Chemistry of Photography

<u>Pre-lab assignment:</u> Collect objects suitable as "subjects" for your photography experiments. The subjects must lie flat on a 3 x 5 -light-sensitive piece of paper or cloth for several minutes. Consequently, your pet collie or roommate, no matter how photogenic in the usual sense, probably are not suitable subjects for your lab work. Materials that will produce beautiful images in this lab on light-induced chemistry (photochemistry) include drawings (either photocopied or hand-drawn) on overhead transparencies, leaves and other objects from nature, silhouettes, and conventional photographic negatives. Images or subjects smaller than 3 x 5 will optimize your opportunities to explore the chemistry of photography. Use your imagination in selecting 4-6 objects for your work, but remember that the resultant photographs (in many colors) will be two-dimensional representations (no enlargement or reduction in size are possible) of these objects.

<u>Overview</u>. Recent work in this course has focused on the dual nature of light, behaving both as a particle and as a wave. Photography relies on the wave-particle duality of light as photographic film varies in its sensitivity to the wavelength of light (color) striking its surface which ejects an electron--a particle--from a light-sensitive chemical on this surface. This photochemical event initiates a series of oxidation-reduction (electron-transfer) reactions to produce a permanent image.

Photographic processes include many of the topics of introductory chemistry:

- ¥interaction of light with matter in the formation of the image,
- ¥oxidation-reduction reactions to develop the image, and
- ¥changing the solubility of chemical compounds with different conditions to preserve the image.

This lab has been designed to aid in your understanding of these chemical topics through the creation of photographic images.

Introduction to the Chemistry of Photography. Early nineteenth century photographers produced crude images using papers impregnated with silver nitrate or silver chloride. Their "photographs" darkened with time; a method to prevent the continued reaction of light with the Ag-treated photographic papers had yet to be discovered. In 1839, however, Louis J. M Daguerre patented the discovery that produced light-fast images. His procedure relied on silver halide photochemistry, but included a process for making the image permanent. Treatment of the exposed photographic plate (copper covered with a surface layer of AgI) with mercury vapors, followed by washing with sodium hyposulfite ($Na_2S_2O_3$), dissolved the silver iodide from the unexposed portion of the plate. This combination of AgI-covered copper plates, mercury vapor, and hyposulfite fixative produced the most popular photographs--daguerreotypes--of the period between 1840 and 1860. William Henry Fox Talbot s improved process for coating silver halides directly on paper in combination with a hyposulfite fixative replaced the daguerreotype by the end of the nineteenth century. Although technologically more advanced, the basic procedures developed by Fox Talbot, the "Inventor of Modern Photography," are used in all silver-based photography today. This lab will explore the chemistry of both silver-based and alternative (non-silver) photographic processes.

Chemical Reactions Involved in Photographic Processes

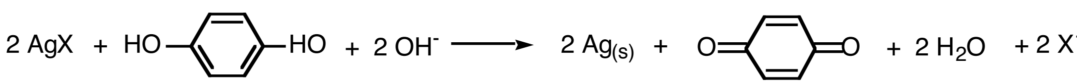
<u>A. Silver-based photographic processes</u>. Capturing light to produce an image utilizes two properties of the silver cation: (1) Ag^+ is reduced to silver metal in the presence of a halide which can be oxidized photochemically (i.e., a photon ejects an electron from the halide). (2) Although the halide salts of silver, AgX, have very low aqueous solubility, many complex ions of Ag^+ (such as that formed with hyposulfite) do dissolve in water. Modern silver-based photography relies on oxidation-reduction chemistry to capture the image. The media-specific solubility of silver halide salts make the initial image permanent. The key reactions are outlined below:

1. <u>Forming the image by exposure to light ($h\upsilon$)</u> : A very small number of X^- ions in the AgX crystals in the film are oxidized to X. The electrons released from this oxidation reduce the Ag^+ to silver metal in the surrounding AgX crystal.

$$X^{-} + h\upsilon \longrightarrow X¥ + e^{-} \qquad (1a)$$

$$Ag^{+} + e^{-} \longrightarrow Ag \qquad (1b)$$

2. <u>Development.</u> The small number of Ag metal atoms formed (the *latent image*) act as a catalyst and sensitizes the surrounding halide salt so that, in the presence of a developer--a reducing agent--the sensitized AgX is reduced, to produce black silver metal in the area exposed to light. Modern developers contain one of many reducing agents for this process. The most common is hydroquinone, which reacts with Ag^+ (in AgX), as shown in equation 2a:



(2a)

Note that the reaction of (2a) occurs in basic medium (OH^-). The development can be stopped, therefore, by dipping the photographic film in acid. The most common "stopper" contains acetic acid. In this experiment, we will remove excess reagents by washing the exposed "film" in water before fixing the image.

