

CHEM 2229 EXP 1: Oxidation of 9-Fluorenol to 9-Fluorenone with Sodium Hypochlorite

Objective: In this experiment you will learn how to perform an oxidation reaction by oxidizing an alcohol (9-hydroxyfluorene) to a ketone (9-fluorenone) using sodium hypochlorite in an acidic environment; how to perform TLC to monitor a reaction; how to perform an extraction to isolate a product; and, how to verify purity of a product using TLC and melting point.

* Chromatography is a useful method for separating components of a mixture of compounds based on their polarity. **Thin layer chromatography** is especially useful for determining the number of components in a mixture, the identity of the compounds, and the purity of a compound.

****Solvent Extraction** is also known as Liquid-liquid extraction (LLE) or partitioning. It is a method used to separate compounds based on their relative solubilities in two different immiscible liquids: usually the polar solvent water and a non-polar organic solvent. Immiscible means that the liquids do not mix and because of this form two distinct layers.

***The **melting point (MP)** is a physical property of a solid also used for the purpose of identification and purity determination.

Reading Assignment:

OCLT: OCLT, pp. 83-108 (chromatography generalities & TLC),
pp. 368-369 (TLC technique summary), pp. 203-246 (extraction);
pp. 376-381 (extraction illustrations); 366 (vacuum filtration);
and 309-315 (melting point).

Solomons Organic Chemistry, 12th ed. (*Note: Pages correspond to 12th ed.*)
pp. 542-547 (12.4 Oxidation of Alcohols)

Concepts:

Acids, Bases, Decantation, Drying Agents, Exothermic Reactions, Extraction, Half Cell Method, Oxidation/Reduction, Oxidizing Agents, Reducing Agents, Reflux, Salting Out

Chemicals:

acetic acid (glacial), acetone, 9-fluorenol, 9-fluorenone, hexane, sodium bicarbonate, sodium chloride, sodium hypochlorite (aq soln) / bleach, sodium sulfate

Safety Precautions:

Wear chemical splash-proof goggles and appropriate attire at all times.

Acetone and hexane are flammable liquids.

Glacial acetic acid is smelly, highly corrosive and toxic.

Sodium hypochlorite is an oxidizing agent.

If you spill an acid or a base on the counter or floor, call for a TA or an instructor to neutralize the spill.

If you spill an acid or a base on your skin, immediately walk to the nearest sink and wash thoroughly with cold water. Do *not* attempt to neutralize a spill on your skin.

Materials Needed:

Oxidation: balance, 5 ml conical vial with cap and septum, magnetic spin vane, ringstand with finger clamp, hotplate with magnetic spinner

TLC: Plastic Beaker (400 ml), filter paper, 4" watchglass, 1 TLC Strip, 6" ruler, dull pencil, TLC capillary tubes (3), disposable vial, glass stirring rod, UV (*black*) light, clear packing tape

Isolation & Recovery: centrifuge tubes (2), 2 disposable pipet and bulbs, 1 rubber stopper, 2 small labels, ring stand with finger clamp, beakers (250 ml, 100ml, 50 ml), microspatula, balance

Melting Point Analysis: melting point apparatus, melting point capillary tubes or microscope slides

Background:

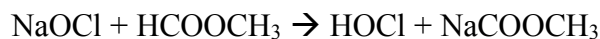
In undergraduate organic labs, extreme caution needs to be taken when using powerful oxidizing agents like Cr(VI) in order to avoid any unnecessary exposure. Traditionally this has been accomplished by binding Cr(VI) to the insoluble polymeric material, Amberlyst A-26 ion exchange resin (from Rohm-Haas). Binding the Cr (VI) allows for easy separation of the chrome from the reaction mixture because the polymer bound chrome by filtration and reused as a reagent. Polymer-bound reagents have been developed for use in a variety of organic syntheses.

