

Octadecanethiol Monolayer on Silver

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Purpose:

Silver is coated with 1-octadecanethiol and the analog alcohol 1-octadecanol to form a non-polar surface. The binding capability of the thiol and alcohol is compared by testing how well water is repelled from each surface. The 1-octadecanethiol may be prepared in advance.

Learning Objectives:

1. Predict how a substance will behave on a particular monolayer given its chemical characteristics.
2. Observe the difference in contact angles between various substances with different chemical characteristics.
3. Explain hydrophobicity in terms of polarity.
4. Apply knowledge of wide and narrow contact angles to demonstrations with water and decalin.

Introduction:

A unique property of thiols (RSH) is their particularly strong attraction to metal surfaces. In any given sample, the thiol will quickly self-assembled into a monolayer to coat the entire metal surface, where the sulfur is attached to the metal with the “tail” end of the molecule pointing away (see Figure 1).

These self-assembled monolayers serve a variety of functions, which is dependent on the group that is used on the tail portion of the thiol.

The tail portion can vary from simple alkyl groups to more complex groupings like carboxylic acids and esters. By changing the functional group of the tail, the properties of the self-assembled monolayers can be changed to fit a particular purpose. An application of this is seen with metallic cloths. Manufacturers will coat metallic cloths with particular thiols to help protect them from specific environmental pollutants and other substances, like water, that can damage them.

The fact that thiols are able to produce self-assembled monolayers on metal surfaces is said to be a distinctive property of this group of molecules, but just how

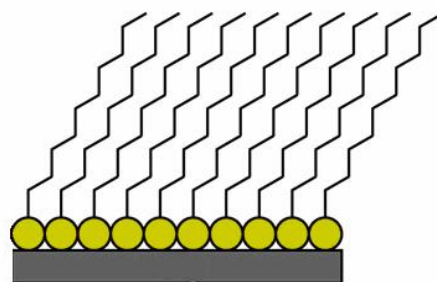


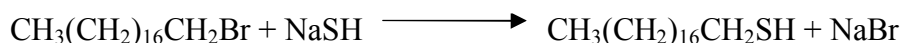
Fig. 1

unique is this phenomenon? Will other elements and molecules with similar characteristics to sulfur and thiols be able to produce monolayers just as effectively?

In the Periodic Table oxygen and sulfur are part of the group 16 elements, and this classification implies that the two share similar chemical bonding characteristics. For example, oxygen and sulfur are both non-metals, and are relatively electronegative. The most common oxidation state for both elements is -2, and they can bond to form similarly structured compounds. One of the most common oxygen-based functional groups in organic chemistry is alcohols (ROH); the comparative sulfur counterparts are thiols.

Although these two types of compounds are similarly structured, there are differences. For example, thiols tend to have a foul odor associated with them, especially the lower molecular weight ones. Also, the O-H bond in alcohols is more polar than the S-H bond in thiols. This difference in polarity leads to the presence of hydrogen bonding in alcohols, but not in thiols.

One of the simplest ways to synthesize a thiol is by using sodium hydrosulfide and a primary alkyl halide. The hydrosulfide ion is very nucleophilic and will undergo S_N2 reaction replacing the halide ion from the alkyl halide in one step. In this experiment 1-bromooctadecane is combined with an excess of sodium hydrosulfide and refluxed in ethanol to produce 1-octadecanethiol:



This experiment examines if the chemical differences between thiols and alcohols will have an affect on the ability to form a monolayer on metallic surfaces. 1-Octadecanethiol and 1-octadecanol both produce non-polar surfaces when they coat the silver. To qualitatively measure which substance produces a more ordered non-polar monolayer, the contact angle of various known substances can be observed and compared between the two. The contact angle is the angle made between the side of a drop and the surface on which it rests. The more attracted a substance is to a surface, the narrower the contact angle will be (Figure 2). In this experiment the non-volatile hydrocarbon decahydronaphthalene, also known simply as decalin, and water are used to compare the hydrophobicity of the surfaces produced.

