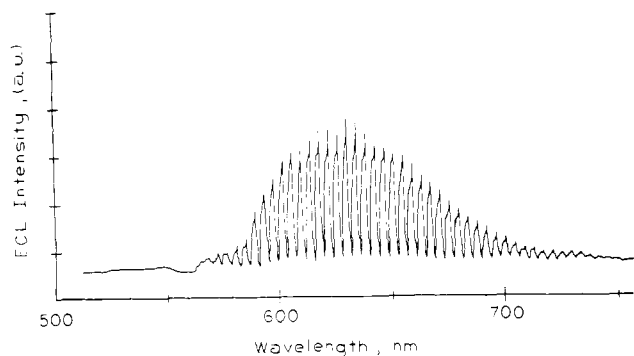
**Figure 1.** Cyclic voltammograms (0.05 V/s) at a glassy-carbon-disk electrode in degassed MeCN-H<sub>2</sub>O (1:1 by volume) solutions containing (a) supporting electrolyte (0.1 M TMAP), (b) 6.6 mM (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, (c) 2 mM Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>, (d) 2 mM Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>, and 6.6 mM (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The supporting electrolyte is 0.1 M TMAP in b-d.



**Figure 2.** Cyclic voltammograms (0.05 V/s) at a Pt-disk electrode in degassed MeCN-H<sub>2</sub>O (1:1 by volume) solutions containing (a) supporting electrolyte (0.1 M TMAP), (b) 6.6 mM (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, (c) 0.4 M NH<sub>4</sub>Cl, (d) 2 mM Ru(bpy)<sub>3</sub><sup>2+</sup>, (e) 2 mM Ru(bpy)<sub>3</sub><sup>2+</sup>, and 6.6 mM (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. The supporting electrolyte is 0.1 M TMAP in b-e.

### Results

**Electrochemical Measurements.** The electrochemical behavior of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in MeCN-water solutions (in all cases 1:1 by volume) containing supporting electrolyte (0.1 M TMAP) is shown in Figures 1 and 2. At a polished glassy-carbon (GC) electrode (Figure 1b) a broad cathodic wave corresponding to  $\text{S}_2\text{O}_8^{2-}$  reduction is observed beginning at 0 V vs. SSCE. No reoxidation wave is observed upon scan reversal within the range of scan rates investigated (up to 0.5 V/s). The drawn out shape of this wave

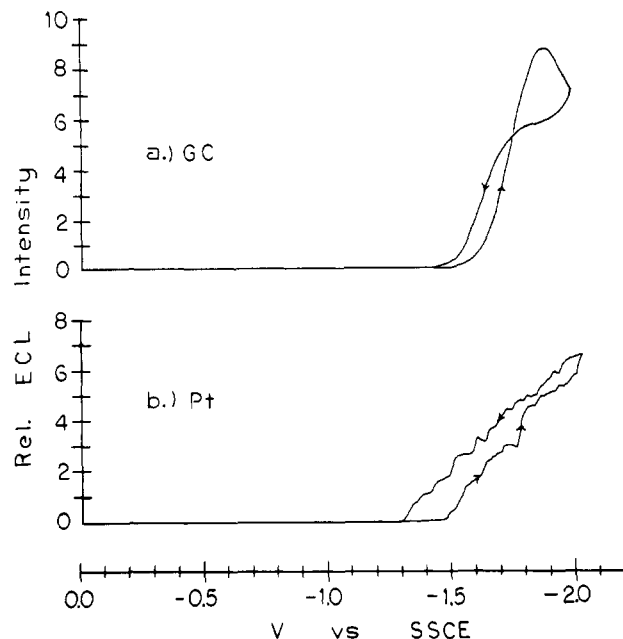


**Figure 3.** Ecl spectrum obtained by repetitively pulsing a Pt-disk electrode between  $-0.5$  and  $-2.0$  V vs. SSCE at 5-s intervals in a MeCN-H<sub>2</sub>O (1:1 by volume) solution containing 1 mM Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>, 10 mM (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and 0.1 M TMAP.

