Luminol lighthouse

These notes accompany the video demonstration **Luminol lighthouse** from *Education in Chemistry* which can be viewed at: <u>https://rsc.li/3Nm4e3q</u>

I was looking for details on oscillating reactions and discovered that not only do changes in colour, sound and heat oscillate, but flashes of light can also oscillate, creating an eerie lighthouse effect. Like all chemiluminescent reactions, this reaction works best in a darkened room.

Level

This demonstration is ideally suited to lessons on catalysis and transition metal chemistry for learners aged 16–18.

Equipment

- 6 cm³ of 30% (100 vol) hydrogen peroxide and 43 cm³ deionised water (for solution A)
- 0.73 g potassium thiocyanate and 50 cm³ of water (for solution B)
- 0.015 g of copper sulfate pentahydrate salt and 100 cm³ of water (for solution C)
- 0.06 g luminol and 50 cm³ of 0.1 M sodium hydroxide (for solution D)
- 500 cm³ demonstration flask (a beaker, conical or similar)
- 3 x 100 cm³ beakers
- 2 L beaker (for a water bath)
- Kettle
- Magnetic stirrer and stirrer bar
- Thermometer

Preparation

These instructions make a 250 cm³ reaction, but it can be scaled up for a larger audience. Make up the following:

- Solution A: dilute 6 cm³ of 30% (100 vol) hydrogen peroxide to 50 cm³ water to make a 1 M hydrogen peroxide solution.
- Solution B: dissolve 0.73 g of potassium thiocyanate in 50 cm³ of water to make a 0.15 M potassium thiocyanate solution.
- Solution C: dissolve 0.015 g of copper sulfate pentahydrate salt in 100 cm³ of water to make a 6 x 10⁻⁴ M copper(II) sulfate solution.

 Solution D: dissolve 0.06 g of luminol in 50 cm³ of 0.1 M sodium hydroxide to make a 7 x 10⁻³ M alkaline luminol solution.

Before the demonstration, boil a kettle of water. Transfer solutions B, C and D into 100 cm³ beakers. Add hot water from the kettle to a larger beaker (I used a 2 L beaker). Place the beakers of B, C and D into the water bath to heat to 50-60°C, taking care not to float them.

Place solution A into the demonstration flask with the stirrer bar. Darken the room.

Safety and disposal notes

- Wear eye protection.
- Hydrogen peroxide can cause serious eye damage. CLEAPSS members should see RB045 (bit.ly/46MzwYE) before diluting 100 vol (30%) hydrogen peroxide.
- Copper (II) sulfate is harmful if swallowed and can cause serious eye damage. Avoid contact with skin.
- Avoid raising dust when measuring out powders.
- Potassium thiocyanate is harmful. Only heat the solution with a water bath and avoid boiling dry.
- Luminol is an irritant (affects the skin and eyes and possibly the respiratory tract).
- Dilute all solutions with plenty of water and dispose in a foul-water drain.

In front of the class

When solutions B–D are between 50–60°C, remove them and adjust the temperature of the water bath to 40–50°C. Ensure the water level is low enough not to float the demonstration flask.

Add solutions B and C to the demonstration flask, then place it into the water bath and stir. To initiate the reaction, add solution D.

There will be an initial flash of blue light, then a faint afterglow associated with a separate reaction of luminol with superoxide ions in solution. Flashes will repeat. At \sim 40°C, the reaction lasts 10–15 minutes with steadily increasing periods ranging from approx 30 seconds initially to 70 seconds after 12 minutes.

Teaching goal

This reaction is a great discussion starter, where students will find the predictable intervals of light captivating, like a slow-motion firefly. All oscillating reactions rely on competing autocatalytic steps broadly fitting the Brusselator model (bit.ly/3usCu6O). This model comprises four reactions with two central competing reactions that share

a reactant and give rise to the oscillations. The overall reaction continually switches between these two central competing reactions.

Although a dark room is best, typically the audience will see the initial burst of light in a classroom setting. Thereafter the solution turns yellow, which fades moments before the next flash of light. The yellow is attributed to copper(I) complexes and suggests that the copper sulfate has catalysed the decomposition of hydrogen peroxide, but before the copper(I) can be re-oxidised by dissolved oxygen or hydrogen peroxide, it is trapped by strong complexation from thiocyanate ions in the mixture. Copper(II) is needed to catalyse the separate luminol reaction (see Lighting up copper, rsc.li/47HEkiq) in its own oxidation by hydrogen peroxide, so as long as the yellow colour is visible, the blue glow will not be.

Meanwhile, hydrogen peroxide and thiocyanate ions undergo a series of reactions to generate OS(O)CN•, which re-oxidises the Cu(I)[SCN]n complexes briefly before the copper(II) is reduced and trapped again.

A range of products are produced including oxygen from the decomposition of the peroxide, sulfate(VI) ions, hydrogen carbonate ions and, crucially, ammonium ions. Therefore, potassium thiocyanate and sodium hydroxide should not be substituted for ammonium compounds that can inhibit the oscillator.