

Tested Demonstrations

Chemiluminescence of Tris(2,2'-bipyridyl)ruthenium(II): A Glowing Experience

submitted by: **Ed Bolton and Mark M. Richter***

Department of Chemistry, Southwest Missouri State University Springfield, MO 65804;
*MarkRichter@smsu.edu

checked by: **Jodye Selco**

Department of Chemistry, University of Redlands, Redlands, CA 92373-0999

Chemiluminescence involves the production of light by species that can undergo highly energetic electron transfer reactions. When Mg powder or turnings are added to a CH₃CN–H₂O (50:50 v/v) solution mixture containing 1 mM Ru(bpy)₃²⁺ and 40 mM S₂O₈²⁻ (CH₃CN = acetonitrile, bpy = 2,2'-bipyridine, S₂O₈²⁻ = peroxydisulfate) at pH 1.2, a bright orange emission results that is easily visible in a darkened room and persists for more than five minutes. Mg is a strong electron donor and is added to the solution to reduce Ru(bpy)₃²⁺ to Ru(bpy)₃⁺ and S₂O₈²⁻ to SO₄^{•-}. The sulfate radical then oxidizes Ru(bpy)₃⁺ to an excited state (*Ru(bpy)₃²⁺) that is able to luminesce.

Experimental Procedure

Materials and Equipment

Tris(2,2'-bipyridyl)ruthenium(II)dichloride hexahydrate
(Strem, Alfa Aesar, Aldrich)

Ammonium persulfate (ammonium peroxydisulfate)

Acetonitrile

Magnesium powder or turnings

Deionized water

Hydrochloric acid (2 M)

100-mL beaker

Stir plate

Magnetic stir bar

Preparation of Solution

Dissolve 0.075 g (0.100 mmol) of Ru(bpy)₃Cl₂·6H₂O in 50 mL of deionized water in a 100-mL beaker. Add ca. 1 g (40 mmol) of (NH₄)₂S₂O₈ with stirring, followed by 50 mL of acetonitrile. Adjust the pH of the solution to 1.2 (±0.05) with 2 M HCl. This solution is stable for more than 24 hours. When you wish to begin the demonstration turn out the room lights and add the magnesium powder or tailings (ca. 1 spatula tipful) with very vigorous stirring (e.g., using a Teflon-covered magnetic stir bar and stir plate) so that the magnesium is suspended and visible. When the magnesium is added an orange glow will be produced around the metal. It may take 1–2 minutes for the reaction to reach full intensity. This is probably due to the oxide coating on the Mg. The chemiluminescence emission lasts approximately 30 min if 5-mm magnesium tailings are used and approximately 5 min

if 70–80 mesh magnesium powder is used. Our preference is to use magnesium powder because it is easier to suspend in solution with stirring. The chemiluminescence may be regenerated by adding more magnesium (ca. 1 spatula tipful), followed by 5–10 mL of 2 M HCl. The acid probably aids in removal of the oxide coating on the magnesium.

Hazards

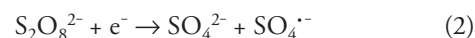
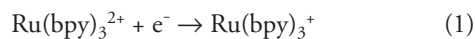
Ru(bpy)₃Cl₂ is a heavy metal complex and its toxicity and carcinogenicity are not known. Ammonium peroxydisulfate is a corrosive material. Acetonitrile is an irritant to the eyes, skin, and respiratory tract. It can also cause damage to liver, kidney, lung, and nervous systems. Therefore, goggles and gloves should always be worn when preparing solutions and performing the demonstration. Please dispose of materials in a manner consistent with local, state, and federal regulations.

Means of venting the small amounts of H₂(g) produced by the Mg reaction should be provided, and this reaction should not be carried out near an open flame.

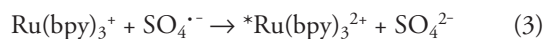
Discussion

Chemiluminescence, converting chemical energy into electronic excited states (the formation of “cold light”), has fascinated students and teachers alike for decades. In fact, light emission from various plants and animals (bioluminescence, a specific type of chemiluminescence) was recorded in many early writings (1). Far from being a mere curiosity, chemiluminescence has found use in probing the energetics and mechanisms of chemical reactions (2, 3) in a variety of analytical applications (e.g., the clinical analysis of biological molecules such as DNA or antibodies) (4) and in the “novelty industry” in the form of Cyalume lightsticks, bracelets, and necklaces.