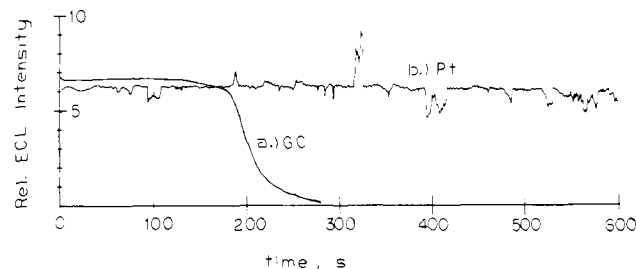
is attributed to the kinetically slow reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> at the GC surface. A corresponding broad wave occurs at a Pt-disk electrode (Figure 2b) beginning at  $\sim 0.4$  V vs. SSCE. At potentials negative of  $-0.7$  V a redox process was observed appreciably before the background reduction, which also occurs in solutions containing only NH<sub>4</sub>Cl (Figure 2c) and is attributed to proton reduction and hydrogen reoxidation. This process is not observed at GC, where proton reduction is slow. An essentially identical voltammetric process was found in solutions containing 7 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and excess NH<sub>4</sub>Cl (buffered to pH 8–9 with sodium borate). However, in solutions of Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (pH 8–9), in the absence of NH<sub>4</sub><sup>+</sup>, no cathodic currents were observed until the applied potential was negative of  $-0.2$  V.

Cyclic voltammograms of Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (2 mM) in MeCN-H<sub>2</sub>O solutions are shown in Figures 1c and 2d. At both Pt and GC a reversible wave corresponding to the oxidation of Ru(bpy)<sub>3</sub><sup>2+</sup> to the 3+ form is observed at 1.15 V. The reduction of Ru(bpy)<sub>3</sub><sup>2+</sup> could not be observed at a Pt electrode because proton reduction occurs first. At GC electrodes a cathodic wave begins at  $-1.35$  V that has a diffusional shape until the potential scan reaches  $-1.53$  V, where a sharp current peak occurs. Upon scan reversal two partially resolved reoxidation peaks are produced centered around  $-1.4$  V. While the details of this reaction in MeCN-H<sub>2</sub>O have not been investigated, the waves occur at potentials corresponding to reduction of Ru(bpy)<sub>3</sub><sup>2+</sup> to the + and 0 species in pure MeCN.<sup>8</sup> The sharp peak in MeCN-H<sub>2</sub>O can probably be attributed to precipitation or strong adsorption of the uncharged complex. A change in this wavelshape was observed when S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (6.6 mM) was added to the Ru(bpy)<sub>3</sub><sup>2+</sup> solution (Figure 1d). The currents at potentials around  $-1.35$  V were increased and the prepeak at  $-1.53$  V was still visible but was slightly diminished. A large increase in the cathodic current negative of  $-1.4$  V occurred and upon scan reversal only a single, more narrow, reoxidation peak was found. These results can be interpreted by invoking the reaction of Ru(bpy)<sub>3</sub><sup>+</sup> with S<sub>2</sub>O<sub>8</sub><sup>2-</sup> (eq 11). The increase in current beyond the Ru(bpy)<sub>3</sub><sup>2+</sup> reduction wave cannot be attributed to solvent reduction, since this large increase is not observed without the addition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. The presence of the small Ru(bpy)<sub>3</sub><sup>+0</sup> prepeak and single reoxidation peak after S<sub>2</sub>O<sub>8</sub><sup>2-</sup> addition indicates that further reduction of Ru(bpy)<sub>3</sub><sup>+</sup> to Ru(bpy)<sub>3</sub><sup>0</sup> competes with the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> mediated reduction. Overall, the results presented here demonstrate the reduction of solution S<sub>2</sub>O<sub>8</sub><sup>2-</sup> by electrogenerated Ru(bpy)<sub>3</sub><sup>+</sup> in MeCN-H<sub>2</sub>O solutions. These results could not be observed at Pt, where scanning into this region results in H<sub>2</sub> evolution.