However, a greener (more environmentally friendly) method has been developed by Jones and Albizati where they use sodium hypochlorite (NaOCl), ordinary household bleach, as the oxidizing agent. The main advantages of NaOCl over Cr(VI) are lower toxicity, easier waste disposal and lower cost. When the pH is below 11, there is the added advantage of absolute selectivity where secondary alcohols need to be oxidized in the presence of primary alcohols. The secondary alcohols are selectively converted to ketones, whereas the primary alcohols are left undisturbed. Thus, the oxidation of alcohols by NaOCl can be performed under a variety of conditions to produce selective compounds with high yields. Primary alcohols can be converted to aldehydes or carboxylic acids. Secondary alcohols can be converted to ketones. The essentially pure products can then be easily extracted using dichloromethane, hexane or ether.

Jones and Albizati note that molecular chlorine becomes a significant product in the decomposition of an aqueous bleach solution, as shown in the following equation:

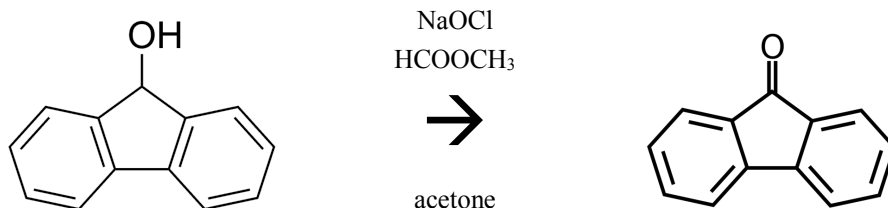


So care needs to be taken to ensure that the pH is kept below 11 by adding a small amount of acetic acid.



When the pH is kept below 11, a significant amount of the sodium hypochlorite (NaOCl) is converted to hypochlorous acid (HOCl). (Composition, 1) The hypochlorous acid then becomes the oxidizing agent as the oxidation number for Cl goes from +1 in HOCl to -1 in the Cl^- , chloride anion.

The oxidation of 9-fluorenone is as follows:



While chlorine bleaches work efficiently and inexpensively and are considered safer to use than Cr (VI) compounds, care still needs to be taken not to introduce chlorine into the environment. Industrial use of chlorine has the potential of adding chlorine to the waste stream which may lead to the formation of polyhalogenated organic compounds like polychlorinated dibenzodioxins (PCDDs) (also known as dioxins) that are significant environmental pollutants. Dioxins have the ability to bioaccumulate and are linked to increased cancer threats.

For oxidation reactions, an environmentally safer alternative to either chrome or bleach is hydrogen peroxide (H_2O_2) because its decomposition products are oxygen and water. However, in the process of decomposing, hydrogen peroxide first releases free radicals which are highly reactive intermediates. These intermediates then oxidize other molecules by stripping electrons from them. This process is very indiscriminate as the free radicals can react with any molecule. So various factors such as pH, temperature, dose, reaction time and/or catalyst addition need to be carefully monitored when trying to maintain selective reactions. Hydrogen peroxide oxidation reactions also require higher temperatures and pressures and longer reaction times than those using sodium hypochlorite.

So for the purpose of this experiment, sodium hypochlorite (bleach) is the preferred oxidizing agent. In this week's experiment, the secondary alcohol 9-fluorenol will be dissolved in acetone. The solution will be made acidic using acetic acid. The 9-fluorenol will be oxidized with NaOCl to form the ketone, 9-fluorenone.

The progress of the oxidation will be monitored by Thin Layer Chromatography, TLC, using fluorescent silica gel sheets $\sim 2.5 \text{ cm} \times 10 \text{ cm}$ developed with the provided 30% acetone in hexane solution and visualized under UV light. The purity of the product will also be verified by measuring the melting point using a Fisher-Johns melting point apparatus.

I. Oxidation of the Alcohol Procedure:

1. Tare a 5ml conical vial.
2. Add ~ 50 mg of 9-fluorenol. Record the actual mass to the nearest 0.001 g.
3. Add 3ml of acetone.
4. To the 5-mL conical vial add a magnetic spin vane and a cap with a septum.
5. Place the conical vial on top of a stirring hot plate and clamp in place. (*Verify heat is off.*)
Magnetically stir the solution until the 9-fluorenol is completely dissolved or 5 minutes.
6. Once the 9-fluorenol dissolves, remove the cap and add 3 drops ($\sim 0.15 \text{ ml}$) of glacial acetic acid and 16 drops ($\sim 0.8 \text{ ml}$) of 5.25% sodium hypochlorite solution (commercial bleach). Replace the cap.
7. Allow the mixture to react for 20 minutes.* While waiting, prepare a TLC chamber.
The color of the solution will turn yellow as all of the alcohol is oxidized. Record any color changes.

