

A Chemiluminescent Clock Reaction: A Dramatic Illustration of Competing Reaction Kinetics

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Received June 24, 2002. Accepted October 17, 2002.

Abstract: In the presence of both rubrene and perylene dissolved in hexanes, oxalyl chloride and hydrogen peroxide react to generate three different colors of light in the order yellow, then white, and finally blue. Student observers with additional TLC data can develop a simple kinetics model involving competing fluorescer decomposition and emission events.

Chemiluminescence, light generation by a chemical reaction, has diverse applications in analytical chemistry and biotechnology [1], is found in living organisms (then termed *bioluminescence*), is the basis for emergency lighting, and has great entertainment value (e.g., light sticks and jewelry). Demonstration of single and two-color fluorescence-based chemiluminescence using the reactants oxalyl chloride and hydrogen peroxide has been described [2, 3]. The reaction involves the formation of a strained dioxetanedione intermediate **I**, which splits into two electronically excited CO₂ molecules (Scheme 1). These excited CO₂ molecules transfer their energy to fluorescer molecules, which emit light visually matching their fluorescence emission spectrum.

In this demonstration, which must be done in a hood or with an overhead laboratory bench ventilator, three solutions have been previously prepared, each using 50 mL of hexanes as the solvent in 250-mL Erlenmeyer flasks equipped with magnetic stir bars: one containing perylene (3 mg), another rubrene (3 mg), and a third with both perylene (3 mg) and rubrene (3 mg). The demonstrator then shines a black-light (365 nm) on each solution showing that perylene fluoresces blue, rubrene fluoresces yellow, and the stirring solution fluoresces mostly white light with a blue tinge. At this point the demonstrator should explain that a mixture of blue and yellow light appears white to the human eye. Oxalyl chloride (0.5 mL) is then added to each of the stirring solutions. Note that oxalyl chloride by itself does not affect the fluorescence of the solutions [4]. After dimming or extinguishing the room lights, 30% hydrogen peroxide (1.0 mL) is quickly injected into each flask [5]. In the perylene and rubrene solutions, blue and yellow light, respectively, will be emitted, as previously described [2, 3]; however, in the flask containing both perylene and rubrene, bright yellow light will immediately radiate from the flask, followed about two minutes later (depending on stir rate) by white light for about one minute, then finally blue to bluish-green light. The bluish light will last for as long as an hour at room temperature. Once the clock reaction produces only blue light, a silica gel TLC is obtained (solvent: hexanes). The TLC plate is spotted with 1 mg mL⁻¹ solutions of perylene (left) and rubrene (right) and with the reaction mixture (center). The *R_f* values of perylene and rubrene in hexanes are 0.25 and 0.15, respectively, and each fluoresces differently under UV light at 365 nm (blue for perylene; yellow for

rubrene). *Neither perylene nor rubrene is present once the reaction produces only blue light.* Only a new compound (*R_f* = 0.8), exhibiting blue fluorescence, is present.

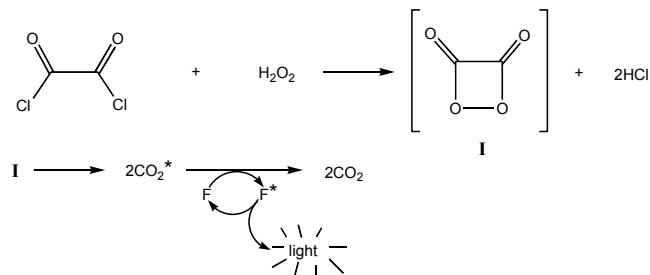
After showing this demonstration and explaining the TLC results (or in a laboratory setting, having the students perform the TLC themselves), some of the questions to be pondered by the students include:

1. Why does the yellow light appear first?
2. Why does the yellow light disappear?
3. Why is the yellow light replaced by white and then blue light?
4. Create a general model that explains what is happening in the chemiluminescent clock reaction. You should not try to specify the chemical reactions involved except to *explain what these reactions do to the fluorescer properties*. Note the following additional information:
 - a. Oxalyl chloride by itself does not affect the fluorescence of the solutions.
 - b. After the reaction produces only blue light, the TLC of the clock reaction shows **no rubrene or perylene left**, but there is a new blue-light-emitting fluorescer present.

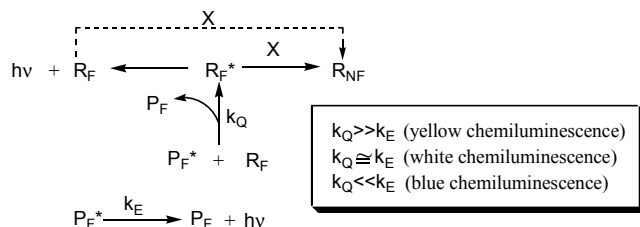
A possible explanation for the chemiluminescent clock reaction is shown in Scheme 2.

Instructors may refer to Moore and Pearson [6] for background on the chemical kinetics of competing reactions. In Scheme 2, initially rubrene (R_F) quenches excited perylene (P_F^{*}) more rapidly than perylene can emit light (*k_Q* >> *k_E*), and only yellow light is observed; however, rubrene is converted into a nonfluorescent compound (R_{NF}) by an unspecified reactant X (probably hydrogen peroxide). Perylene is also transformed, but into a different blue fluorescent compound, a perylene derivative (*R_f* = 0.8). This perylene derivative could even be a conjugate of rubrene and perylene. Excited state rubrene (R_F^{*}) and/or ground state rubrene (R_F) could be converted into R_{NF}, which could be identical to the new perylene derivative if it is a perylene-rubrene conjugate. Because of rubrene's decomposition, eventually the rate of perylene and/or perylene derivative emission will dominate rubrene's quenching event, producing an intermediate white light stage (*k_Q* ≅ *k_E*), and finally only blue light (*k_Q* << *k_E*).

Scheme 1.



Scheme 2.



This demonstration has also been successfully tested for several years as a laboratory exercise with students in second-semester organic chemistry, who found the three-color chemiluminescence intriguing and who mostly grasped the basic idea of fluorescence quenching; however, the concept that one fluorescer could "steal" energy from another fluorescer was rarely presented in a student model of this process.

Handling and Disposal

This demonstration must be performed in a hood or with an overhead laboratory bench ventilator! The demonstrator must also wear gloves. Oxalyl chloride is a lachrymator, and its vapors and liquid are corrosive to skin, eyes, and lungs. Hydrogen peroxide 30% is a strong oxidizing agent that is also corrosive to skin, eyes, and lungs. Both perylene and rubrene are suspected carcinogens. The waste mixture from this demonstration should be allowed to stop reacting in the hood, as evidenced by cessation of CO_2 bubbling, and then placed in a halogenated waste bottle and properly labeled.

References and Notes

- DeLuca, M. A.; McElroy, W. D. *Bioluminescence and Chemiluminescence*; Academic Press: New York, 1981.
- Summerlin, L. R.; Borgford, C. L.; Ealy, J. B. *Chemical Demonstrations: A Sourcebook for Teachers*; American Chemical Society: Washington, D.C., 1987; Vol. 2, p 110.
- Shakhashiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry*; The University of Wisconsin Press: Madison, WI, 1983; pp 153, 175.
- The author has tried to replace oxalyl chloride with less toxic diaryl oxalates without success. Unfortunately, commercial 3% hydrogen peroxide produces very little discernible light by eye.
- Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley & Sons: New York, 1981.