**Electrogenerated Chemiluminescence (ecl).** A bright orange luminescence from the electrode surface occurred at GC or Pt electrodes immersed in a MeCN-H<sub>2</sub>O solution containing both Ru(bpy)<sub>3</sub><sup>2+</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and biased negative of  $-1.4$  V vs. SSCE. The ecl emission spectrum produced in this manner is shown in Figure 3. The band shape and emission maximum at 625 nm coincide with previously reported<sup>8</sup> ecl and emission spectra of Ru(bpy)<sub>3</sub><sup>2+\*</sup>. Ecl was not observed under these conditions with MeCN-H<sub>2</sub>O solutions containing only Ru(bpy)<sub>3</sub><sup>2+</sup> or only S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.



**Figure 4.** Relative ecl intensity-potential curves at (a) glassy-carbon and (b) Pt-disk electrodes in MeCN-H<sub>2</sub>O containing 1 mM Ru(bpy)<sub>3</sub><sup>2+</sup> and 10 mM S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. The scan rate is 50 mV/s. The noise in b is due to H<sub>2</sub> evolution.

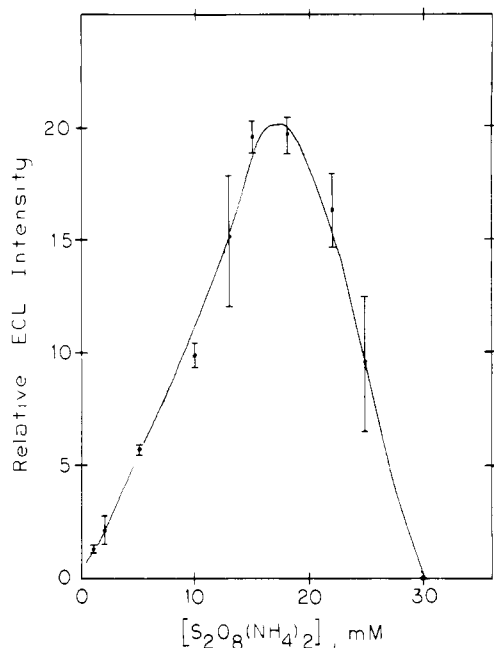


**Figure 5.** Ecl intensity with time obtained at RDE (100 rpm) in the same solution as in Figure 4 at (a) GC and (b) Pt. The noise in b is due to H<sub>2</sub> evolution.

The ecl intensity was essentially unaffected by saturation of the solution with O<sub>2</sub>.

The ecl intensity-potential curves shown in Figure 4 are useful in probing the reaction pathway responsible for production of excited-state Ru(bpy)<sub>3</sub><sup>2+\*</sup>. No ecl was observed at potentials up to  $-1.4$  V, where S<sub>2</sub>O<sub>8</sub><sup>2-</sup> is reduced directly at both GC and Pt electrodes. When the potential was biased negative of the onset of the Ru(bpy)<sub>3</sub><sup>2+/+</sup> reduction wave ( $-1.4$  V), ecl was observed, indicating that the direct electrogeneration of Ru(bpy)<sub>3</sub><sup>+</sup> is necessary to produce the Ru(bpy)<sub>3</sub><sup>2+\*</sup> excited state. Note that though the Ru(bpy)<sub>3</sub><sup>2+/+</sup> voltammetric wave cannot be observed at the Pt electrode, the onset potential of ecl at Pt occurs at the same potentials as at GC, suggesting that reduction of Ru(bpy)<sub>3</sub><sup>2+</sup> occurs at the same potentials at Pt and GC.