1. <u>"Fixing" the image (making it permanent)</u>. Unexposed AgX on the photography film (plate or paper) is removed by complex formation with thiosulfate (eq. 3). The soluble complex, $[Ag(S_2O_3{}^{2-}]_2{}^{3-}$, can be readily washed away to leave only the dark silver metal image.

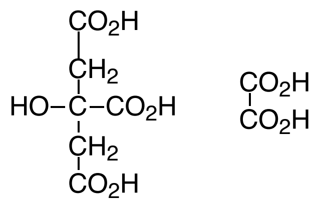
$$AgX + 2\, S_2O_3{}^{2-}[Ag(S_2O_3{}^{2-}]_2{}^{3-} \qquad (3)$$

The process described above forms the negative in conventional black-and-white photography; light shining through the negative produces the final photograph (the positive) using this same chemistry.

2. Toning (coloring) the image. The silver-based black and white photographs may be altered by *toning*, using chemistry to produce different colored images. For example, reactions of Ag with thiosulfate in acid solution produces sulfur that then reacts with the Ag-image to yield the brown Ag_2S of *sepia* photographs.

B. Cyanotypes. The blue photographs on formation of insoluble Prussian Blue through photoreduction of Fe(III) to Fe(II) are called cyanotypes. Toning reactions may alter the color of the initial image. In this lab, one or more toning treatments as well as the wavelength dependence of the iron photoreduction will be explored.

Photoreaction and formation of insoluble Prussian Blue. The two photoactive iron compounds most commonly used for photography are ferric ammonium citrate, $Fe(III)NH_4(C_6H_6O_7^{2-})_2$, and ferric ammonium oxalate, $Fe(III)(NH_4(C_2O_4^{2-})_2$. .



citric acid oxalic acid

Citrate and oxalate are the anions generated by loss of two acidic protons from citric and oxalic acids, respectively. Interaction of light with these anions leads to their oxidation and releases carbon dioxide and an electron (equation 4a) which then reduces Fe(III) to Fe(II) (4b). Although we will be using ferric ammonium citrate in this lab, the redox chemistry is more readily apparent in the reaction of oxalate (equation 4a):

$$C_2O_4^{2-} + h\upsilon \longrightarrow 2\,CO_2 + 2\,e^- \qquad (4a)$$

$$Fe^{3+} + 1\,e^- \longrightarrow Fe^{2+} \qquad (4b)$$

Overall reaction

$$2\,Fe^{3+} + C_2O_4^{2-} + h\upsilon \longrightarrow 2\,Fe^{2+} + 2\,CO_2 \qquad (4c)$$

The Fe(II) formed in (4c) combines with CN^- present in the solution to form the complex $[Fe(CN)_6]^{4-}$ which, in turn, gives the insoluble blue Prussian blue, $Fe(III)_4[Fe(CN)_6]_3$, adhering to the fibers of the cloth or paper on which the reagents had been coated (5a and 5b, respectively):

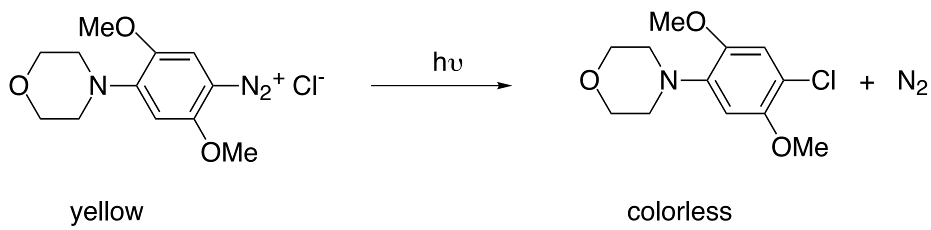
$$Fe^{2+} + 6\,CN^- \longrightarrow [Fe(CN)_6]^{4-} \qquad (5a)$$

$$3\,[Fe(CN)_6]^{4-} + 4\,Fe^{3+} \longrightarrow Fe(III)_4[Fe(CN)_6]_3 \qquad (5b)$$