***Note:** If at any time after 10 minutes a white ppt is noticeable, add 4 more drops of NaOCl. The white ppt, NaCl, is insoluble in acetone. The ppt should dissolve within 5 minutes. If it does not, dissolve, contact a TA or instructor for advice.

II. Thin Layer Chromatography Procedure:

(Note: Students may share chambers. Each student needs their own TLC strip.)

1. Prepare a TLC chamber with 30% acetone in hexane. (See page 7 for directions.)
2. Prepare a single TLC strip to be spotted with three spots:
ketone standard (9-flourenone), alcohol standard (9-fluorenol) and reaction solution.*

***Note:** Ketone and alcohol can be spotted at this time. Wait the 20" before checking the reaction solution.

3. After the mixture has reacted for 20 minutes,* check for progress of the reaction using TLC.

***Note:** Do **not** perform TLC if the solution is still colorless, instead contact a TA or an instructor for help.

4. To prepare the reaction mixture for TLC
 - a. Acquire a disposable vial from the cart.
 - b. Add ~1/4 inch of acetone to the vial.
 - c. Dip a clean glass stirring rod in the reaction mixture, then into the vial. Stir.
 - d. Use a clean capillary to spot the TLC strip with the reaction mixture.
5. Double check under the UV light that all of the spots are visible and not overlapping.
6. Allow the mixture to continue to react while the TLC strip is developing.
7. Mark the solvent front immediately after removing the TLC strip from the chamber.
8. View the TLC strip and mark the outlines of the spots.*
9. Attach labeled TLC strips to a page in lab notebook
with the 2" clear packing tape that can be found on the supply cart.

***Note:** If the TLC analysis reveals the presence of unreacted alcohol, check with the instructor or the TA to determine if it is necessary to add extra NaOCl solution. If necessary, prepare a second TLC strip to verify the total transformation of the alcohol to the ketone.

III. Isolation of Product

1. Acquire 2 pipets, 1 rubber bulb, 2 - 10 ml centrifuge tubes, 1 rubber stopper and 2 small labels.
2. Label one centrifuge tube Hexane Solution (H) and the other Aqueous Soln (A).
3. Once the alcohol is completely oxidized, transfer the contents of the 5 ml conical vial
to the H centrifuge tube.
4. Rinse the 5 ml conical vial twice with 1 ml hexane each time. Add the rinsings to the (H) centrifuge tube.
5. Using finger clamps, clamp the H centrifuge tube to the ringstand.
Make sure the centrifuge tube is in a vertical upright position.
6. Place the Aqueous Solution centrifuge tube in a 250 ml beaker.

A. Extraction:

1. To extract the 9-fluorenone, place a rubber stopper in the centrifuge tube. Shake the centrifuge tube to thoroughly mix the solutions. Clamp the centrifuge tube to the ringstand. Allow the layers to settle.*

***Note 1:** Both layers should be clear – not cloudy – with a distinct phase separation line between the layers. If the layers are cloudy, contact a TA or an instructor for help.

***Note 2:** If you have difficulty seeing the phase separation line, place a burette card (a piece of white paper with a thick black line) behind the centrifuge tube. Move the card up and down until the line is visible.

2. Using a pipet, extract the lower aqueous layer and add it to the Aqueous (A) centrifuge tube.
3. Repeat the extraction by adding 2 ml of hexane to the Aqueous centrifuge tube. Place a rubber stopper in the centrifuge tube. Shake the centrifuge tube to thoroughly mix the solutions. Clamp the centrifuge tube to the ringstand. Allow the layers to settle.*
4. Using a pipet, extract the lower aqueous layer and add it to a waste beaker.
5. Pour the remaining hexane solution into the original Hexane (H) centrifuge tube.
6. Set the empty Aqueous centrifuge tube in the 250 ml beaker.

