

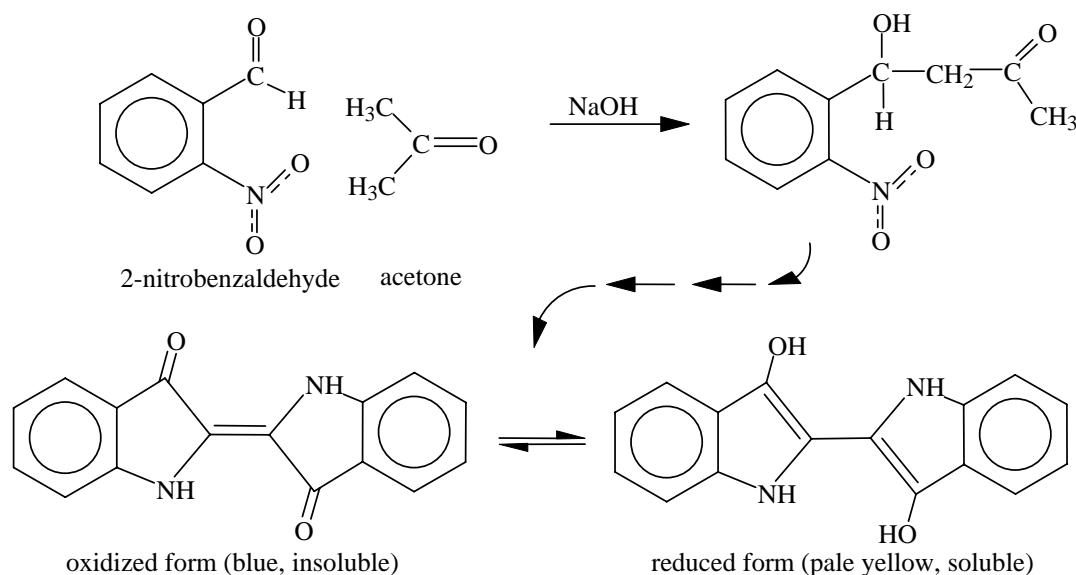
CHEM 321

Synthesis of Indigo and “Vat Dyeing”

Adapted from James R. McKee and Murray Zanger, *Journal of Chemical Education* **68**, A242-244 (1991)

Indigo is a dark blue/purple dye that has been known since antiquity. Egyptian mummies have been found wrapped in cloth dyed with indigo. The natural source is a leguminous plant which is ground up to produce a juice which contains a colorless, water soluble precursor of the dye. If the juice is fermented, a colorless liquid is recovered. If this liquid is allowed to stand in contact with air, perhaps after soaking some fabric with it, a chemical reaction (oxidation) takes place, and a dark blue pigment (indigo) precipitates.

Several methods are now known to produce indigo from commercially available chemicals. This protocol combines 2-nitrobenzaldehyde with acetone in the presence of sodium hydroxide to make the dye. The chemistry is complex, involving at least 5 steps that occur spontaneously. Some of these steps will be discussed in the second semester of this course. Don't try to understand the chemistry at this time. The reaction sequence that is thought to occur is shown below using compact representations of molecules.



Indigo can be chemically reduced under alkaline conditions. When this is done, it becomes pale yellow and soluble in water. In this form it is called "leucoindigo". If the surrounding environment later becomes oxidizing again, the dye re-oxidizes, turning blue and becoming insoluble. If oxidation happens while the soluble form is inside the fibers of a fabric, the dye becomes permanently trapped in the fabric. This permits one to “vat dye” fabrics: the dye is used in its soluble reduced form to soak the fabric. The cloth is then air-dried, which oxidizes the dye. It quickly turns blue, and the color stays pretty well through multiple washings because the dye has precipitated inside the fibers.

The objectives of this experiment are to learn how to measure and mix reactive chemicals, isolate a solid using the technique of vacuum filtration, and dye a piece of fabric. (Cloth dyed in this experiment will "bleed", so do not wash it with good clothes...)

Pre-lab Your Table of Properties should have entries for acetone, 2-nitrobenzaldehyde, and ethanol. For NaOH and sodium dithionite, only list hazards.

Experimental Protocol

1. Synthesis of indigo

Put three labeled clean small test tubes in a test tube rack. To the first, add about 1 mL of 1 M NaOH; to the second, 2-2.5 mL of acetone; and to the third, about 4 mL of 95% ethanol. Obtain a clean Pasteur pipet (long glass eyedropper) and rubber bulb to fit.

