Arenediazonium Ions in Organic Synthesis: Para Red and *para*-Iodonitrobenzene

**Background**
An arenediazonium salt will be prepared from *para*-nitroaniline and used in two different reactions—with iodide ion to produce *para*-iodonitrobenzene and also with β-naphthol to produce an azo dye, Para Red. The Para Red will be used to dye fabric, its uV-visible spectrum will be determined, and its acid-base properties will be investigated.

**Synthesis of *para*-nitrobenzenediazonium chloride.** This arenediazonium salt will be prepared by the reaction of paranitroaniline with an aqueous solution of sodium nitrite and hydrochloric acid at low temperature (*Reaction 1*). The mechanism of this reaction is discussed in the amine chapter of the Klein text used for Chem 21 and Chem 22.

![Synthesis of *para*-nitrobenzenediazonium chloride](image)

**Synthesis of *para*-iodonitrobenzene.** Nitrogen gas can be displaced from arenediazonium salts by various nucleophilic reagents to produce a variety of different substituted aromatic rings. Here, addition of iodide ion (as KI) to *para*-nitrobenzenediazonium chloride will be used to prepare *para*-iodonitrobenzene (*Reaction 2*). Nitrogen gas is released during this reaction. Note that in the azo-coupling reaction used to produce Para Red, no nitrogen gas is released. The purity of the product will be assessed by measurement of the melting point (Technique 10).

![Synthesis of *para*-iodonitrobenzene](image)

**Synthesis of Para Red.** Arenediazonium salts can also react as electrophiles with strongly activated aromatic rings in electrophilic aromatic substitution reactions. The aromatic ring must be highly activated in order for the reaction to occur at the low temperatures (< 5°C) necessary to prevent decomposition of the arenediazonium salt. Here, *para*-nitrobenzenediazonium chloride will be reacted with β-naphthol to produce the azo dye Para Red (*Reaction 3*). The electrophile reacts with the ring carbon that is *ortho* to both the activating group (OH in this case) and the other ring.

![Synthesis of Para Red](image)
**Fabric Dyeing** Fabric strips containing six different types of cloth will be used for the dyeing. We note which type of cloth is dyed by the Para Red most effectively. The effectiveness of the dye is determined, at least in part, by the efficiency of the interactions between the dye and the cloth. A diagram of this type of fabric strip is shown below, after dyeing with a yellow dye. Our strips contain the same fabrics in the same order as in this example.

*Acetate* is cotton-derived fabric that has been modified to remove many OH-groups found on the surface of the threads. *Cotton* is natural cellulose found in plant material. *Nylon* is a synthetic material made of many linked amide groups, somewhat similar in structure to wool or silk. *Polyester* (Dacron) is a synthetic material made from many linked ester groups. *Acrylic* (Orlon) is another synthetic fabric made from many acryonitrile (CH$_2$=CHCN) units linked together. *Wool* and silk are natural polyamide or protein materials made from animal sources. This end of the strip is easily recognized by its thick "furry" appearance.

Para Red is an example of an azo dye and was the first azo dye used. The vivid colors of azo dyes are due to the delocalization of electrons in the aromatic rings and through the nitrogen-nitrogen double bond (the azo bond). Para Red will be synthesized in the fiber of the fabric by first dipping it in a basic solution of β-naphthol and then in the solution of the arenediazonium salt. This process is called "ingrain" dyeing and is typically used for azo dyes.

Once the fabric has been dyed the remaining portions of the β-naphthol and arenediazonium solutions will be combined to isolate the solid Para Red product.