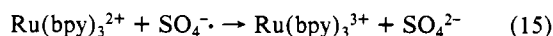
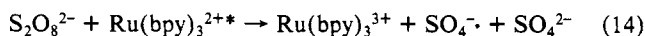
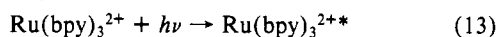
The ecl intensity-time profiles obtained at GC or Pt electrodes are different, however. When a GC electrode was pulsed repetitively between 0.0 and  $-1.8$  V at 5-s intervals the ecl intensity decayed to negligible background levels after approximately 20 pulses, while the ecl intensity at Pt under the same conditions was constant for several hours. The ecl intensity at the GC electrode could be restored by removing the electrode from the cell, wiping it with a paper towel, and returning it to the same solution. The decay of ecl at GC is thus caused by irreversible filming of Ru(bpy)<sub>3</sub><sup>0</sup> or products on the electrode surface. Although this probably occurs at Pt, the continuous evolution of H<sub>2</sub> gas during pulsing prevents buildup of this passivating film. Ecl intensity-time profiles obtained at rotating GC- and Pt-disk electrodes (RDE) confirm that filming by reduction products is responsible for the decay in ecl intensity of GC electrodes. The ecl intensity for both



**Figure 6.** Relative ecl intensity as a function of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  concentration in degassed MeCN– $\text{H}_2\text{O}$  solution (1:1 by volume) containing 1 mM  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ .

GC and Pt RDEs at 100 rpm (Figure 5) is relatively constant for  $\sim 200$  s. After this initial period a rather rapid decay in ecl intensity is observed only at the GC RDE. This rapid drop in ecl intensity at GC instead of a gradual decay indicates that the deterioration of ecl signal is due to a surface process rather than slow loss of reactants (e.g.,  $\text{S}_2\text{O}_8^{2-}$  or  $\text{Ru}(\text{bpy})_3^{2+}$ ) because of a side reaction. The decay in ecl intensity can be attributed to processes involving the  $\text{Ru}(\text{bpy})_3^0$  form, since the decay could be slowed considerably by pulsing only potentials of  $-1.45$  V vs. SSCE, where  $\text{Ru}(\text{bpy})_3^{2+}$  is reduced only to the  $1+$  form. Even under these conditions, a slow decay in the ecl intensity was observed after 15–20 min.

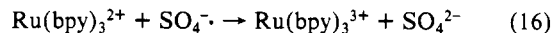
**Quenching of  $\text{Ru}(\text{bpy})_3^{2+*}$  by  $\text{S}_2\text{O}_8^{2-}$ .** Recently,  $\text{S}_2\text{O}_8^{2-}$  has been used as an effective quencher of excited-state  $\text{Ru}(\text{bpy})_3^{2+*}$  (with a quantum efficiency of 2),<sup>9</sup> and this system was employed in designing water photolysis cells.<sup>10,11</sup> Photoproduction of  $\text{Ru}(\text{bpy})_3^{3+}$  occurs by the reactions



The quenching of  $\text{Ru}(\text{bpy})_3^{2+*}$  by  $\text{S}_2\text{O}_8^{2-}$  in aqueous solutions suggests that the ecl efficiency should show a strong dependence on the  $\text{S}_2\text{O}_8^{2-}$  concentration. The relative ecl intensity of a 1 mM  $\text{Ru}(\text{bpy})_3^{2+}$  solution as a function of  $\text{S}_2\text{O}_8^{2-}$  concentration is shown in Figure 6. Although the quenching reaction was  $\sim 50$  times slower in MeCN– $\text{H}_2\text{O}$  than in water,<sup>13</sup> the  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$  solutions were prepared in the dark prior to the measurements to prevent any change in concentrations because of the photo-reaction. The intensity– $\text{S}_2\text{O}_8^{2-}$  concentration curve in Figure 6 was obtained by integrating the ecl intensity while repetitively pulsing the potential of a Pt-disk electrode between 0.0 and  $-1.8$  V vs. SSCE at 5-s intervals. Each point represents the average of five trials, each consisting of the initial four pulses. The relative ecl intensity increases with  $\text{S}_2\text{O}_8^{2-}$  concentration up to 15–20 mM. At higher concentrations the intensity drops off sharply and is less than 1% of its maximum level at 30 mM. A further increase in  $\text{S}_2\text{O}_8^{2-}$  concentration completely suppresses emission ( $<0.01\%$  of the maximum intensity). Ecl was not observed in purely aqueous solutions (0.2 M  $\text{Na}_2\text{SO}_4$ , pH 6) of  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{S}_2\text{O}_8^{2-}$  at either Pt or GC electrodes, probably because  $\text{Ru}(\text{bpy})_3^+$  is not

produced or is unstable under these conditions and because of the much faster quenching reaction in water.