B. Neutralization of Acid:

1. To wash the hexane extract, add 2.5 ml of 5% (w/v) sodium bicarbonate (aq) solution to the Hexane (H) centrifuge tube. Clamp the H centrifuge tube to the ringstand. Using a pipet, mix the two layers of the solution by drawing the lower layer up into the pipet and releasing the lower layer into the upper layer. Do this several times to make sure the layers are thoroughly mixed. Allow the layers to settle.
2. Using a pipet, extract the lower aqueous layer and add it to a waste beaker.
3. Repeat process in steps 1 & 2 once using a second 2.5 ml of 5% (w/v) sodium bicarbonate.
4. Repeat process in steps 1 & 2 twice more using 1 ml of saturated NaCl (aq) soln each time.
5. After the last rinsing with NaCl soln, pour the hexane solution from the H centrifuge tube into a clean dry 100 ml beaker.
6. Add 0.5ml hexane to the H centrifuge tube to rinse it. Swirl. Add the rinsing to the hexane solution in the beaker.

C. Drying the Product

1. Add a heaping microspatula spoonful of anhydrous sodium sulfate, Na₂SO₄, to the hexane solution in order to dry it. Swirl the beaker to increase contact of sodium sulfate with the solution. The sodium sulfate will clump as it removes any remaining water in the solution. If only relatively large clumps form, add more sodium sulfate until it is “free-flowing.” Swirl occasionally for 5 minutes.
2. Weigh a clean dry 50 ml beaker. Record the mass to the nearest 0.001 g.
3. Decant the hexane solution into the 50 ml beaker.
4. Rinse the sodium sulfate twice with 0.5 ml portions of hexane. Add the rinsings to the 50 ml beaker.

D. Recovery of Product

1. Remove the hexane from the 9-fluorenone by heating the beaker on a hotplate (~100 °C) under a mini-hood*or by gentle evaporation using a hair dryer under the hood.*
2. Record physical appearance of the product.
3. Record the mass of the beaker and product to the nearest 0.001 g.
4. Determine the mass of the product to the nearest 0.001 g and record it.

***Note 1:** Do *not* directly inhale the hexane vapors as they may cause dizziness.

***Note 2:** The MP of 9-fluorenone is relatively close to the BP of the solvent hexane. The melted solid may look like residual solvent. To test if all of the solvent has evaporated, remove the beaker from the heat source. Place the beaker on the counter. Using a microspatula, scrape through the liquid. If it solidifies and is powdery, all of the solvent has been removed. If it is “tacky” or does not form a powder when scraped, there is still residual solvent present. Place the beaker back on the hotplate and wait 5 minutes.

IV. Melting Point Analysis

1. Using an AFON-DMP100 or a Fisher-Johns melting point apparatus, determine the melting point range of the product. Refer to Melting Point handout for directions.
2. Record the melting point range. Record the model and number of the MP apparatus.

V. Post Lab Information:

A. Calculations: (*Label and show all calculations along with the answers in your lab report.*)

1. Determine the theoretical yield of the ketone based on the starting mass of the alcohol.
2. Determine the percent yield of the ketone.
3. Determine the percent error for the MP.
4. Determine the R_f values for the pure 9-fluorenone, pure 9-fluorenol and reaction mixture.
5. Determine the percent error for the R_f value.

B. Conclusion:

In your conclusion, discuss whether the experiment was successfully performed and / or any problems that arose during the experiment and your recommendation for how to avoid those problems if you were to redo the experiment.

Concepts To Consider Before Answering Prelab Questions on Canvas

(See Solomon's Organic Text for more information on oxidation reactions.)

1. Write the reactions showing the general structures of the products in which Cr(VI) is used to oxidize the following: a.) primary alcohols; b.) secondary alcohols; and c.) tertiary alcohols.
2. Name and draw the structural formulas for the two 2° alcohols that can be oxidized to form camphor.
3. Write a balanced equation for the oxidation of cyclohexanol with sodium dichromate in the presence of sulfuric acid.