**Visible spectrum of Para Red.** The visible spectrum of Para Red will be taken to determine whether or not the spectrum is consistent with the literature spectrum of Para red and its observed color. A compound appears colored when it absorbs light in the visible portion of the spectrum. Conversely, if no visible light is absorbed, the compound appears colorless or white. The apparent color of the compound is due to the portion of the visible spectrum that is not absorbed. A color wheel, or color circle, can be used to correlate the observed color to the wavelength absorbed: the observed color is on the opposite side of the wheel from the absorbed color (wavelength). The wavelengths given on the wheel at the right are of the absorbed light. Different azo dyes absorb light of different wavelengths due to their different structures. For example, more highly conjugated systems will absorb light with longer wavelengths (lower frequency; lower energy). Also, having electron-donating and electron-withdrawing groups para to each other on an aromatic ring increases both the wavelength of light absorbed and the intensity of the absorption (absorptivity in Beer’s law).

**Acid-Base Properties of Para Red.** This compound can act as an acid-base indicator because the structures of its acid and conjugate base forms absorb light at different wavelengths. We will explore this property by adding acid and base, in turn, to a solution of the Para Red.

**Pre-lab Reading**
• Dyes and Dyeing Essay (link)
• Techniques
  • Vacuum Filtration - Chapter 9 of Mohrig Techniques book, 4th edition
  • uV-vis Spectroscopy - Chapter 25 of Mohrig Techniques book, 4th edition; Section 16.11 in Klein, end edition
• Color - Section 16.12 in Klein; also information in Mohrig’s uV-vis Chapter

Procedure

Safety Notes
Wear gloves throughout this experiment. Sodium nitrite is an oxidizing agent and highly toxic. para-Nitroaniline is highly toxic and is readily absorbed through the skin. β-Naphthol is an irritant and a suspected carcinogen. Solutions of HCl and NaOH are caustic. Para Red may be a carcinogen. Avoid touching the dyed fabric strip with your hands. If your gloves become stained red, take them off immediately and put on a new pair.

List of Chemicals and Materials Needed
• para-nitroaniline (0.35 g/pair)
• β-naphthol (2-naphthol, 0.13 g/pair)
• potassium iodide (0.05 g/pair)
• 3 M HCl (8 mL/student)
• 10% NaOH (5 mL/student)
• Chilled 7% aqueous sodium nitrite solution (5 mL/pair) - a batch for class use will be prepared by the instructor (5 g in 70 ml)
• acetone (15 mL/student)
• fabric strips with six types of material, cut in 2-cm wide strips

Overview
We will first make the basic naphthol solution and dip the fabric in that, then chill that solution, and then prepare the diazonium salt and immediately use it in the two reactions. It is a good idea to weigh out the KI needed in step #11 before you start to prepare the diazonium salt solution. For any solid reagents, masses used need to be within 10% of those specified and the actual mass used (read all digits off balance!) must be recorded in your notebook.

β-Naphthol Solution
1. Obtain a fabric strip and, to keep track of which end of the strip is acetate and which end is wool, cut a notch in the wool end.
2. Place 0.13 g β-naphthol in about 10 mL hot water (60-80 °C) in a 50-mL beaker. Then add 10% NaOH in 0.2-mL portions until the solid just dissolves. Do not add too much base, as the fabric decomposes in base.
3. Soak the fabric strip in this solution for 2-3 minutes, remove it with forceps, pat it dry, and place it flat on a paper towel.
4. Chill the remaining naphthol solution in an ice-water bath and keep it at 0-5°C.

Preparation of para-Nitrobenzenediazonium Chloride
5. Obtain 5 mL of the 7% NaNO_2 solution and keep it in an ice-water bath until ready to use.
6. Place 0.35 g of p-nitroaniline and 10 mL of water in a 50-mL Erlenmeyer flask. The solid won’t significantly dissolve at this point.
7. Add 4 mL of 3 M HCl and warm on a hot plate to dissolve the solid. You may use a magnetic stirring
bar to stir the solution. Add more HCl dropwise, if necessary, to complete the dissolution of the
solid.
8. Cool the solution in an ice-water water bath until it reaches 0–5 °C. Some solid may come out of
solution at this point.
9. Add the chilled 7% NaNO₂ solution all at once to the reaction mixture in the flask.
10. Stir for 10 minutes, keeping the reaction mixture in the ice-water bath. The solution should become
clearer during this time.