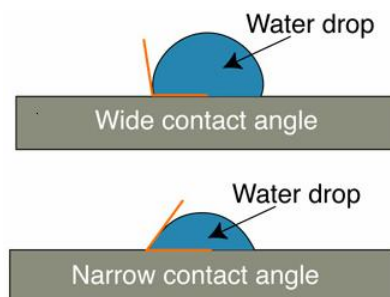


Fig. 2

Materials:

1-bromooctadecane
sodium hydrosulfide (NaSH)
3 M hydrochloric acid (HCl)
sodium sulfate (Na_2SO_4)
ethanol
chloroform
*0.5 M glucose

*0.8 M potassium hydroxide (KOH)
*0.1 M silver nitrate (AgNO₃)
6 M nitric acid (HNO₃)
15 M concentrated ammonium hydroxide (NH₄OH)
1-octadecanethiol
1-octadecanol
decahydronaphthalene (decaline)
1 - separatory funnel
1 - pleated filter paper
1 - funnel (plastic or glass)
2 - 10 x 10 cm glass plates
large crystallizing dish
magnifying glass

*Prepared pre-lab

Procedure:

Part I: Synthesis of Octadecanethiol

Note: Part 1 can be time consuming so it would be best to use two lab sessions to complete. Sections A and B can be done the first week, with section C and Part 2 done the following week.

A. Refluxing Reaction and Evaporating Solvent

1. Set up heating mantle on top of magnetic stirrer.
2. In a 100-mL 14/20 round bottom flask, measure out 1.00 g (nearest 0.01g) of 1-bromooctadecane (MM = 333.38 g), and add a stirbar.
3. Clamp this flask to a ring stand and lower into the mantle.
4. Weigh out 0.50 g of NaSH (MM = 56.07 g) in a weighboat and add to the flask using a 14/20 glass funnel.
5. Measure 20.0 mL of ethanol and add to flask. Replace the funnel with a water condenser.
6. Turn the variac setting to ~55 and begin stirring. Start a water flow through the condenser.
7. Once reaction heats up enough to reflux, let it continue for 1 hour.
8. Remove water condenser and insert a glass tube attached to the aspirator. Run aspirator for about 15 minutes or until most of the solvent has evaporated. Alternately, the ethanol may be removed using the rotary evaporator.

B. Washing and Separating Product

1. Remove flask from the heating mantle and stop the stirrer. Add 20.0 mL of 3M HCl and 20.0 mL of chloroform. Swirl mixture until the solid is dissolved.

2. Remove the stirbar from the flask, and pour the contents into a separatory funnel. Rinse the flask with a pipet full of chloroform and pour this into the funnel as well. Let the solution separate into 2 layers.

Describe what the two layers look like. Which layer is the chloroform (organic)? How do you know this?

3. Empty the bottom layer into a clean 50-mL 14/20 Erlenmeyer flask. Drain the top layer into a 250-mL beaker (waste).
4. Wash the bottom layer with 15 mL of water and place back into funnel. After shaking, allow the layers to separate. Repeat step 3 and then wash the bottom layer with an additional 15 mL of water, and pour it back into the funnel for shaking.
5. Making sure the stop cock is completely shut, rinse the inside of the tip of the separatory funnel with some acetone and let it air dry. Empty the bottom layer into a new, clean 50-mL 14/20 Erlenmeyer flask, and discard the top layer.
6. Add two spoonfuls of the drying agent Na_2SO_4 and swirl mixture around until solution no longer appears murky. Meanwhile, set up a hot water bath in a crystallizing dish with the temperature around 75°C .
7. Filter this solution into a clean and dry 50-mL 14/20 Erlenmeyer flask using pleated filter paper in a funnel. Rinse out the original flask with a pipet full of chloroform and filter this into the solution.
8. Clamp flask to ring stand and lower into the hot water bath. Set up the aspirator air flow as before, and evaporate until the solvent is gone. Once every several minutes or so, gently remove the aspirator tube and give the contents of the flask a swirl to ensure no film is forming on the surface of the liquid. Alternatively, the dry solution may be filtered into a 50-mL 14/20 round bottom flask, and the chloroform removed on the rotary evaporator.
9. When product is completely dry, transfer into a 50-mL 14/20 round bottom flask if it is not already in one. Cap and store until the following week when the Kugelrohr Distillation can take place.

C. Kugelrohr Distillation

1. Place flask with the crude octadecanethiol inside the Kugelrohr oven and attach two collection bulbs. Apply aspirator suction and begin rocking the system. Turn on the variac to a setting of 70.
2. Once solution is heated to $\sim 220^\circ\text{C}$, clear distillate will be noticeable. Keep the oven temperature somewhere between 220°C and 235°C (adjust variac setting if necessary) throughout the distillation.
3. Preweigh another 50-mL 14/20 round bottom flask and record the mass below. When most of the original contents have distilled, turn off the variac, the rocker and the aspirator suction.
4. Disconnect the collection bulbs from the Kugelrohr oven. **The distilling flask will be very hot so handle with thermal gloves.** Add a pipet full of chloroform

to the collection bulb containing the distillate. Swirl it around and collect the solution in the preweighed 50-mL round bottom flask. Repeat with another pipet full of chloroform.

