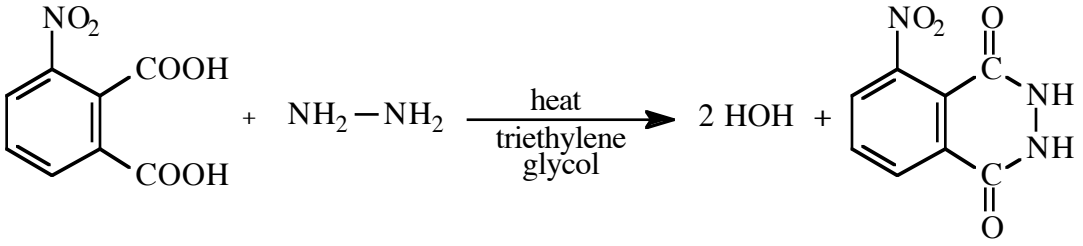
Luminol Synthesis

Source: AEM Handout adapted from K. L. Williamson *Macroscale and Microscale Organic Experiments*. 2nd ed. Lexington, MA: D. C. Heath, 1994. p 647-654.

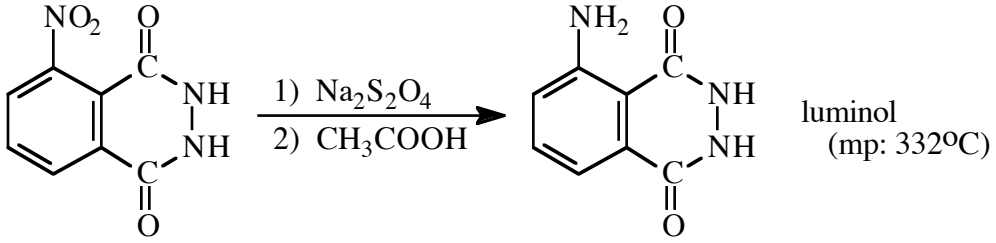
Luminol is a substance that is chemiluminescent. Chemiluminescence is defined as the release of visible light (instead of heat) as the energy by-product of a chemical reaction. Over the next two lab periods, we will synthesize luminol using standard organic reactions and then let it react with reagents that will result in the release of light.

Synthesis Overall Reactions:

Step 1:



Step 2:



Experimental:

Reaction Procedure and Work-Up: Step 1.

First heat a flask containing at least 15 mL of water on your hot plate; you will need this at the end of Step 1.

Next, combine ~0.8 g of 3-nitrophthalic acid (know exact amount!) and ~3 mL (know exact amount!) of an 8% aqueous solution of hydrazine (a very nasty material -- be careful and wear gloves!) in a very large (~20 x 150 mm) test tube. Next, add 3 mL of triethylene glycol, and clamp the tube in a vertical position in a hot sand bath IN THE HOOD. Insert a thermometer (clamp it with the bulb of the thermometer all the way into the liquid, but not touching the glass) and a boiling chip, and boil the solution vigorously to distill the excess water. The temperature should hover at about 110 to 130°C for awhile. Eventually the temperature will rise rapidly (over ~3 min) until it reaches 215°C. (During this heating, the mixture may turn dark gold or even black; the color of the mixture at this point does not matter!) Note the time that the temperature reaches 215°C, and by adjusting the amount of sand around the base of the test tube, maintain a temperature of 215 to 220°C for 2 full min. Lower the sand bath from the tube, so the reaction mixture can cool slowly to below 100°C (crystals of the nitro product often appear).

When the mixture temperature is below 100°C, remove the thermometer, add the 15 mL of hot water, and mix thoroughly. Let this mixture continue to cool slowly to RT, and then cool it further in an ice bath. Separate the solid granular nitro compound (which ranges from light yellow to gold in color) from the liquid reaction mixture. (See “Cleaning Up” discussion below for processing the liquid!)

Reaction Procedure and Work-Up: Step 2.

Immediately put the slightly moist nitro compound back into the uncleaned large test tube in which it was prepared. Add ~2.5 g (know exact amount!) of fresh sodium hydrosulfite. Now add 5 mL of 3 M sodium hydroxide solution, which you can use to wash the solids down the sides of the tube if you need to. Stir with a glass rod. You may further wash the solid down the walls with water (no more than 5 mL!).

Heat to the boiling point, stir, and keep the mixture hot for 5 min, during which time some of the reduction product may separate. Lower the sand bath from the tube. Carefully add 2 mL of glacial acetic acid to the mixture, and allow it to cool slowly to RT. Cool further in an ice bath and collect the resulting precipitate of light yellow to gold colored luminol using suction filtration. The filtrate (also called the mother liquor) usually deposits a second "crop" of luminol on standing overnight, if you would like to collect it.

Purification and Characterization. We will not recrystallize this crude luminol, but you will characterize it in two ways: measure its mp (note that this will be a "crude" mp!) and carry out its chemiluminescence reaction. You should also calculate the theoretical and percent yield for the synthesis.

