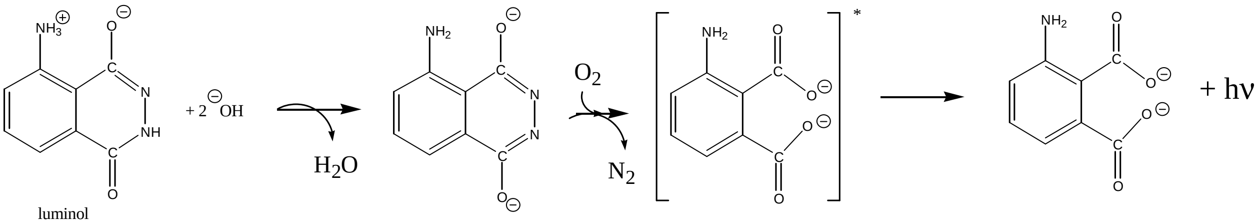
Want to light up your life? Try chemiluminescent esters!! During the previous laboratory session we performed the Fischer esterification method of producing an ester from a carboxylic acid and an alcohol. This week we will synthesize esters from and acid chloride and alcohol. Bruice section 17.8 describes the mechanism.

Chemiluminescence is the production of light through a chemical reaction which ends up producing very little heat.

The television show CSI: Crime Scene Investigation is a good example of how chemiluminescence is used in real world situations. The CSIs use luminol (5-amino-2,3-dihydro-1,4-phthalazinedione/ $C_8H_7N_3O_2$) which is a yellowish solid and is soluble in water and most polar solvents. Luminol is used to detect trace amounts of blood. To create this luminol solution, it is first mixed with a solution of hydrogen peroxide (the oxidant) and a hydroxide salt (the activator). When the luminol solution is introduced to iron, which is found in the hemoglobin of blood, it reacts and becomes unstable. As the "excited" electrons relax, excess energy is released as photons of blue light. The blue glow lasts for about 30 seconds and can be photographed.[1]

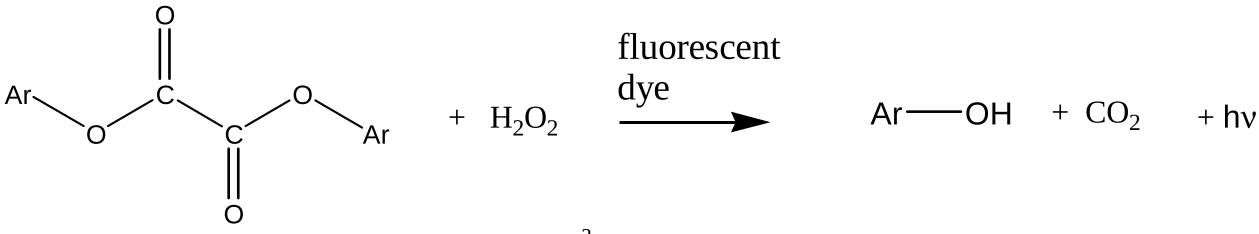


Another popular way to see chemiluminescence in action is through the use of glowsticks. In order to activate the "glowing" action of the glowstick, a person has to bend the stick. Inside the stick is a casing which keeps two solutions from mixing. When this casing is broken, the chemicals are able to mix and start the chemical reaction. In the specific reaction of this experiment, esters become oxidized by hydrogen peroxide in the presence of a suitable fluorescent dye acceptor molecule such as 9,10-diphenylanthracene. The energy from the decay of an unstable intermediate catapults an electron in the fluorescent dye to an excited state. The light is then emitted when the fluorescent dye finds its way back to a relaxed state.[2] The wavelength of light emitted depends on the structure and electronic configuration of the fluorescent dye.

> *"The one sitting on the throne was as brilliant as gemstones – jasper and carnelian. And the glow of an emerald circled his throne like a rainbow." Revelation 4:3, Holy Bible*

[1] http://en.wikipedia.org/wiki/Luminol
[2] Experiment 48: Luminol, in Pavia, Lampman and Kriz, "Introduction to Organic Laboratory Techniques: A Contemporary Approach" (1976) Saunders

The chemiluminescence produced by oxidation of bis(aryl) oxalates, the compounds that will be synthesized in this experiment, in the presence of fluorescent dyes is more impressive than that produced from luminol. Bis(aryl) oxalate chemiluminescence is the chemical reaction in "light sticks" used for a variety of purposes. Since the 1980s this reaction has become widely used in scientific investigations as an analytical tool for trace analysis. It is currently a sensitive and versatile chemiluminescence detection method for research purposes. The overall reaction (not balanced) may be represented by



where Ar- is an electronegative aryl group.[3] The bis(aryl) oxalates we will synthesize are; bis(4-nitrophenyl)oxalate (NPO), bis(2,4-dinitrophenyl)oxalate (DNPO), and bis(2,4,6-trichlorophenyl)oxalate (TCPO).

There are several parameters that can be varied in this experiment.