5. Remove the chloroform on the rotary evaporator. Once all the chloroform has been removed, let the distillate cool and white crystals of octadecanethiol should start to form. Once it is cool enough to handle, reweigh the 50-mL 14/20 round bottom flask with the product in it and record its mass in Table 1.

Part II: Silver Mirror Formation and Comparisons

A. Preparing Active Silver Solution

In the fume hood:

1. Add 10.0 mL of 0.1 M AgNO₃ to 50-mL flask
2. Add 15 M NH₄OH dropwise. A precipitate will initially form. Continue adding drops of NH₄OH until this precipitate is dissolved (~9 drops).
3. Add 5.0 mL of 0.8 M KOH to the flask. Another precipitate will form.
4. Add NH₄OH dropwise until this precipitate dissolves (~7 drops).

B. Formation of the "Silver Mirror" on Glass Plates

1. Obtain and clean two 10 x 10 cm glass plates with water and acetone
2. Place 500 µl of 0.5 M glucose in the center of each of the glass plates as evenly as possible
3. On top of this, add 1500 µl of the active silver ion solution to each plate (this can be done with two 750 µl portions of solution). A grey precipitate will start to form.
4. Release the tip of the micropipetter and use it to stir the two solutions together.
5. Wait five minutes. Carefully bring glass plates to the sink and rinse them off with water followed by acetone. This solution will stain your hands, so gloves are recommended.
6. To facilitate drying, use a hot air blower on low heat on each plate for about 15 seconds.

****C. Preparing Octadecanethiol and Octadecanol Solutions**

1. Obtain two Wheaton 5-mL vials, and weigh out 0.002 g (nearest 0.001 g) of the synthesized octadecanethiol into one.
2. Weigh out 0.002 g (nearest 0.001 g) of octadecanol into the other Wheaton 5-mL vial.
3. Add 5.0 mL of ethanol to each vial. Swirl contents to dissolve solid. If it is not readily dissolving, place a spin vane into the vial and set on magnetic stirrer for 30 seconds.

** Note: this step is only required if you have synthesized octadecanethiol. Otherwise materials will be prepared ahead of time, so you can proceed to part D

D. Formation of Monolayers and Comparison

1. If octadecanethiol and octadecanol solutions are pre-made, obtain 1-2 mL of each in small glass vials.
2. On one of the glass plates, add 5 drops of the octadecanethiol-ethanol solution to the center of the silver mirror.
3. Repeat above using the octadecanol-ethanol solution on the other glass plate.
4. Wait 2 minutes or until all the ethanol has evaporated from each plate (this is readily visible).
5. To each plate, add two separate drops of water to one side of the coated mirror. To the other side of each mirror, add 2 separate drops of decalin (see Figure 3). Use a magnifier to observe the contact angles between the drops and the surfaces. Are they wide, narrow, or non-existent? Write down any observations or illustrations in Table 2.

Figure 3. Silver Mirror Illustration

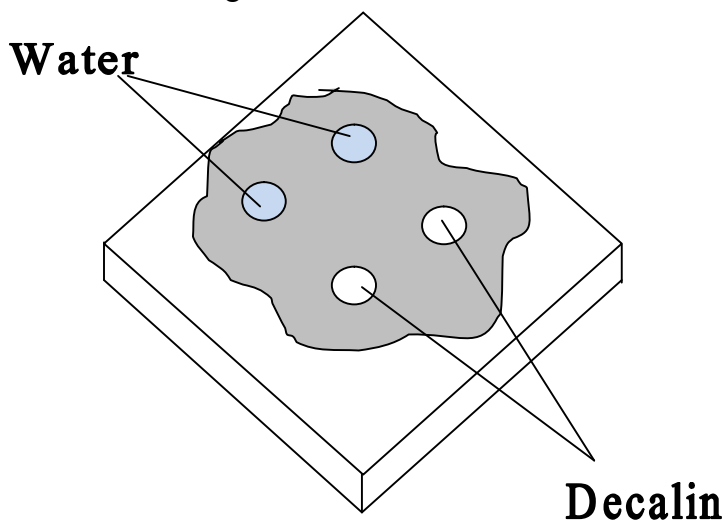


Table 1. Masses from Octadecanethiol Synthesis

| | |
|-----------------------------|--|
| Mass container + product | |
| Mass container | |
| Mass product | |

Table 2. Contact Angle Observations

| | Thiol Coated Silver | Alcohol Coated Silver |
|---------|---------------------|-----------------------|
| Water | | |
| Decalin | | |

E. Clean up

1. Once the experiment is completed, the silver-coated glass plates can be cleaned by submerging them in a glass container with enough 6 M HNO₃ to cover the surface completely. Wear gloves to remove the plates, and rinse them off with water followed by acetone.
2. All other solutions can be washed down the sink with plenty of water.