Cleaning Up: Combine the filtrates from the first and second reactions, and do the following steps:

* dilute with an equal volume of water,
* neutralize with sodium carbonate (i.e. add aqueous Na_2CO_3 until the mixture does not bubble!)
* add 40 mL of household bleach (5.25% sodium hypochlorite solution), and
* combine with other students' treated materials in the very large Erlenmeyer flask in the designated hood.

We will heat the mixture to 50°C for a minimum of 1 h. This process will oxidize any unreacted hydrazine and hydrosulfite, allowing us to convert hazardous waste into non-toxic, non-hazardous waste which can be flushed down the drain.

Chemiluminescence of Luminol

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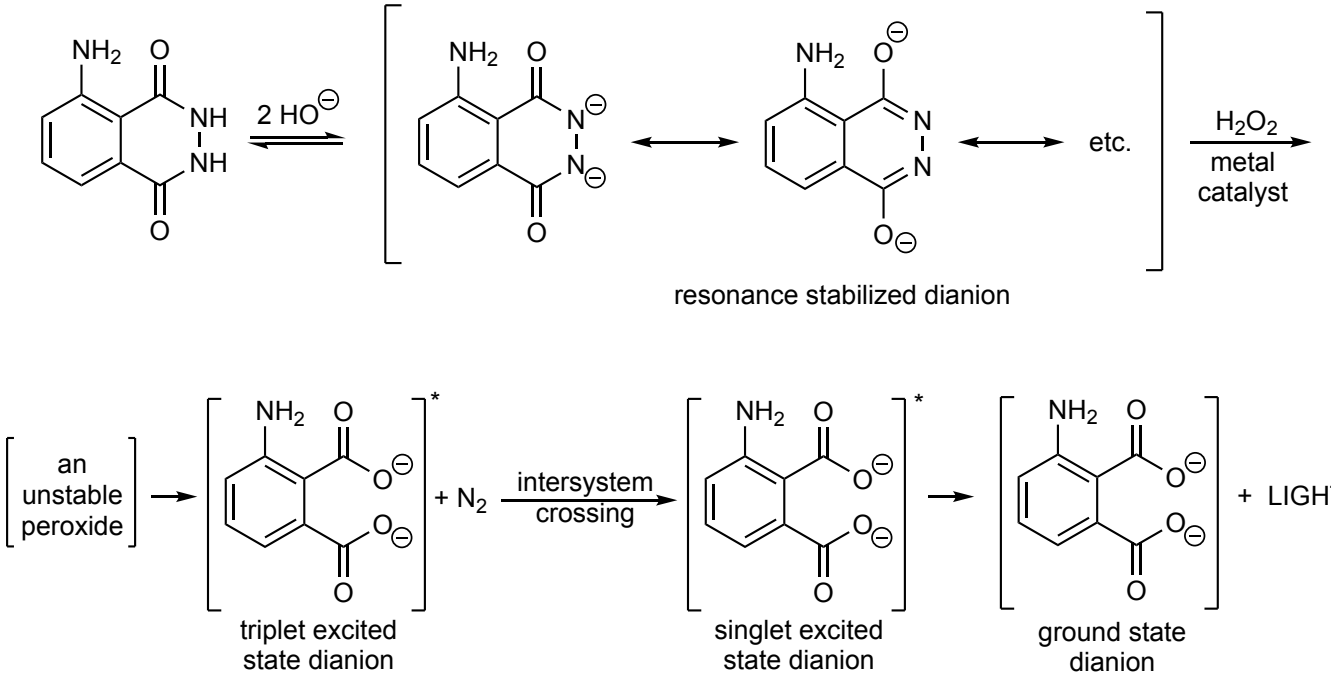
Remember to calculate the theoretical and % yield of the luminol synthesis that you have previously performed!

Note that you will use only a small portion of your product to do the chemiluminescence procedure below; the rest of your sample will be turned for a grade and for use in Science Demonstrations in the coming year. (Thanks!)

Chemiluminescence Reaction:



Experimental

You will make two stock solutions and combine them for the "light show".

Stock Solution A in a 125 ml Erlenmeyer flask:

combine 0.5 g sodium carbonate
+ 0.05 g luminol
+ ~60 ml H_2O.

Stir to dissolve (as much as possible), then add
3.0 g sodium bicarbonate
+ 0.05 g ammonium carbonate
+ 0.035 g copper (II) sulfate.

Stir to dissolve (as much as possible), then dilute to 125 ml.

Stock solution B in a large beaker that will hold at least 250 mL:

Mix 7 ml 3% hydrogen peroxide with enough water to make a 125 ml solution.

When everyone has prepared their stock solutions, we will turn out the lights to see the chemiluminescence. Pour Stock Solution A into Stock Solution B (make sure beaker holds at least 250 mL!) to see the glow.

Cleaning Up. Since all the reagents in this part of the experiment are water soluble and in very small quantities, this reaction mixture can be flushed down the drain with plenty of water. Any unused solid $Cu(SO_4)_2$ should be put into solid hazardous waste.