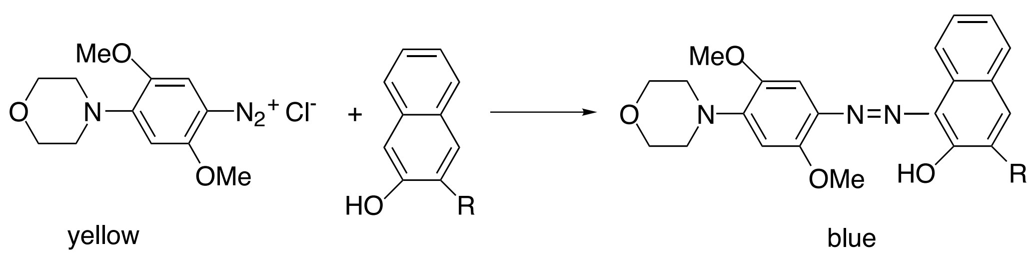
The blue color results from interaction between the iron in two different oxidation states. (Similar compounds, all containing both Fe(III) and $[Fe(CN)_6]^{4-}$, but with either K^+ or NH_4^+ ions also are blue or greenish-blue in color and are also called Prussian Blue as well. Only compounds containing iron in these two oxidation states of iron are blue).

Treatment of Prussian blue of cyanotypes with base changes the blue to yellow, probably $Fe(OH)_3$; whereas, toning with a combination of tannic acid and sodium carbonate give rich purplish color. The chemistry of this latter reaction is not well known.

C. Blue Print Paper or Diazo Prints. Most photographic processes using organic compounds rely on an initial photochemical reaction, followed by a second reaction between the photochemical product or the unexposed reactant with another chemical a *coupler* impregnated in the paper. The following reactions, occurring on the blueprint paper; the photosensitive compound belongs to a group called diazo dyes. Consequently, the prints made with paper covered with these dyes are also called diazo prints.



(6a)



(6b)

Notice that original diazo paper is yellow; whereas, the exposed paper will contain a blue image on a white background. Identify the coupler in the above set of equations.

Experimental Procedures

General Directions. All the experiments involve coating papers or cloth with photosensitive reagents or using prepared photosensitive paper. Consequently, these materials should not be exposed to strong light except when the desired photographs are made. Taking a photograph" in this lab consists of placing the "subject, " one of the objects selected by the student, on top of the photosensitive paper or cloth, covering the object with glass to hold it in place, and exposing this package to light. In some cases, a filter will be placed between the light source and the paper to evaluate the wavelength dependence of the photographic process. Development of the photographs consists of dipping the exposed papers in aqueous solutions and washing with water.

Safety Considerations. The materials which will be used to make photographic papers (Ag^+ and Fe(III) solutions) are toxic and will, at the least, stain the skin. Consequently, care should be taken to avoid getting them on your hands; gloves should be worn when preparing these photosensitive papers. **Ultraviolet light will damage the eyes; do not look directly at the light sources.**

Lab Notebook. The photographic prints constitute the main results of this lab and should be carefully labeled and numbered. The narrative in the *Results/Discussion* section(s) should explicitly refer to these figures.

Disposal of Wastes. All waste solutions should be discarded in the labeled bottles.

A. **Silver-Based Photography.**

1. Comparison of the photosensitivity of silver halides. Pour 2 mL portions of 0.1 M solutions of sodium chloride (NaCl), sodium bromide (NaBr), and sodium iodide (NaI) into three separate test tubes. To each test tube, add 0.5 mL (10 drops) of 0.1M silver nitrate ($AgNO_3$). Filter each solution through filter paper into clean test tubes. Save the filter paper and discard the filtrate. Unfold the filter papers, label each according to the silver halide which you filtered, place a coin in the center of each and expose to sunlight or UV light for about 10 minutes.

a. Record the type light source used (*Experimental*).
b. Record your observations (*Results*).
c. Write equations for all reactions occurring (*Results/Discussion*).
d. In most commercial photography, AgBr is the silver salt used. Explain this choice based on your data (*Discussion*).

