Catalytic Hydrogenation of Cyclohexene

http://en.wikipedia.org/wiki/Hydrogenation
http://en.wikipedia.org/wiki/Gas_chromatography
Write-up for this lab to be completed on 10/20 and 10/23

Reagents and Equipment

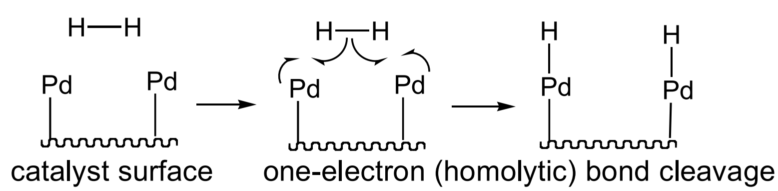
Cyclohexene (1-2 mL)
10% palladium on carbon (100 mg)

Test tube
Open tube (as air condenser)
Boiling chips
Sand bath
Cotton wool
Disposable pipettes

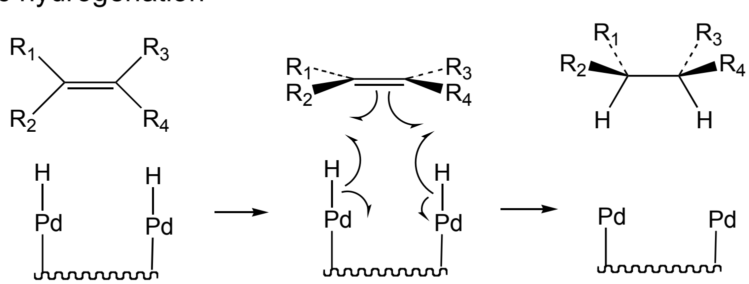
Purpose

This lab will introduce the technique of gas chromatography for the analysis of volatile product mixtures. The reaction that we will explore is the catalytic hydrogenation of an alkene. The general scheme for catalytic hydrogenation of an alkene is shown below. H_2 adsorbs to the catalyst, and the binding of hydrogen atoms to the palladium weakens the H-H bond to the extent that hydrogen atoms are available for addition to double bonds. Notice that the hydrogen adds *syn* (same side) across the double bond. Consequently we can predict the stereochemistry of the product(s) of this reaction with confidence.

Step 1. Adsorption of hydrogen

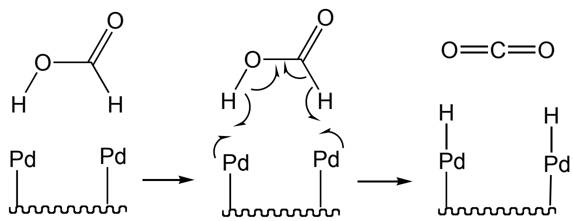


Step 2. Catalytic hydrogenation

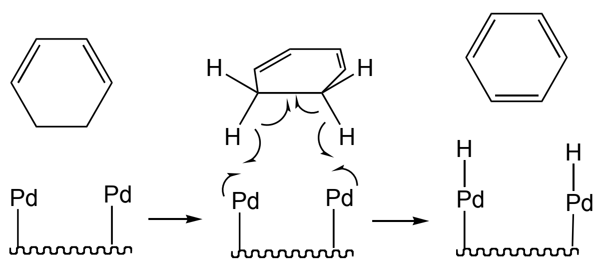


In the reaction above, the source of hydrogen is molecular H_2 gas. This is not always convenient, and other molecules can be used as the source of H_2. Common examples are 1,3-cyclohexadiene and formic acid.

Formic acid:

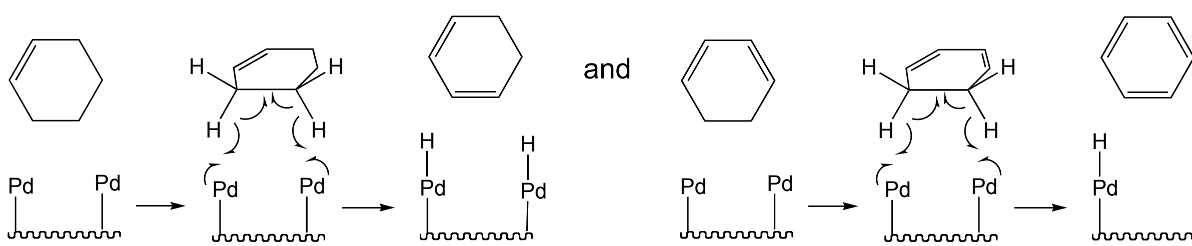


1,3-Cyclohexadiene

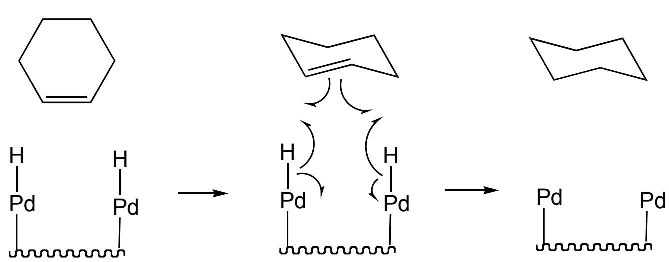


When non-H_2 sources are used, the reaction is called *transfer hydrogenation*: hydrogen atoms are transferred from a donor molecule to the reactant to be hydrogenated. The stability of the oxidized donor molecule drives the dehydrogenation. Benzene and CO_2 are both much more stable than 1,3-cyclohexadiene and formic acid, respectively. In this lab we will use cyclohexene as the hydrogen donor in the transfer hydrogenation of… cyclohexene! The reaction occurs as follows:

Adsorption of hydrogen



Catalytic hydrogenation



There are 3 possible products from this reaction: unreacted cyclohexene, the hydrogenated product (cyclohexane) and the oxidized hydrogen donor (benzene). We will use gas chromatography (GC) to identify the relative amounts of each.

GC is based on the partition equilibrium of analyte between a solid stationary phase and a mobile carrier gas (most often Helium). The stationary phase is packed inside a long coiled tube. The stationary phase may be hydrophilic (e.g. silica), in which case polar molecules will be retained more strongly than apolar molecules, or it may be hydrophobic (e.g. a liquid silicone-based material), in which case apolar molecules will be retained more strongly. As its name suggests, the technique only works for samples that are stable in the gas phase at elevated temperatures. The high temperatures used in GC make it unsuitable for high molecular weight, or thermally unstable analytes. The GC has a detector that reports the presence of eluting analytes, and the signal from the detector is relayed to a chart recorder as peaks in a chromatogram.

Experimental Procedure

1. Weigh approximately 100 mg of Pd/C catalyst and place in a clean, dry test-tube. Add 1 – 2 mL of cyclohexene to the test-tube and add one or two boiling chips.
2. Attach an air-condenser to the test-tube. This is an open-ended tube around which is wrapped a wet paper towel. The wet towel is held in place around the air condenser using a test-tube holder. The air condenser is attached to the test-tube using a rubber stopper.
3. Clamp the assembly to a ring stand and place the bottom of the test-tube in a sand bath. Turn on the variac controller and boil the reaction mixture for 15 minutes.
4. After 15 minutes remove the heat and allow the reaction to cool to room temperature.
5. Filter off the catalyst using a cotton-wool plug in a disposable pipette. Use a pipette bulb to blow the reaction solution through the plug into a pre-weighed sample vial. Record the weight of the product mixture, and cap and label the vial.
6. Take a GC of your product mixture. Cyclohexane elutes first, then cyclohexene, and benzene elutes last.

Write-up

Use the peak areas in the chromatogram to report the yield as a percent conversion of cyclohexene to products. Does your chromatogram accurately reflect the stoichiometry of the reaction? Predict the products of this reaction if you were to use 3,3,4,4,5,5,6,6-octadeuterocyclohexadiene as the starting material (deutero compounds have hydrogen atoms substituted for deuterium, atomic symbol D).

Waste disposal

Catalyst that is wet with organic liquids is flammable. Rinse your catalyst residue into the appropriate waste container with acetone. Product mixtures are flammable and should be disposed of in the appropriate waste container. Pipettes containing catalyst should be disposed of as solid waste and collected in a container in a hood.

Safety

Your pre-lab should include a comprehensive safety assessment of all the solvents and chemicals used in this lab. The sand-baths can get extremely hot, and will remain so after they have been turned off.