Preparation of para-Iodonitrobenzene
11. Weigh 0.10 g of KI into a small, labeled beaker.
12. Use a syringe pipet setup to measure 2.0 mL of the cold diazonium salt solution you just prepared.
and add it to the KI in the beaker. Swirl the mixture until gas evolution ceases. A murky, black
reaction mixture is expected.
13. Isolate the solid by vacuum filtration with a Hirsch funnel. Wash the solid with two 1-mL portions of
cold water. Dry the solid by pulling the vacuum for a few minutes, and then transfer it to a small
labeled and weighed beaker.
14. Leave it to dry in your locker until the following lab period when the mass and melting point will be
determined.

Fabric Dyeing
15. Place the fabric strip that has already been treated with naphthol in the chilled diazonium salt
solution for 2-3 minutes. This make Para Red within the fibers of the various fabrics.
16. Remove the strip with forceps, rinse it with water by dunking it in a beaker of water, and lay it flat on
a paper towel.
17. Note the different colors observed on the different fabrics and how effectively the dye was accepted
onto each fabric.
18. Draw a diagram of the relative intensities in your notebook, with the fabric types identified. Take a
photo to use in your typed report. Dispose of the fabric strip in the waste.

Preparation and Isolation of Para Red
19. After the fabric is removed from the diazonium salt solution, pour the diazonium salt solution into the
basicified chilled β-naphthol solution from step #4 to yield the solid Para Red product.
20. Isolate the solid by filtration on a Buchner funnel and wash thoroughly with water. Let it dry a bit on
the funnel and then transfer it to a beaker. Leave it to dry in your locker.
21. Weigh it and, if you instructor indicates, determine the melting point the following week.

Acid-Base Properties
22. This can be done with damp or dry Para Red.
23. Place a tiny (~1-3 mg) sample of the un-dry product in a small test tube. Add about half a milliliter
each of acetone and deionized water. Note the color.
24. Experiment with adding small amounts of NaOH and then HCl, using the solutions that are available
in the lab. Note what happens to the color as you add base and then acid. You should see a color
change; seek assistance if you don’t or the solution seems impossibly dark.

Visible Spectroscopy
25. You may do this using either dry or damp Para Red.
26. Prepare a solution consisting of a tiny amount (1-2 mg) of Para Red dissolved in about 25 mL
acetone in a clean dry test tube. The solution should be a pale orange or even slightly yellow at this
point. If it is too orange, or red, you will need to dilute it further in order to get a good spectrum.
27. Record the visible spectrum from 400-800 nm with the help of your instructor. Sketch the spectrum
in your notebook, being sure to write down the absorbance maximum or maxima.
28. Transfer the solution back into the test tube and add just enough 10% NaOH solution that it changes color and the new color remains when the solution is mixed. Transfer the the solution back to the cuvette and take its spectrum, again sketching the spectrum and recording the absorbance max in your notebook.

**Cleanup and Waste Disposal**
Put all filtrates, excess reagents, and your dyed fabric strip in a waste container. Do not take your fabric strip home. Wash your glassware and filtration apparatus with soap and water. Any dye that remains may be rinsed with acetone. The stockroom will probably not accept Buchner funnels that are stained with Para Red.

**Practice Questions**
1. Why is para-nitroaniline more soluble in HCl than in water?
2. Why is it better for the diazonium salt to be used as quickly as possible after its preparation?
3. Why is the reaction between naphthol and diazonium salt more efficient at higher pH? Think about the form of the naphthol that is present at higher pH as opposed to at lower pH.
4. Why is the diazonium salt more stable at low pH than it is at a higher pH?
5. What causes the bubbling that is observed when KI is combined with the diazonium salt solution? Why is no bubbling observed when the naphthol is combined with the diazonium salt solution?

*Credits: This procedure is based on a lab done at the University of Colorado at Boulder and was originally adapted by Dr. Jamey Anderson of Santa Monica College.*

*Last revised 8/2/2018*