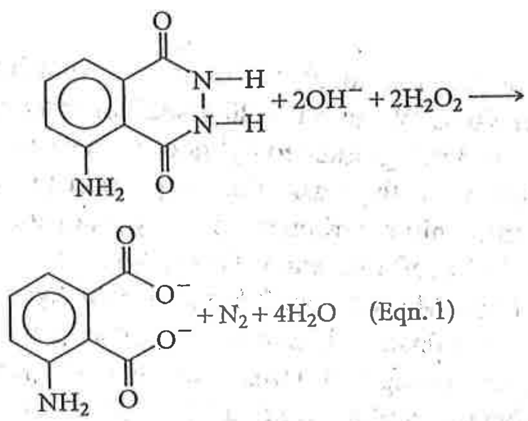
Experiment 9

Chemiluminescence: Glow Stick in a Beaker

Introduction

A glow stick, also called a light stick, is generally composed of a transparent plastic case that holds chemicals in two compartments. One compartment is a separate glass or plastic tube that is sufficiently brittle to be broken when the outer plastic case is bent, releasing the components into the larger compartment. The mixing of the chemicals from the two compartments results in a chemiluminescence reaction. Generally the reactions use hydrogen peroxide as an oxidant; luminol (Equation 1), oxalates (Equation 2), or oxalyl chloride as reductants (Equation 3); and possibly a sensitizer, a molecule that can absorb energy from a chemical reaction and then releases the energy as photons.



(Eqn. 1)

$$R{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OR + H_2O_2 \longrightarrow + 2ROH + 2CO_2$$
(Eqn. 2)

$$Cl{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}Cl + H_2O_2 \longrightarrow 2HCl + 2CO_2$$
(Eqn. 3)

A chemiluminescence reaction is a chemical reaction that produces a molecule in an excited electronic state and releases the excitation energy as a photon of light, rather than heat, to reach its ground electronic state. Chemiluminescence reactions are rather uncommon as they have several requirements. For example, this type of reaction must generate an atom, ion, or molecule capable of being excited electronically at a reasonable rate and produce a sufficient amount of energy to generate this species in an electronically excited state. Also the excited species must be capable of returning to its ground state by releasing a photon. Additionally, this process must be able to compete with other processes by which the excited molecule could relax, most notably loss of the excess energy as heat or by transfer of the energy to another molecule, exciting it electronically. The latter process is called quenching. If the quenching molecule, the quencher, in turn releases the transferred energy as a photon, then it is a sensitizer; such luminescence is called sensitized luminescence.

In this experiment, you will be performing one or two chemiluminescence reactions and observing the effects of sensitizers on the reaction.

SAFETY NOTES: Safety goggles are required for all experiments.

Fluorescent molecules are often carcinogenic; dichloromethane is a potential carcinogen. Wearing gloves is recommended when handling these chemicals. Similarly, wearing gloves is a good precaution when handling hydrogen peroxide solutions.

Halogenated hydrocarbons, such as dichloromethane, and their solutions need to be placed in appropriate waste containers, separate from aqueous waste and non-halogenated organic waste.

Experimental Procedures

Part A: Aqueous Version

The experiment may be performed individually or in groups; your instructor will provide details. Obtain a 500 mL Erlenmeyer flask. Weigh out 1.20 g sodium carbonate; add it to the flask along with 250 mL of water. Use a 100 mL graduated cylinder to measure the water. Swirl to dissolve. Weigh out and add the following to the flask: 0.06 g luminol (3-aminophthalhydrazine), 7.2 g sodium bicarbonate, 0.15 g ammonium carbonate monohydrate, and 0.12 g copper sulfate monohydrate. Swirl to dissolve and add 250 mL water. This is solution A.

Obtain a second 500 mL flask. Measure out 2.5 mL of 30% hydrogen peroxide using a 10 mL graduated cylinder and add to the flask. Add 298 mL of water. This is solution B.

Obtain three 200 mL beakers. Using a 100 mL graduated cylinder, add 75 mL of solution A to each beaker. To the second beaker, add approximately 1 mL of fluorescein solution. To the third beaker, add approximately 1/4 mL of the rhodamine B solution. (If you are using a dropping bottle, add about 1/4 a dropper full of the dye solutions).

The addition of solution B will initiate the chemiluminescence reaction. The reaction is best observed if the lights are turned down. (Your instructor will determine how low the lights can safely be turned down. Your instructor may ask everyone to wait to add solution B until the entire class is ready.) Using a 100 mL graduated cylinder, measure out 75 mL of solution B. Add to the first beaker; stir with a glass stirring rod. Record your observations including color and intensity. Similarly, add 75 mL of solution B to the second beaker and stir; record the results. Finally, add 75 mL of solution B to the third beaker and stir; record the results. Dispose of the solutions in the appropriate waste containers.

Part B: Non-Aqueous Version

Obtain a 10 mL and 25 mL graduated cylinder and a 20 mL and two 100 mL beakers. Measure out 1.5 mL of 30% hydrogen peroxide and place in the 20 mL beaker. Also add 13.5 mL of water to the beaker. Add 7.5 mL of the diluted hydrogen peroxide solution that you just made to each of two 100 mL beakers. Add 20 mL of dichloromethane to each beaker. Add 0.005 g of 9,10-bis(phenylethynyl)anthracene to one beaker; label the beaker C. Add 0.005 g of 9,10-diphenylanthracene to the other beaker; label the beaker D. Cover with plastic wrap or parafilm and place the mixture in a hood until ready to add the oxalyl solution. (As water and dichloromethane are immiscible, two layers should be present.)

In the hood, uncover beakers C and D; subsequent steps should all be performed in a hood. Using a 100 mL graduated cylinder, obtain 100 mL of oxalyl solution in dichloromethane from the instructor. Add 50 mL of the solution to beaker C; immediately stir rapidly with a glass stirring rod. Record the results. Add 50 mL of the solution to beaker D; immediately stir rapidly with a glass stirring rod. Record the results.

Literature Cited

1. Shakhashiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry*; The University of Wisconsin Press: Madison, WI, 1983; Vol. 1; pp. 125–204.

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Pre-Laboratory Questions

1. Search the Internet to find the structure of fluorescein and rhodamine B. Draw the structures below. Do they have any similarities? What is the role of these molecules in the experiment?

2. Find the MSDS's on the Internet for 30% hydrogen peroxide, dichloromethane, and oxalyl chloride. What hazards do they represent?

3. What parts of the experiment require the use of a hood?

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Report Sheet

Part A

Record your observations. (Note the appearance of any bubbles, formation of any precipitants, any color changes, etc.)

Part B

Record your observations.

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Questions

1. A particular sensitizer can absorb photons of one wavelength and release photons of a longer wavelength. Why must the radiation be at a longer wavelength? (Hint: it may be helpful to think in terms of frequency.) Are your results in part A consistent with this? Explain.

2. When a glow stick is placed in a freezer, its chemiluminescence lasts a significant time longer. How might this come about?