

Lab 7. Geometric Isomers

Prelab Assignment

Before coming to lab:

- Read this lab handout thoroughly and then answer the **pre-lab questions** at the end (i.e. pp. 9 – 10) of this lab exercise and be prepared to hand them in at the start of your lab period.
- This lab exercise does not require a report in your lab notebook. The report for this exercise consists of completing the attached Report pages (pp. 5 – 8) as you carry out the procedures on pp. 2 – 4.

Purpose

In this lab you will observe some of the physical properties (melting point and solubility in water) of two unknowns and then identify each unknown as either maleic or fumaric acid. You will then treat each unknown with heat and hydrochloric acid (HCl acts as a catalyst) to break the double bond (i.e. break the π -bond). The product that reforms after this treatment should be the more stable isomer. You will confirm this by testing the product's solubility in water.

Introduction

This experiment deals with the topic of isomerism. **Isomers** are chemical compounds that have the same chemical formula, but different chemical structure. A special type of isomerism, called *cis/trans* isomerism, may occur in molecules which possess a double bond. **Cis/trans isomers** are also called **geometric isomers**.

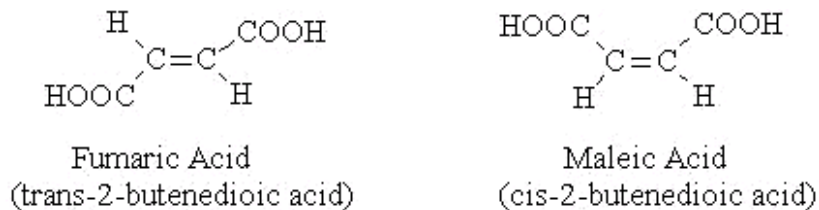
Why is geometric isomerism important? In many instances, the shift from one geometric structure to another turns out to have profound chemical or biochemical significance. The chemistry of vision provides an interesting example. As you may know from biology, the retina is our light detector at the back of the eye. Photoreceptor cells in the retina (rod cells) contain **11-cis-retinal**, a compound derived from **vitamin A**. When light reaches the retina, the cis-retinal compound rapidly flips into the trans-isomer, and the process gives out a signal to nerve cells and hence to the brain. Then, an enzyme catalyzes the reverse process by flipping trans-retinal back to the cis-isomer, ready for the next light signal. This is the role of cis-trans isomerism in vision.

Criteria for a compound to exhibit geometric isomerism

Geometric (cis-trans) isomers are compounds which have the same chemical formula but differ in the spatial arrangement of the groups that are attached to a double bond or to a ring. How does this come about?

- The molecule must have a double bond or a ring structure. There is free rotation around a single (sigma) bond, and restricted rotation around a double (1 sigma + 1 pi) bond. Therefore, groups which are attached to the carbon atoms of a double bond are held fixed on one side of the double bond or the other. A similar argument applies to a cyclic (ring) compound.
- The two groups attached to the first carbon atom involved (in a double bond or ring) must be *different from each other*. The other two groups attached to the other carbon atom must also be different from each other. Otherwise the two isomers will be indistinguishable!

To see *cis-trans isomerism* more clearly, look at the two molecules below:



Notice that the two molecules have identical chemical formulas—they are both $C_4H_4O_4$. The difference is in the way the atoms and groups are arranged around the double bond. In Maleic Acid, the *cis isomer*, the two *carboxylic acid groups*, $-COOH$, are on the *same side* of the double bond. In fumaric Acid, the *trans isomer*, the carboxylic acid groups are on *opposite sides* of the double bond and are connected to *different* carbon atoms.

Despite their similar chemical structure, maleic and fumaric acid are *different* compounds, with different chemical and physical properties. Some of the physical properties are summarized below.