The nature of the phenol used to synthesize the bis(aryl) oxalate may be important to the overall results. Evidently, phenols with electron withdrawing substituents behave well. By reacting the oxalyl chloride with a mixture of two phenols mixed bis(aryl) oxalates may be synthesized.

The choice of fluorescent dye (fluorophor) has the effect of changing the wavelength, duration, and intensity of the light emitted. The Wikipedia “Glow Stick” page lists no less than 18 different fluorophors that can be used. The fluorophors need only be present in small amount because they are effectively recycled during the glowing process. The fluorophors have the role of adjusting the wavelength of the light emitted by the decaying bis(aryl) oxalate to the desired value.

The concentration of hydrogen peroxide also may have an effect on wavelength, duration, and intensity of the light emitted.

Various solvents have been employed for the reaction and subsequent chemiluminescence. The choice of solvent may also influence the outcome of the chemiluminescence.

This experiment was adapted for use at Dominican Univeristy by Ashley, Becki, Karl, and Megan during Spring 2008.

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[3] **Experiment 26** DNPO - a Chemiluminescent Rainbow (Chemiluminescence of oxalate esters) http://www.chem.leeds.ac.uk/delights/texts/VV_exp_26.htm

Procedure[4]:

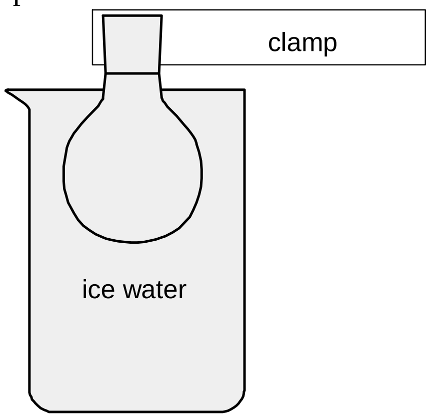
Note: All Glassware Must be Dry Before use!

Part I: Making the Ester

1. You will be assigned one of the three phenols listed here:

Assignments	phenol
1R, 4R, 7R, 2R, 5R, 8R	4-nitrophenol
3R, 6R, 9, 1L, 4L, 7L	2,4-dinitrophenol
2L, 5L, 8L, 3L, 6L, 10	2,4,6-trichlorophenol

2. Measure out 1.0 x 10^{-2} moles of your phenol into a clean, dry 100mL round-bottom flask.
3. Add a stirring bar.
4. Add 16mL of acetone to your round-bottom.
5. Add 1.4mL of triethylamine to the flask using a graduated pipette.
6. Place the mixture in an ice bath and obtain 0.4mL of oxalyl chloride in a 1 mL syringe.
7. Using the syringe, add the 0.4mL dropwise to the mixture in the ice bath. Stir vigorously for a while after each drop is added. Wait for the vapor to clear before adding the next drop.



8. Remove from the ice bath and stir for 30 minutes at room temperature.
9. The color of the solution should be either white or pale yellow. If the color of the solution becomes dark, add one or more drops of oxalyl chloride until the color of the reaction mixture turns pale yellow.
10. When the reaction is complete, recover the solid with a Buchner funnel. Wash the solid with a few mL of water to wash off the excess triethylamine. Dry completely.
11. Record the mass of your bis(aryl) oxalate.
12. Set aside a portion of your solid in a 20 mL vial for UV-vis and GC analysis.

Part II: Testing the Ester

1. Add the remainder of your product to a dry 100 – 150 mL beaker.
2. Add 10mL of 0.002M solution (ethyl acetate/dichloromethane 1:1 is used as a solvent) of a fluorescent dye: 9,10-diphenylanthracene, rhodamine 6G, or anthracene.
3. Mix well.
4. Go to a dark place.
5. Add 10mL of 3% hydrogen peroxide/acetonitrile solution.
6. Mix and record any observations.
7. Report your data so that a table of class data can be compiled. This table will be available on MyDU and should be in your lab report.

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[4] This procedure is an adaptation of the procedure found in Duarte, Robert, Janne T. Nielsen, and Veljko Dragojlovic. "Synthesis of Chemiluminescent Esters: a Combinatorial Synthesis Experiment for Organic Chemistry Students." Journal of Chemical Education 81 (2004): 1010-1015.

Disposal: All liquids should be disposed of in the liquid disposal container under the fume hood in the front of the classroom. All solid waste should be placed in the solid disposal container under the same fume hood. The solid waste also includes any gloves, weight boats, and paper towels.

Safety Concerns: Acetone, ethyl acetate, and acetonitrile are highly flammable. They should be used under the fume hoods. Phenols can cause skin burns. Gloves and safety goggles should be worn at all times. Students should not touch anything around the laboratory with their gloves on because of the risk of spreading chemicals and harming others. Make sure to keep gloves dry because the chemicals from the phenols leak through and turn hands yellow. Avoid contact with the phenols as much as possible. Also, some of the phenols have extremely strong scents and should therefore be weighed under the fume hood. Caution should also be taken when cleaning out glassware. Gloves should remain on until the completion of the experiment and clean-up.