(*Note: Use the half-cell method to balance the redox equation. Dichromate is reduced to Cr³⁺.*)

References:

Experiment 19: Oxidation of 9-Fluorenol. Available at: <https://slideplayer.com/slide/4627512/>

Galvin, Jennifer M. and Eric N. Jacobsen. Composition of Aqueous Solution as a Function of pH.

Available at: <http://reag.paperplane.io/00002530.htm>

A Greener Bleach. Contributed by Ed Vitz, John W. Moore, Justin Shorb, Xavier Prat-Resina, Tim Wendorff, & Adam Hahn. Available at:

https://chem.libretexts.org/Ancillary_Materials/Exemplars_and_Case_Studies/Exemplars/Environmental_and_Green_chemistry/A_Greener_Bleach

Hydrogen Peroxide is a Powerful Oxidizer. Available at:

<http://www.h2o2.com/products-and-services/us-peroxide-technologies.aspx?pid=112&name=Hydrogen-Peroxide>

Jones, C. Susana and Kim Albizati. Sodium Hypochlorite Oxidation of 9-Fluorenol to 9-Fluorenone: A Reaction Monitored by Thin Layer Chromatography. *J. Chem. Ed.*, 1994, Vol. 71, No. 11, A271-A272.

How to Perform TLC Reminder Notes

1. Prepare TLC chamber:
 - a. Add $\sim \frac{1}{4}$ inch of 30% acetone in hexane to plastic beaker.
 - b. Place filter paper along wall of beaker and watch glass on top of beaker to create a space for vapor to saturate.
2. Prepare TLC strip:
 - a. Avoid touching TLC strip – handle only by the edges.
 - b. Using a pencil, draw a horizontal line $\sim \frac{1}{2}$ inch from and parallel to the bottom of the strip. This is the origin line.
 - c. Using a capillary, spot strip with reference ketone, alcohol and reaction mix.
3. Develop TLC strip:
 - a. Place TLC strip in chamber being careful to make sure strip does not touch filter paper and solvent front is parallel to drawn starting line.
 - b. Once solvent front has move to $\sim \frac{1}{2}$ inch from top of strip, remove strip and with a pencil mark the solvent front.
4. Visualizing TLC strip:
 - a. Allow TLC strip to dry. A hair dryer may be used to help evaporate solvent.
 - b. View strip under UV lamp and mark exterior of sample spots.
 - c. Once reaction mixture does not have a spot corresponding to the ketone, the reaction is complete.
5. Determine the Retention Factor, R_f , values for each spot.
 - a. Mark center of each spot. Measure distance from origin to center of spot.
 - b. Measure distance from origin to solvent front.
 - c. $R_f = \text{distance spot travelled} / \text{distance solvent front travelled}$

Recall: If the spots appear in a horizontal row or clumped together, then separation has not been achieved. The spots should have different distances vertically from the start line to the solvent front in order to have good separation. The **retention factor (R_f)** is the ratio of the distance the spot moved from the starting line to the distance the solvent front moved above the origin.

$$R_f = d/D. \text{ (See Figure 2.)}$$

The R_f value will be a unitless number between 0.0 and 1.0. The R_f value is consistent to a certain degree for a given compound using the same solvent and the same type of TLC plate. Thus, one can compare the R_f values for the components of the mixture to the R_f values for the known compounds and easily identify the components by matching the R_f values. [Note: The width of the spot (w) is used to calculate the number of theoretical plates, N , which will not be necessary for this experiment as the most efficient solvent has already been chosen.]



Figure 1: Spots on TLC plate.

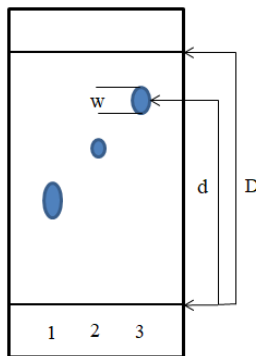


Figure 2: For the calculations, d , D and w are measured vertically, where d is from the starting line to the center of the spot being measured, D is from the starting line to the solvent front and w is the width of the spot from top to bottom.