	Melting Point (°C)	Solubility in water @ 25 °C (g/Liter H ₂ O)
Maleic Acid (cis-2-butenedioic acid)	139	788
Fumaric Acid (trans-2-butenedioic acid)	287	7

The molecules do not normally interconvert between the two structures because there is no free rotation about the double bond. Additionally, one of the two structures is usually more stable because there is less *steric hindrance* (i.e. less crowding) between the functional groups of atoms. *Which isomer would you predict to be the more stable molecule, maleic or fumaric acid?* Although the double bond is fairly strong, the π -bond can be broken with the input of energy—we will use heat as the source of energy and enlist the help of a *catalyst* to speed up the reaction. When the π -bond reforms, it will do so in a way that gives the most stable geometric isomer that minimizes steric hindrance.

Procedure (Work in Teams of Two)

Part 1. Observing the Physical Properties of the Unknowns A and B

1. Test the relative melting points of **unknowns A and B** by placing approximately equal amounts of each unknown (about the size of a pea) in two separate test tubes. The unknowns are maleic and fumaric acid.
2. Place each test tube in a test tube holder and warm both samples over a Bunsen burner. Be sure to heat gently (the flame of a properly adjusted Bunsen burner has a temperature of about 800 °C!), by waving each test tube *over* the flame—i.e. **Do not heat either of them directly in the flame.** Record your observations in table 1 noting which sample melts first. After this test, you should be able to predict which compound is which.
3. Empty the contents of each tube into the waste container under the hood.
4. Test the solubility of each unknown by placing approximately equal amounts of each unknown (about the size of a pea) in two separate test tubes. Add about 2 mL of DI water to each tube and shake vigorously. Record your observations in table 1 and note the relative solubilities of each unknown. **At this point you should know the identity of each unknown!**

Part 2. Breaking the Double Bond in an Isomerization Reaction

1. Set up an hot water bath by adding 200 mL water to a 400 mL beaker and placing on an electric hot plate. Allow the water to come to a boil. Meanwhile, while the water bath is warming up...
2. *Accurately* weigh out about 1.0 g of the *more soluble* compound (record the mass in [table 2](#) to $\pm 0.001\text{g}$) and add it to a clean 125 mL Erlenmeyer flask (it's O.K. if the flask is a little wet).
3. Use a small graduated cylinder to add 10 mL of DI water to the flask. Gently swirl the flask to dissolve as much of the solid as possible. Any undissolved solid will dissolve when the solution is heated.
4. Take the flask to the HCl dispenser under the hood and use the pipette pump to add 10 mL concentrated HCl (i.e. 12 M HCl). HCl acts as a *catalyst* in the isomerization reaction.

**Caution!!! Concentrated HCl is extremely Hazardous—
It's Corrosive and Burns the Skin!
Use Gloves and Wear Goggles at all Times!**

5. Set up the isomerization apparatus as shown in [figure 1](#).
 - Insert into the flask a one-hole stopper with a long glass tube to act as a reflux condenser to trap and limit the escape of gaseous HCl while heating.
 - **Caution!** After the isomerization reaction the reflux condenser will be contaminated with concentrated HCl.
 - Rinse the reflux condenser with water in the sink immediately after removing it from the flask at the end of the isomerization reaction.
 - Clamp the neck of the flask to a ring stand
 - Submerge the flask slightly in the boiling water.
6. Allow gentle heating for 10 minutes. Then turn off the hot plate. Record your observations during the course of the reaction in [table 2](#).
7. Remove the flask from boiling water and allow it to cool for 10 minutes.
8. While you wait for the flask to cool...
 - Set up an ice bath in a 400 mL beaker and begin cooling 20 to 25 mL of DI water.
 - Carry out [steps 2- 4](#) above with the other unknown—**stopper the flask to prevent the release of HCl gas into the room.**
9. After the flask ([in step 7](#)) has cooled for 10 minutes place it in the ice bath. ([Why do we do this?](#))



Figure 1. Experimental set-up for the isomerization reaction.

