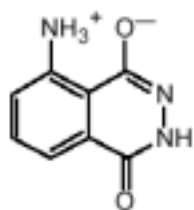
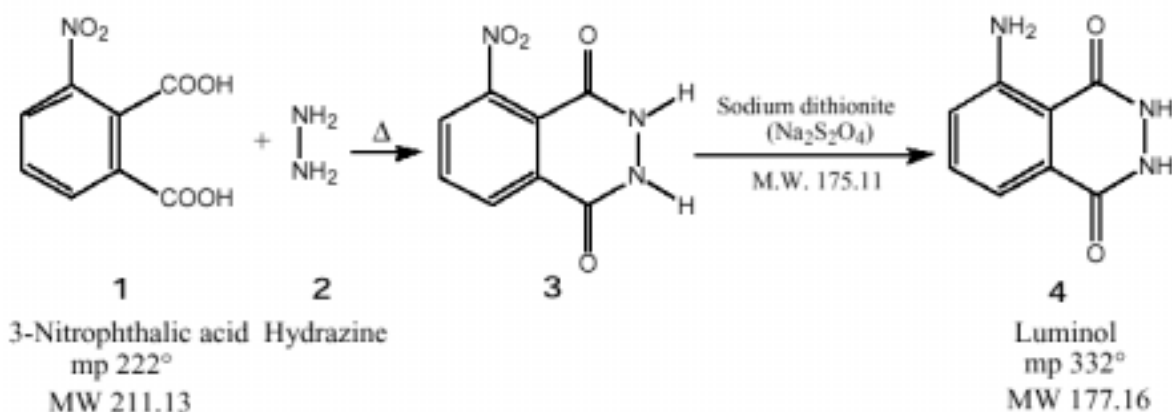


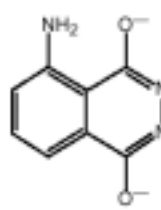
The Synthesis Of Luminol And A Test Of It's Chemiluminescent Properties.

Luminol is an interesting molecule because, when oxidized, it releases energy in the form of light. Fans of the CSI television series will recognize it as part of a forensic test for blood.¹

The first step in the preparation of luminol involves the reaction of 3-nitrophthalic acid, **1**, with hydrazine, **2**. This reaction is most conveniently carried out in the high-boiling solvent triethylene glycol, which is added to an aqueous solution of the hydrazine salt. The excess water is then boiled off, and the temperature is raised to the point where the dehydration has gone to completion within a few minutes. The nitro- group of the resulting compound, nitrophthalhydrazide, **3**, is then reduced to an amine group using sodium dithionite to form luminol, **4**. Compound **3** is soluble in alkali due to enolization, thus the reduction is carried out in basic solution.²



In neutral solution, luminol is zwitterionic.

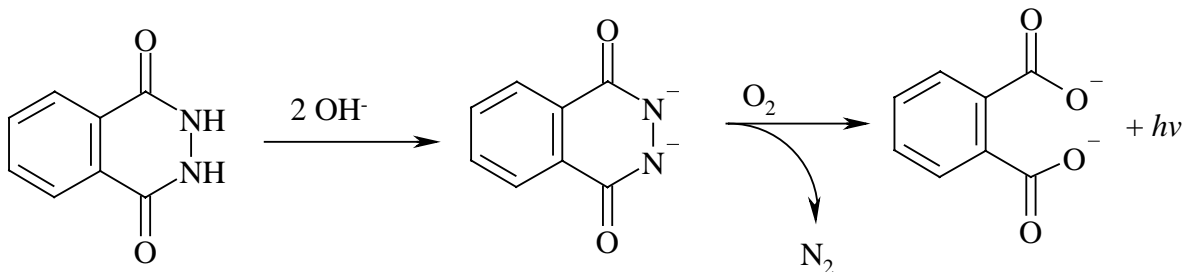


When dissolved in a basic solution, luminol becomes dianionic.

The dianion can be oxidized to form a peroxide of unknown structure. This peroxide decomposes, releasing nitrogen gas and producing the 3-aminophthalate ion which exists in an excited state. As this molecule relaxes to the lower energy (ground) state, a photon of visible light is emitted resulting in the observed chemiluminescence.

¹ http://dsc.discovery.com/fansites/onthecase/toolbox/tool_01.html;
http://www.deakin.edu.au/forensic/Chemical%20Detective/Luminol_test.htm
<http://www.clubs.psu.edu/sciencelions/demos/LuminolDemo.doc>

² <http://chemserv.bc.edu/ugrad/lab/org/orgexp.html>



Procedure for the synthesis of luminol:³

1. Heat a flask containing 15 mL of water in a boiling water bath. (Used in step 6.)
2. Heat a mixture of 1g of 3-nitrophthalic acid and 2 mL of an 8% aqueous solution of hydrazine (caution) in a 20x150-mm test tube over a sand bath until the solid is dissolved.
3. Add 3 mL of triethylene glycol and clamp the tube in a vertical position in a hot sand bath.
4. Add a boiling chip, and an aspirator tube connected to an aspirator. Boil the solution vigorously to distill the excess water (110-130 °). Let the temperature rise rapidly until (3-4min) it reaches 215 °. You can check the temperature of the reaction with a thermometer but make sure that the thermometer has temperature markings over 200 °C!
5. Remove heat, note the time, and by intermittent gentle heating maintain a temperature of 215-220 ° for 2 min.
6. Remove the tube, cool to about 100 °(crystals of the product often appear), add the 15 ml of hot water, cool under the tap, and collect the light yellow granular nitro compound (**3**).
7. Return the nitro compound at once to the uncleaned test tube in which it was prepared. Add 5 mL of 3 M NaOH solution, stir with a rod, and to the resulting deep brown-red solution add 3g of fresh sodium hydrosulfite dihydrate. Wash the solid down the walls with a little water.
8. Heat to the boiling point, stir, and keep the mixture hot for 5 min, during which time some of the reduction product may separate.
9. Add 2 mL of acetic acid, cool under the tap, and stir. Collect the resulting precipitate of light-yellow luminol. On standing, the filtrate usually deposits a further crop of luminol. *Make sure to record your and yield.*

Procedure for the luminescent reaction with O₂:

1. Cover the bottom of a 125 ml Erlenmeyer flask with KOH pellets.
2. Add enough DMSO to cover the pellets.
3. Add a "tip of a spatula" amount of the luminol to the flask. Add some O₂ to the flask.
4. Stopper well and shake vigorously until a blue glow appears. *Make sure to record your observations.*

Post Lab Questions:

1. The aspiration in step 4 is obviously used to help remove something, in this case water. Write a mechanism for the reaction of **3** going to **4** being sure to show where the water is coming from.
2. Find a mechanism in your book similar to this mechanism and provide me with just the section and the page the mechanism is described on.

³ <http://cas.bellarmine.edu/chem117a/lab/luminol.htm>