2. Making salted paper prints with gelatin-immobilized AgCl on paper. Paint a solution of ammonium chloride, NH_4Cl onto watercolor paper. Allow the paper to dry (to touch). Then paint a solution of $AgNO_3$ onto the NH_4Cl-coated paper and let dry with minimum exposure to light. Place one of your images on this paper and expose to an intense light until image shows (less than10 minutes). Rinse with tap water and fix (soak) in a solution of sodium thiosulfate for 10 minutes. Rinse again with water and dry.

a. Record the type light source used (*Experimental*).
b. Record your observations. (*Results*).
c. Write equations for all reactions occurring (*Results/Discussion*).

B. **Cyanotypes**

1. In the dark, mix 5 mL each of a potassium ferricyanide, $K_3[Fe(CN)_6]$ solution and a ferric ammonium citrate solution, $Fe(III)NH_4(C_6H_6O_7^{2-})_2$ in a paper cup. Using a brush, paint the mixture onto a piece of watercolor paper or a piece of cotton cloth. Let soak in and then wipe evenly with a paper towel. Coat once more and wipe evenly. Allow to dry completely by air drying or with a hair dryer. Expose to light source (instructor or student assistant will demonstrate) until the exposed regions turn gray. Rinse with water and let dry.

a. Make sure you record the type light source used (*Experimental*).
b. Record your observations. (*Results*).

c. Identify the equations for all reactions occurring (*Results/Discussion*).

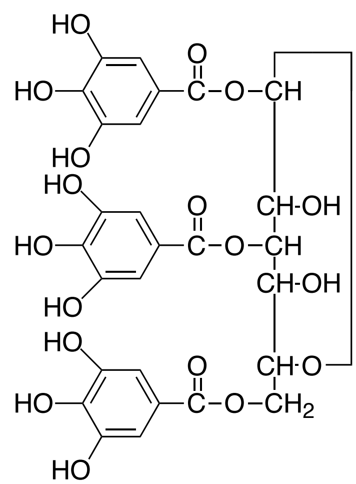
C**. Students may choose at least one of the following experimental options to explore.**

1. Timed exposure with a single light source either with salted silver prints or cyanotypes. Suggestion: Remove a mask from film as a function of time.

2. Toning of cyanotypes.
    a. Treat with NaOH. After rinsing the print in water, place paper or cloth into 0.1 M NaOH. Rinse with water and let dry.

    b. Treat with tannic acid and sodium carbonate. After rinsing the print with water, place it into a tannic acid solution and agitate for 1 minute. Rinse print with water and transfer it into a solution of sodium carbonate for 30 seconds. Rinse again and return print to tannic acid solution and wait until it turns a purple-brown color. Rinse with water and let dry.

The chemistry of this latter toning process is not well understood. You might be able to make some guesses about it based on the structure of tannic acid below (found in the bark of most trees) and knowing that the H-atoms on the HO-groups on the rings can be lost as H^+ ions:



a. Make sure you record the type light source used (*Experimental*).
b. Record your observations. (*Results*).

D. Diazo Paper

Take a sheet of diazo paper (bright yellow) and with an image, expose it to light source. Place in a developing chamber with ammonia to develop the image.

a. Record the type light source used (*Experimental*).
b. Record your observations (*Results*).
c. Identify the equations for all reactions occurring (*Results/Discussion*).

Summary and Conclusions. Use your photographic prints (and/or those of other students in your section) to discuss your own conclusions regarding the strengths and weaknesses of the photographic processes you explored in this lab.

Related reading:

1. Silver prints, cyanotypes, and toning

Paul Mueller s Chemistry 103 (Hampton-Sidney College): Chemistry and Art Web page: http://cator.hsc.edu/~mollusk/ChemArt/photo/index.html.

2. Cyanotypes

Mike Ware s Alternative Photography web page http://www.mikeware.demon.co.uk/cyano.html

3. *Chemistry and Artists' Colors,* Mary Virginia Orna, Chemical Heritage Foundation, 1998, p. 333-354, 357-369.

McCarthy and MMerritt, August, 1999; revised January, 2001