10. While the flask containing the reaction product is cooling in the ice bath, prepare the apparatus for suction filtration as shown in [figure 2](#). Connect the hose to a vacuum line. You must **clamp the flask**, and keep it clamped throughout (otherwise the funnel or the flask, or both, will tip over and break!).
11. Carry out suction filtration as follows:
 - Weigh a piece of filter paper of correct size (record the mass in [table 2](#)) and place it in the Büchner funnel. Use a squirt bottle to wet the filter paper with distilled water and make it snugly fit over the holes.
 - Turn on the vacuum.
 - Hold the cooled reaction flask and swirl it before rapidly pouring its contents onto the filter paper in the Büchner funnel. Your isomerization product is the solid that collects on the filter paper.
 - Add 5 to 10 mL of ice cold DI water to the 125 mL flask, swirl to dislodge any remaining solid product and then pour into the Büchner funnel.
12. Wash the solid on the filter paper with another 5 to 10 mL of ice cold DI water—why use ice water? (*Hint*: see the solubility data in the table on page 2.) Continue suction for another five minutes to dry the solid. While the solid is drying...
 - Repeat the isomerization reaction with the other unknown—i.e. repeat [steps 5 – 13](#) with the unknown having the lowest solubility in water.
13. After at least 5 minutes of drying, remove the filter paper and product from the funnel. Weigh the filter paper and product in a plastic weighing boat of known mass. After weighing, label the boat so that you remember which sample is which. Record the mass and your observations about the appearance of the product in [table 2](#).
14. Test the solubility of both samples by placing approximately equal amounts of each product in two separate test tubes. Add 2 mL of deionized water to each tube and shake vigorously. Record your observations in [table 2](#).
15. **Clean-up**: Place your unknown samples and the filtrate from suction filtration in the waste containers under the hood.
 - **Caution!!** The filtrate and the reflux condenser each contain concentrated HCl!! After emptying the filtrate into the waste container, rinse the Büchner flask and the reflux condenser with copious amounts of tap water and flush down the drain. Use DI H₂O for the final rinse.



Figure 2. Büchner funnel set-up for suction filtration.

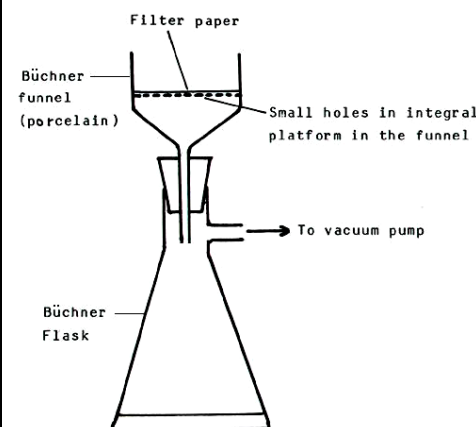


Figure 3. How does suction filtration work? The vacuum pump creates *reduced air pressure inside the flask*. Since the atmospheric pressure outside the flask is greater than the air pressure inside the flask, the material in the funnel is pushed through the filter paper from above. This speeds up the filtration process.

Lab 7 Report Sheet – Chem 162
Geometric Isomers

Name _____
Team No. ____ Date _____ Section _____

Experimental Results (Use a *pen* to record all data and observations!)

Table 1. Observations of the physical properties of unknowns A and B in part 1 of the procedure.

Compound	Observations	
	Heating over a Bunsen burner flame	Unknown and a few mL H ₂ O
Unknown A		
Unknown B		

Table 2. Observations of unknowns A and B during and after the isomerization reaction (part 2 of the procedure).