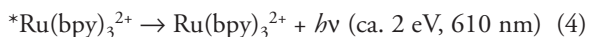
The chemical reaction that produces the chemiluminescence in this demonstration involves the reduction of Ru(bpy)₃²⁺ and S₂O₈²⁻ by Mg (5):



Production of the electronic excited-state complex occurs via an electron-transfer reaction involving the strong oxidant SO₄^{•-} (5, 6) that is produced as an intermediate in reaction 2:



where $^*\text{Ru}(\text{bpy})_3^{2+}$ is the excited state species able to emit light:



Although it is not known whether the oxidant producing the excited state is $\text{SO}_4^{\cdot-}$ or another highly energetic species, the origin of the bright orange luminescence (eq 4) is well known. The excited state formed in the chemiluminescent reaction is probably the same as that formed during photoluminescence and electrochemiluminescence (5–8). In photoluminescence, an electron is excited from metal-based $d\pi$ orbitals to ligand-based π^* orbitals (a metal-to-ligand charge transfer [MLCT] transition). The excited electron then undergoes intersystem crossing to the lowest triplet state of $^*\text{Ru}(\text{bpy})_3^{2+}$, from where emission occurs (7). Electrochemiluminescence involves the production of light near an electrode surface by the generation of species that can undergo highly energetic electron transfer reactions (5, 8). Since photoluminescent, chemiluminescent, and electrochemiluminescent spectra are nearly identical, the emission process in the present system most likely involves the MLCT state of $^*\text{Ru}(\text{bpy})_3^{2+}$. This state may be formed if the oxidizing agent (i.e., $\text{SO}_4^{\cdot-}$) removes an electron from the $d\pi$ orbital of the reduced metal complex.

The bright orange chemiluminescence characteristic of $^*\text{Ru}(\text{bpy})_3^{2+}$ may also be generated using an oxidizing agent, followed by interaction with a strong reducing agent. For example, in a chemiluminescent experiment reported in this *Journal*, PbO_2 was used to oxidize $\text{Ru}(\text{bpy})_3^{2+}$ to $\text{Ru}(\text{bpy})_3^{3+}$ followed by reduction to $^*\text{Ru}(\text{bpy})_3^{2+}$ using the powerful reducing agent tetrahydridoborate ion (BH_4^-) (9). In our work the excited state results from the reduction of $\text{Ru}(\text{bpy})_3^{2+}$, followed by interaction with a strong oxidizing agent. Although the end results are the same, the use of lead compounds (lead and lead compounds are toxic) in the $\text{Ru}(\text{bpy})_3^{2+}/\text{BH}_4^-$ system, the relatively poor stability of reagent solutions (≤ 30 min) (10), and the considerable frothing that occurs upon direct addition of the $\text{Ru}(\text{bpy})_3^{2+}$ solution to an aqueous BH_4^- solution (9, 10) make it less attractive for classroom demonstrations.

Acknowledgment

We gratefully acknowledge the financial support of Southwest Missouri State University.

Literature Cited

1. Harvey, E. N. *A History of Luminescence*; American Philosophical Society: Philadelphia, PA, 1957.
2. Faulkner, L. R.; Glass, R. S. In *Chemical and Biological Generation of Excited States*; Waldemar, A.; Giusseppe, C., Eds; Academic: New York, 1982; Chapter 6.
3. Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Plenum: New York, 1994; p 185 and references cited.
4. During, K. J. *Chromatography* **1993**, *618*, 105–131. Lanzillo, J. J. *Anal. Biochem.* **1991**, *194*, 45–53. Yang, H.; Leland, J. K.; Yost, D.; Massey, R. J. *Biotechnology* **1994**, *12*, 193. Blackburn, G. F.; Shah, H. P.; Kenten, J. H.; Leland, J.; Kamin, R. A.; Link, J.; Pterman, J.; Powell, M. J.; Shah, A.; Talley, D. B.; Tyagi, S. K.; Wilkins, E.; Wu, T.-G.; Massey, R. J. *Clin. Chem.* **1991**, *37*, 1626.
5. White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6891–6895.
6. Bolletta, F.; Rossi, A.; Balzani, V. *Inorg. Chim. Acta* **1981**, *53*, L23–L24.
7. See, for example: Meyer, T. *Acc. Chem. Res.* **1989**, *22*, 163–170. Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Plenum: New York, 1994; Chapter 5. Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic: New York, 1992; Chapter 1.
8. Tokel, N.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 2862.
9. Gafney, H. D.; Adamson, A. W. *J. Chem. Educ.* **1975**, *52*, 480–481.
10. Shakhshiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry*, Vol. 1; University of Wisconsin Press: Madison, 1983; pp 194–199.