Two alternative paths appear likely for the production of  $\text{Ru}(\text{bpy})_3^{2+*}$ . The first, analogous to that proposed for the  $\text{Cr}(\text{bpy})_3^{3+}$  in ref 3, involves eq 12. However,  $\text{SO}_4^{\cdot-}$  can also oxidize the  $2+$  species leading to the sequence

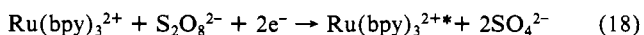


Both mechanisms involve the direct reduction of  $\text{Ru}(\text{bpy})_3^{2+}$  at the electrode surface, in agreement with the observation that ecl is not observed until potentials where  $\text{Ru}(\text{bpy})_3^+$  is produced. Two sources of  $\text{SO}_4^{\cdot-}$  are possible: that formed from reaction of  $\text{S}_2\text{O}_8^{2-}$  with  $\text{Ru}(\text{bpy})_3^+$  (eq 11) and that produced at the electrode surface (eq 8). However, because  $\text{SO}_4^{\cdot-}$  will be immediately reduced at the electrode, the path of eq 11 is probably more important in excited-state production. Note that in both routes at least two electrons must be passed in the reduction step for each photon emitted.

The quenching reaction of  $\text{Ru}(\text{bpy})_3^{2+*}$  by  $\text{S}_2\text{O}_8^{2-}$  (eq 14) is interesting in that the two strong oxidants generated in the reaction  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{SO}_4^{\cdot-}$ , can be recycled to produce another  $\text{Ru}(\text{bpy})_3^{2+*}$ . This recycling reaction is probably partly responsible for the strong emission observed in a solution containing such an effective quencher. However, at high  $\text{S}_2\text{O}_8^{2-}$  concentration ( $>30$  mM) not only is the excited state quenched but electrogenerated  $\text{Ru}(\text{bpy})_3^+$  may be removed by reaction with  $\text{S}_2\text{O}_8^{2-}$  to give  $\text{Ru}(\text{bpy})_3^{2+}$ , decreasing the  $\text{Ru}(\text{bpy})_3^+$  steady-state concentration near the electrode surface.