Questions

1. Calculate the percent yield of 1-octadecanethiol (MM = 286.55 g). Show all steps and formulas.
2. Using arrows for reactive electron pairs, illustrate the mechanism of nucleophilic attack used to produce the octadecanethiol (hint: S_N2 reaction).
3. During the octadecanethiol synthesis, 3 M HCl is added to the product flask prior to the washing and separation steps. What is the purpose of adding this acid?
(hint: side reaction $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{SH} + \text{NaSH} \rightleftharpoons \text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{SNa} + \text{H}_2\text{S}$)
4. In general, which has a wider contact angle—the water or the decalin? Explain in terms of polarity and hydrophobicity.

5. Describe the shape of the water droplets on the thiol-coated surface vs. the alcohol-coated surface. Between the monolayer of octadecanethiol and octadecanol, which repels water more strongly? Does this support the conclusion that thiols have a unique attraction to metal surfaces?

Note to teacher and TA:

1. The active silver solution has a temporary shelf-life, which is dimensioned greatly when the solution is exposed to air. To ensure it lasts for the duration of the lab, make sure students cover the flask with either parafilm or a stopper when the solution is not in use.
2. After the silver has been coated with either the thiol or alcohol, it can be rinsed with acetone, air dried and used again.

Pre-lab Preparation: Individual

A. 0.5 M glucose

Measure 0.90 grams of glucose in a 50-mL 14/20 flask and dissolve in 10 mL water

B. 0.8 M KOH

Measure 0.45 grams of KOH in a 50-mL 14/20 flask and dissolve in 10 mL of water

C. 0.1 M AgNO₃

Measure 0.17 grams AgNO₃ in a 50-mL 14/20 flask and dissolve in 10 mL of water

*D. 1-octadecanol-ethanol solution

Measure 0.008 g 1-octadecanol in a 50-mL 14/20 flask and dissolve in 20 mL ethanol

*E. 1-octadecanethiol-ethanol solution

Measure 0.008 g 1-octadecanethiol in a 50-mL 14/20 flask and dissolve in 20 mL ethanol, heating to dissolve all the solid if necessary

*Note: Parts D and E need only be done ahead of time if you do not plan on synthesizing octadecanethiol as part of the procedure.

Pre-lab Preparations: 25 students

A. 0.5 M glucose

Measure 3.6 g of glucose in a 50-mL 14/20 flask and dissolve in 40 mL water

B. 0.8 M KOH

Measure 6.75 g of KOH in a 250-mL 14/20 flask and dissolve in 150 mL of water

C. 0.1 M AgNO₃

Measure 5.1 g AgNO₃ in a 500-mL 14/20 flask and dissolve in 300 mL of water

D. 1-octadecanethiol-ethanol solution

Measure 0.016 g 1-octadecanethiol in a 50-mL 14/20 flask and dissolve in 40 mL ethanol

E. 1-octadecanol-ethanol solution

Measure 0.016 g 1-octadecanol in a 50-mL 14/20 flask and dissolve in 40 mL ethanol, heating if necessary to dissolve all the solid

Supplies for 10 students

10.0 g 1-bromooctadecane

5.0 g of NaSH

0.3 L of ethanol

0.2 L of 3M HCl

0.3 L of chloroform.

20.0 g of Na₂SO₄

0.10 L of 0.1 M AgNO₃

20.0 mL of 15 M NH₄OH

50.0 mL of 0.8 M KOH

20 10 x 10 cm glass plates

10.0 mL of 0.5 M glucose

0.10 g of octadecanethiol

0.10 g of octadecanol

10.0 mL of decalin

1.0 L 6 M HNO₃

Suggestion for Placement:

This experiment deals with new methods of synthesizing that are not commonly used in entry level organic chemistry (i.e. Kugelrohr distillation), and would therefore be better suited for an advance organic chemistry lab.