Pre-Lab

Title

Purpose

Physical constants.

Name	Formula	M.W g/mole	m.p. ^oC	b.p. ^oC	Density g/mL
4-nitrophenol	$C_6H_5NO_3$	139.11	110 -115°C	279°C	
2,4-dinitrophenol	$C_6H_4N_2O_5$	184.11	112°C		
2,4,6-trichlorophenol	$C_6H_3Cl_3O$	197.45	69°C	246°C	
triethylamine	$C_6H_{15}N$	101.2	-115°C	89°C	0.726
oxalyl chloride	$C_2O_2Cl_2$	126.93	−16 °C	63–64 °C	1.4785
hydrogen peroxide	H_2O_2	34.0147	-11 °C	150.2 °C	1.4
acetone	C_3H_6O	58.09	−94.9 °C	56.53 °C	0.79
9,10-diphenylanthracene	$C_{26}H_{18}$	330.42	248-250 °C		
rhodamine 6G	$C_{28}H_{31}N_2O_3Cl$	479.01			
anthracene	$C_{14}H_{10}$	178.23	218	340	
acetonitrile	C_2H_3N	41.05	- 45	82	0.786
ethyl acetate	$C_4H_8O_2$	88.105	-83.6	77.1	0.897
dichloromethane	CH_2Cl_2	84.93	-96.7	39.6	1.33

Safety data.

Name	Solubility	Safety Information
4-nitrodiphenol 2,4-dinitrophenol 2,4,6-trichlorophenol	Poor solubility in water. Soluble in alcohol and non-polar solvents	Combustible. Gives off irritating or toxic fumes (or gases) in a fire. May cause eye redness. Avoid all contact.
triethylamine	Soluble in water and alcohol. Some soluble in non-polar solvents	Highly flammable. Gives off irritating or toxic fumes (or gases) in a fire. Irritating to eyes, skin, and respiratory system.
oxalyl chloride	decomposes in water	May be fatal if inhaled, or absorbed through skin. Causes severe burns. Extremely destructive of mucous membranes.
hydrogen peroxide	miscible in water and alcohols. Immiscible with non-polar solvents	Corrosive, cause irritation to the eyes, mucous membranes and skin. May also bleach clothing.

9,10-diphenylanthracene rhodamine 6G anthracene	insoluble in cold water some soluble in alcohol soluble in non-polar solvents	Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.
acetone acetonitrile	miscible in water, alcohol, some miscible with hydrocarbon solvents	Inhalation may lead to hepatotoxic effects (causing liver damage) Flammable
ethyl acetate	immiscible in water, miscible with alcohol, and hydrocarbon solvents	Inhalation may lead to hepatotoxic effects (causing liver damage) Flammable
dichloromethane	immiscible in water, miscible with alcohol, and hydrocarbon solvents	Inhalation may lead to hepatotoxic effects (causing liver damage)

1. http://www.inchem.org/
2. Wikipedia.org
3. https://fscimage.fishersci.com/msds/08812.htm

Structures and equations.(4 points)
__ Draw the structural formulas for the reaction between oxalyl chloride and your phenol. Balance the reaction.

__ Draw the chemical structure of 9,10-diphenylanthracene. Cite your source, please.

__ Calculate the number of grams of the phenol you will be using.

__ Calculate the number of moles of oxalyl chloride that you will be using.

__ Calculate the theoretical yield of your bis(aryl) oxalate.

__ *Flowchart*. (1 point) Refer to "Procedure"

__ *Safety Question*: (1 point) Glowsticks containing chemiluminescent chemicals are often used by children and teens at events like parades, sporting events and parties. Many times kids will put glowsticks in their mouths and think it is okay because manufacturers label them as "Non-toxic." Are they truly *non-toxic*? What should be done if someone were to swallow a small glowstick? Cite any sources used please.

Experimental Observations and Data: (4 points)

Lab Report:
Results.

__ (1 point) calculate your percent yield. Show your calculations please.

__ (1 point) Summarize your chemiluminescence results. Compare your results with the results of your classmates. There are three bis(aryl) oxalates and three flourophores. This makes 9 different combinations. Which combination(s) gave the best results?

__ (1 point) Interpret the GC-FID chromatogram in terms of identity and purity

Discussion and Conclusion.

__ (1 point) What is the purpose of the triethylamine?

__ (2 points) Define and differentiate between a) luminescence, b) chemiluminescence, c) fluorescence, and d) phosphorescence. Reference any sources you use.

___ (2 points) Search an ACS journal such as the Journal of Organic Chemistry for articles with "chemiluminescent" or "chemiluminescence" in their title. Reference on of these articles and describe what you learned from reading the abstract and introduction.

Green Question:

__ (2 points) Compare and contrast the Fischer Esterification and the acyl chloride methods of synthesizing esters. Which method may be more environmentally friendly? Why?

"The glow of one warm thought is to me worth more than money."

~ Thomas Jefferson quotes (America's 3rd US President (1801-09)