**Efficiency.** The ecl efficiency ( $\phi_{\text{ecl}}$ ) is usually discussed in terms of photons emitted per redox event; when the luminescence efficiency is known, the number of excited states generated per redox event can be estimated. For the  $\text{Ru}(\text{bpy})_3^{3+}$ – $\text{Ru}(\text{bpy})_3^+$  system in MeCN the ecl efficiency has been estimated at 25 °C as  $\sim 5\%$ .<sup>4,8</sup> Since this number is near that for the luminescence efficiency at 25 °C, the efficiency of producing  $\text{Ru}(\text{bpy})_3^{2+*}$  upon  $1+/3+$  annihilation approaches unity.<sup>4a,b</sup> The complexity of the reaction mechanism for the  $\text{Ru}(\text{bpy})_3^+$ – $\text{S}_2\text{O}_8^{2-}$  precludes measurement of  $\phi_{\text{ecl}}$  and we have chosen to estimate the coulometric efficiency ( $\phi_{\text{coul}}$ , photons generated per electron injected) by comparing the integrated intensity of the  $\text{Ru}(\text{bpy})_3^{2+}$ – $\text{S}_2\text{O}_8^{2-}$  system to that of the  $\text{Ru}(\text{bpy})_3^{2+}$  ( $3+/1+$  reaction) system. The integrated ecl intensity of the  $\text{Ru}(\text{bpy})_3^{2+}$ – $\text{S}_2\text{O}_8^{2-}$  system was measured in a MeCN– $\text{H}_2\text{O}$  solution containing 1 mM  $\text{Ru}(\text{bpy})_3^{2+}$  and 18 mM  $\text{S}_2\text{O}_8^{2-}$ , which corresponds to the optimized conditions in Figure 6. A 1 mM  $\text{Ru}(\text{bpy})_3^{2+}$  MeCN solution was used in the reference system. The ecl efficiency was estimated by comparing the ratio of integrated emission intensity to the total coulombs passed for both systems at a GC-disk electrode, pulsed repetitively at 5-s intervals. In the  $\text{Ru}(\text{bpy})_3^{2+}$ – $\text{S}_2\text{O}_8^{2-}$  solution the electrode potential was pulsed from 0 to  $-1.45$  V vs. SSCE. In this potential range the filming problem at GC is minimized. Under these conditions the relative integrated ecl intensity of the  $\text{Ru}(\text{bpy})_3^{2+}$ – $\text{S}_2\text{O}_8^{2-}$  system was found to be about 6–7 times larger than that observed during the cathodic pulse from the  $\text{Ru}(\text{bpy})_3^{3+/+}$  annihilation reaction. However, the charge obtained by integrating the current pulse during the 5-s step in the  $\text{S}_2\text{O}_8^{2-}$  was 12–14 times larger than the integrated current during the cathodic pulse in the  $+3/+$  system. Thus the coulombic ecl efficiency for the  $\text{S}_2\text{O}_8^{2-}$  is about half that of the annihilation system.

One can estimate the maximum efficiency for this system by considering the pathway represented by eq 10–12, which yield the overall reaction



The occurrence of the reactions in eq 16 and 17 and even the quenching reactions (eq 14 and 15) will not perturb the overall stoichiometry of eq 18, assuming no other loss processes occur. The maximum predicted coulombic efficiency for the  $\text{S}_2\text{O}_8^{2-}$  system would then be two cathodic electrons consumed per excited

(13) Unpublished results: H. S. White, W. Becker, and A. J. Bard.

state generated compared with one cathodic electron per excited state for the annihilation system. The observed ratio between these systems corresponds to these expectations and implies that losses in the  $S_2O_8^{2-}$  system, e.g., by direct reduction of  $SO_4^{\cdot-}$  at the electrode (eq 9), by reaction of  $SO_4^{\cdot-}$  with solvent, or by oxidation of  $Ru(bpy)_3^+$  in side reactions, are small.

Note also that the observed intensities in the  $S_2O_8^{2-}$  system can be much higher than those in the 1+/3+ system because of the higher reactant concentrations that can be employed in the MeCN-H<sub>2</sub>O solvent.

**Chemiluminescent Systems.** Chemiluminescence can also be generated in a MeCN-H<sub>2</sub>O solution containing  $Ru(bpy)_3^{2+}$  and  $S_2O_8^{2-}$  when a strong reductant capable of producing  $Ru(bpy)_3^+$  is added to the solution. Thus, when Mg powder or turnings were added to a MeCN-H<sub>2</sub>O solution mixture of 1 mM  $Ru(bpy)_3^{2+}$  and 20 mM  $S_2O_8^{2-}$ , a bright orange emission resulted that was easily visible under room light and persisted for several hours. The production of luminescence presumably follows a pathway similar to that discussed for the ecl, with the external circuit and electrode replaced by a strong electron donor. Addition of  $S_2O_8^{2-}$  or Mg to the solution after the luminescence had decayed to low levels resulted again in a bright emission, indicating that the system is limited by consumption of Mg or  $S_2O_8^{2-}$ . Analogous chemiluminescent systems involving  $Ru(bpy)_3^{2+}$ , oxalate, and a strong oxidant have been reported.<sup>2c</sup> An interesting aspect of this system is that no apparent reaction occurs when Mg,  $S_2O_8^{2-}$ , and  $Ru(bpy)_3^{2+}$  are mixed in MeCN alone. This is probably due to the low solubility of  $(NH_4)_2S_2O_8$  and the Mg oxide coating in MeCN. The reactants can be mixed in MeCN and stored for long durations (>50 h) with no or very low emission detected. However, the bright chemiluminescence is observed simply upon addition of water, which dissolves the reactants. In carrying out this