Data and Observations	Unknown ____ (the more soluble unknown)	Unknown ____ (the least soluble unknown)
Name of the Unknown Compound		
Initial mass of unknown (g)		
Mass of Product and filter paper and boat (g)		
Mass of filter paper (g)		
Mass of weighing boat (g)		
Mass of product (g)		
% Yield		
Observations <i>during</i> the Isomerization Reaction (e.g. Appearance of the <i>Unknown</i> and any other noteworthy observations.)		
Observations <i>after</i> the Isomerization Reaction (e.g. Appearance of the <i>isomerization product</i> and any other noteworthy observations.)		
Observations of the Solubility Test of the Isomerization Product in water		

4. a.) Calculate the % *yield* for *each* isomerization reaction involving each unknown. Show your work below using units and sig. figs. Circle your answers and record the results in [table 2](#)

Unknown A:

Unknown B:

- b.) Discuss the % yields for unknowns A and B and give likely reasons that accounts for your % yields being either over or under 100%.

- c.) Compare the % yield for the isomerization reactions involving unknowns A and B and explain any differences.

5. Which is the **more stable isomer**, maleic or fumaric acid? Why is it the more stable isomer? Explain using specific experimental evidence obtained in this lab activity.
6. Draw a complete **3-D Lewis structure for Maleic Acid**. Label the geometry, bond angle and hybridization at all carbon and oxygen atoms.
7. Compare the relative **molecular polarity** of maleic and fumaric acid—i.e. which isomer is more polar? Explain your reasoning, using words and both chemical structures (label the polar bonds with $\delta+$ and $\delta-$ in each structure). Then discuss specific experimental evidence that supports your choice of the most polar isomer.
8. Make a diagram or sketch showing how the C=C double bond is formed by the overlap of sp^2 and unhybridized p-orbitals. In your diagram, identify the sigma (σ) and pi (π) bonds.

Lab 7. Geometric Isomers
Prelab Questions

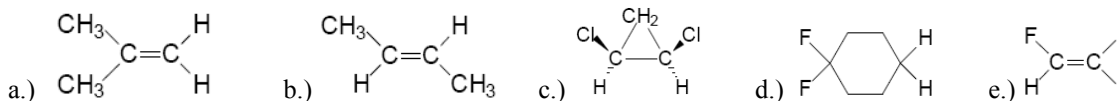
Name _____
Section _____ Team # _____

Instructions: Complete the following questions and hand in at the start of your lab period or when instructed by your instructor. Show your work with units and correct significant figures for all questions that involve a calculation.

- What mass in grams of each isomer (i.e. maleic and fumaric acid) would you expect to dissolve in 10 mL of water at room temperature (e.g. ? Show your work below using units and correct sig. figs. Circle your answers.
 - Maleic acid
 - Fumaric acid
- What two special experimental conditions will be used to facilitate the isomerization reaction? List each condition below and the role each plays in facilitating the isomerization reaction in [part 2](#) of the lab.
 - _____ Role it plays:
 - _____ Role it plays:
- Starting with 1.00 gram of the more soluble isomer in [step 2 of part 2](#) of the procedure, what is the maximum mass of the other isomer you could get in the reaction? Explain your answer. (Hint: Compare the two chemical formulas)
- Draw the structure of maleic and fumaric acids.
Maleic acid: _____ Fumaric acid: _____
 - Which would you predict to be the more stable isomer? Explain.

5. The solid on the filter paper is washed with ice cold DI water in [step 12](#) of the procedure in part 2. Why use ice water? What is the disadvantage of using DI water at room temperature?

6. Some but not all of the compounds below are capable of geometric isomerism. Circle all structures below that are capable of geometric isomerism.



7. Two compounds are named below. In each case, draw the 3-dimensional chemical structure and then decide whether or not the compound can have geometric isomers (i.e. cis – trans isomers).

a.) **1,2-dichlorobutane:** Geometric isomers? **Yes** or **No**? (Circle your choice and explain your reasoning below.)

Hint: Recall that alkanes have the general formula, C_nH_{2n+2} , and that $n = 4$ for butane.

b.) **2-butene:** Geometric isomers? **Yes** or **No**? (Circle your choice and explain your reasoning below.)

Hint: Recall that alkenes have the general formula, C_nH_{2n} , and that $n = 4$ for butene.

8. Label the geometry, bond angles and hybridization at each carbon atom of the structures in [questions 7a and 7b](#), above.