Take the smallest beaker available (make sure it is clean) to a balance and tare it (this means put it on the pan and press the “tare” button to make the balance display read zero). Weigh 2-nitrobenzaldehyde (0.2 g +/- 0.02 g) into this beaker. *[The best way to weigh any solid reagent is to slightly tip the reagent bottle over your beaker while tapping it with a knuckle. If you do this correctly you will be able to control the amount of solid that flows out of the reagent bottle. Don't stick a spatula into the bottle!]* **Always replace caps on reagent bottles when finished!**

Add all the acetone to the beaker and swirl until all of the solid dissolves. Now add about 2 mL of water to the solution while swirling. Some cloudiness will form, but should disappear as it is mixed. While continuing to swirl, add the NaOH solution slowly dropwise with the Pasteur pipet (addition should take about a minute). The contents of the beaker will show almost instant blue color, and may get warm. This is when the two reagents join (“couple”) and then undergo several other reactions, including oxidation by O₂ in the air. Add the NaOH slowly enough so that the mixture does not get very warm. After all the NaOH has been added, let the mixture stand for 5 minutes. During this time, the reaction reaches completion, and the indigo dye, which is poorly soluble in water, precipitates.

While waiting, attach a vacuum hose from an aspirator to the side arm of a 125 mL vacuum flask and clamp the flask to a ring stand so that it cannot fall over. Find a filter paper circle that exactly fits the bottom of a Hirsch funnel (the funnel is white and conical; the paper should cover all the holes but not have any wrinkles). The Hirsch funnel should have a properly sized rubber stopper on its stem. Put the funnel on the flask and the paper in the funnel. When the 5 min wait is over, center the paper, turn on the aspirator as shown, push the funnel down onto the flask, and squirt a little water onto the paper. Make sure the paper is seated properly so that there are no leaks around it. This set-up is for the technique called “vacuum filtration”, which is much faster than gravity filtration. One always seats the paper using the solvent that is about to be poured through it (not always water!).

Swirl the dark sediment in the beaker and rapidly pour as much of the slurry as possible into the funnel. If there isn't enough room, wait until the level in the funnel drops, then swirl again and quickly pour the rest into the funnel. Dark liquid should come through the filter. Use a water wash bottle to rinse most of the remaining dye from the beaker into the funnel and wait until all the water has been pulled through. Then wash the solid with at least 4 mL of clean water. Finally, wash it with 4 mL of ethanol. The water and ethanol wash away most unreacted reagents that may still be present.

2. Dyeing of cloth

Put about 4 mL of 3 M NaOH plus 10 mL of water into the original reaction beaker. Put the paper with dye into it; also scrape dye from the sides of the funnel into the beaker. Swirl and heat until it begins to steam (try not to boil it, but watch out for spattering!). While keeping it hot and continuing to swirl, add solid sodium dithionite a little at a time until the mixture becomes clear and yellow and the paper has no more dark dye on it (the liquid surface and walls of the beaker above the solution will stay blue). Pour the yellow solution into about 40 mL of cool water contained in a 250 mL beaker. The solution should stay clear and yellow except for a blue skin at the surface. If there are lots of blue solids in suspension, add a little more dithionite and heat if necessary. Remove the filter paper at this time. Use this solution to paint a design on a small piece of fabric – maybe using an eyedropper (which keeps the solution away from air until it's on the fabric in the desired pattern). Avoid getting any on your skin – it is alkaline and also will

dye you blue for a long time. As the “fabric art” dries it should turn blue. After it doesn’t seem to be getting any darker, wash it with a lot of water to rinse away the NaOH and other water-soluble chemicals.

Report Follow “Guidelines for writing the Introduction section” in your lab syllabus. Present the main goals of the experiment in your own words.

Attach your fabric to your report.

Introductions often include pertinent background material whose purpose is to set the stage for the work about to be described. Look up one piece of background information related to the main topics in this protocol. Incorporate your findings into your introduction. Some suggestions:

- 1) Another protocol to make indigo [just summarize how the alternate protocol resembles and differs from current protocol]
- 2) A deeper look into how vat dyeing works
- 3) A brief history of how fabrics can be colored

Remember to cite the source in American Chemical Society (ACS) format. The direct link on our website which can help with proper citation format is:

<http://www.linfield.edu/chem/assets/files/Courses/CHEM%20321/ACSQuickRefGuide.pdf>

To cite an internet source, use the following format:

Author (if any). Title of Site. URL (accessed date), other identifying information.

The date of access is mandatory. *Example:*

Weisstein, E. W. Molecular Orbital Theory. <http://scienceworld.wolfram.com/chemistry/MolecularOrbitalTheory.html> (accessed 12/15/03), part of Eric Weisstein's World of Science. <http://scienceworld.wolfram.com/> (accessed 12/15/03).

In addition, answer the following enrichment question at the end of your report:

1. Circle and name all of the functional groups in acetone, 2-nitrobenzaldehyde**, ethanol, and both the reduced and oxidized form of the dye. **Note: In this compound’s name, there are clues to the names of the three functional groups in this molecule.