reaction, means of venting the H<sub>2</sub> produced by the Mg reaction must be provided. Similar experiments were performed with Me<sub>2</sub>SO replacing water. Although H<sub>2</sub> evolution was eliminated under these conditions, the observed emission was not as intense as in the MeCN-H<sub>2</sub>O system, probably because of the lower solubility of the  $(NH_4)_2S_2O_8$  in this medium

### Conclusion

The chemical or electrochemical reduction of  $S_2O_8^{2-}$  produces a strongly oxidizing intermediate,  $SO_4^{\cdot-}$ , that generates a very intense emission in the presence of electrogenerated  $Ru(bpy)_3^+$ . The ecl mechanism involves several reaction pathways and includes the quenching of  $Ru(bpy)_3^{2+*}$  by  $S_2O_8^{2-}$  to produce several strong oxidants also capable of generating the excited state. The ecl and chemiluminescent intensity of this system is several times larger than that of previously reported systems based on  $Ru(bpy)_3^{2+}$  and may be useful in practical devices. Other ecl and chemiluminescent systems based on reaction of the intermediate  $SO_4^{\cdot-}$  with suitable reduced species, A<sup>-</sup> (e.g., radical anions of aromatic hydrocarbons), to produce A\* have also been studied. These will be the subject of a separate communication.

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**Registry No.** [ $Ru(bpy)_3$ ]( $S_2O_8$ ), 83632-61-5;  $Ru(bpy)_3^+$ , 56977-24-3;  $SO_4^{\cdot-}$ , 14808-79-8;  $Ru(bpy)_3^{2+}$ , 79736-55-3;  $S_2O_8^{2-}$ , 15092-81-6; MeCN, 75-05-8.

(14) **Note Added in Proof:** Findings similar to those reported here have just appeared: Bolletta, F.; Ciano, M.; Balzani, V.; Serpone, N. *Inorg. Chim. Acta* 1980, 62, 207-213.

## Solution Thermodynamic Studies. 6.<sup>1</sup> Enthalpy-Entropy Compensation for the Complexation Reactions of Some Crown Ethers with Alkaline Cations: A Quantitative Interpretation of the Complexing Properties of 18-Crown-6

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**Abstract:** The interactions of 18-crown-6, 15-crown-5, and 12-crown-4 with Na<sup>+</sup> and K<sup>+</sup> were studied in methanol and water as solvents at 25 °C.  $\Delta G^\circ$  values for both 1:1 and 2:1 complexation reactions were determined by potentiometric titrations. Used in conjunction with these values, calorimetric measurements led to  $\Delta H^\circ$  and  $\Delta S^\circ$  values. The thermodynamic parameters obtained cannot be correlated with the cations or the crown ethers "hole" sizes in any 1:1 or 2:1 reactions. Moreover, the  $\Delta G^\circ$  values are the result of quite different but permanently compensating combinations of the  $\Delta H^\circ$  and  $\Delta S^\circ$  values. These arise from several thermodynamic processes in which the role of the solvent must be considered. In the case of 18-crown-6, we present a quantitative interpretation in which this crown ether develops interactions that are stronger with Na<sup>+</sup> than with K<sup>+</sup>.

Since Pedersen's pioneering work,<sup>2</sup> the interest in complexing agents like crown ethers and cryptands has increased considerably. These complexing agents are known to effect a dramatic change in the interactions of cations with their counterions and give rise to the so-called "naked anions"<sup>3</sup> for instance. The association

properties of crown ethers with alkaline cations have been mainly described in terms of similarities between cation size<sup>4-7</sup> and the size of the inner "hole" of the crown ether. This kind of oversimplified qualitative description does not take into account the role of the solvent.<sup>8,9</sup>

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