Questions regarding lab:

It is understood that thiols have a particularly strong attraction to metal surfaces, and will form a self-assembled monolayer, lining up on the surface of the metal with the tail end of the molecule pointing outward at a 30 degree angle away from the surface. However, in any of the text or sources looked at, there is no explanation given as to why the sulfur in a thiol group can react with the metal in this way. What are the characteristics of sulfur that allow it to behave this way, and has a mechanism for this reaction been discovered?

In continuation of the previous question, the analog alcohol to the thiol used in this experiment was used to coat the surface of silver. Both oxygen and sulfur are in group 16 of the periodic table, and share similar chemical bonding properties, so the thought was that both the coated surfaces would behave similarly. Both repelled the water, but the thiol-coated surface had a much wider contact angle. I assumed that unlike the thiol, the alcohol did not form a self-assembled monolayer on the surface of the silver, but that the molecules are less organized. My question is what characteristic differences between the oxygen in the alcohol and the sulfur in the thiol can account for this observation?

Answer Key

1. Calculate the percent yield of 1-octadecanethiol (MM = 286.55 g). Show all steps and formulas.

Theoretical yield

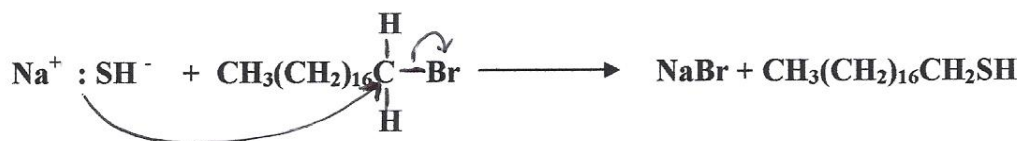
$$1.00 \text{ g bromo} \left(\frac{1 \text{ mol bromo}}{333.38 \text{ g bromo}} \right) \left(\frac{1 \text{ mol thiol}}{1 \text{ mol bromo}} \right) \left(\frac{286.55 \text{ g thiol}}{1 \text{ mol thiol}} \right) = 0.860 \text{ g thiol}$$

Actual yield = 0.700 g (for example)

% Yield

$$\left(\frac{\text{Actual}}{\text{Theoretical}} \right) \times 100 = \left(\frac{0.700 \text{ g}}{0.860 \text{ g}} \right) \times 100 = 81.4 \%$$

2. Using arrows for reactive electron pairs, illustrate the mechanism of nucleophilic attack used to produce the octadecanethiol (hint: S_N2 reaction).



3. During the octadecanethiol synthesis, 3 M HCl is added to the product flask prior to the washing and separation steps. What is the purpose of adding this acid? (hint: side reaction $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{SH} + \text{NaSH} \rightleftharpoons \text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{SNa} + \text{H}_2\text{S}$)

During the reaction, excess sodium hydrosulfide could react with the wanted product, 1-octadecanethiol, to produce octadecanethiolate. By adding acid to the product, the equilibrium of the thiolate reaction would shift to the reactant side (left) to produce more of the wanted thiol.

4. In general, which has a wider contact angle—the water or the decalin? Explain in terms of polarity and hydrophobicity.

The water has a wider contact angle than the decalin. The surface of each coating is non-polar, meaning that it is hydrophobic and will repel polar substances like water, which creates a wider contact angle. Unlike water, decalin is non-polar and it is attracted to the surface, which creates a narrow contact angle.

5. Describe the shape of the water droplets on the thiol-coated surface vs. the alcohol-coated surface. Between the monolayer of octadecanethiol and octadecanol, which repels water more strongly? Does this support the conclusion that thiols have a unique attraction to metal surfaces?

Water is repelled on both the thiol-coated and alcohol-coated surfaces, and the drops are rounded on each surface. However, the thiol-coated surface's water drops are almost completely beaded up (very wide contact angle), where as the alcohol-coated surface's water drops are only slightly beaded. This would suggest that octadecanethiol repels water more strongly, supporting the conclusion that thiols have a unique attraction to metal surfaces.

Citations

Carey, F.A. (2006). *Organic chemistry* (6th ed.). Boston: McGraw Hill.

Lisensky, G. (2006). Octadecanethiol monolayer on silver. *Interdisciplinary Education Group*. Retrieved May 12, 2008, from <http://mrsec.wisc.edu/Edetc/nanolab/Agthiol/index.html>

Masterson, W. L., & Hurley, C.N. (2004). *Chemistry principles and reactions* (5th ed.). United States: Thompson Brooks/Cole.

Ulman, A. (1991). *An introduction to ultrathin organic films: from Langmuir-Blodgett to self-assembly*. Boston: Academic Press, Inc.