Catalytic Hydrogenation of Methyl Oleate


PreLab Exercise:

1. How many mL of H\(_2\) are required to reduce 3.5 mmol acetylene completely to ethane at STP?

Introduction:

Catalytic reduction is a very important and widely used industrial process; usually no harmful wastes are produced in the process. Catalytic hydrogenation and dehydrogenation are carried out on an enormous scale, for example, in the catalytic cracking and reforming of crude oil to make gasoline.

Nitrobenzene can be reduced catalytically to aniline with water the only by-product:

\[
3\text{H}_2 + \text{NO}_2 \xrightarrow{\text{Catalyst}} \text{NH}_2 + 2\text{H}_2\text{O}
\]

Styrene is made by the catalytic dehydrogenation of ethylbenzene at very high temperature, but it also can be hydrogenated back to ethylbenzene very easily. Palladium, as a catalyst, lowers the energy barrier for the reaction in both directions.

The addition of hydrogen to alkenes is one of the most common reactions. The alkene is more reactive toward this process than is the aromatic ring or functional groups such as esters or ketones.

Hydrogenation is stereospecific, so alkynes are reduced to cis-alkenes. The metal is usually supported on a high-surface-area material such as charcoal. The alkene and the hydrogen probably are both adsorbed onto the surface of the catalyst before the transfer occurs. This heterogeneous reaction, a reaction that involves reactants in the liquid or gas phase and a catalyst in the solid phase, is difficult to study.

In the present experiment, catalytic hydrogenation is carried out using hydrogen gas from an external supply to hydrogenate the unsaturated fatty acid methyl ester, methyl oleate, \(\text{1}\), to the corresponding saturated fatty acid ester, methyl stearate, \(\text{2}\).

It uses one of the most common commercially available noble metal catalysts, palladium, which is dispersed on activated carbon to provide a very large catalyst surface area. A large surface area is important because the carbon-carbon double bond interacts with the atomic hydrogen formed at the surface of the palladium metal. The one or two mg of Pd in the 20 mg of 5 or 10\% Pd on activated carbon used here has a much greater surface area of exposed palladium than if it was a 2 mg lump of foil or pure Pd metal. 5\% Pd/C costs about $3.00 to $4.00 per gram, but on a microscale, the cost to run this experiment is only a few cents.

The apparatus for hydrogenation has many different forms. If quantitative measurement of the hydrogen uptake is desired, the volume of hydrogen absorbed as a function of time can be measured can be followed as water rises in the hydrogen reservoir (a graduated cylinder) as shown below.
A simple and easy to construct apparatus for measuring the amount of hydrogen gas reacting with unsaturated organic compound.

If you merely want to hydrogenate a double bond and are not concerned about the quantitative aspects of the reaction, you can use a rubber balloon that holds the hydrogen. As soon as the balloon has reached a constant size, hydrogen uptake is over and the product can be isolated. This apparatus is shown below and is the type you will use in this experiment.

CAUTIONS:

Hydrogen gas is flammable and explosive as the typical freshman chem "popping balloon" demonstration effectively shows. The finely powdered 5 or 10% Pd on Carbon can catalyze the explosive reaction of hydrogen/air mixtures if it comes in contact with these mixtures as a dry solid or dust. Therefore, it is important to have the Pd/C powder suspended in a liquid to avoid an explosion or fire.

A freshly filtered catalyst is pyrophoric (spontaneously flammable in air), so do not dispose of the filter pipet immediately. Since the amount of catalyst used is so small, the chances of fire inside the pipet are quite remote, but care is warranted. Follow the instructions below carefully to minimize the hazards of handling hydrogen in this experiment.

Assembly and Testing of the Hydrogenation Apparatus:

Assemble the hydrogenation apparatus as shown above, but do not put anything into the flask except the 1/2" magnetic stirring bar. [Balloons are available from the Hooded shelves.]

Push a needle through the rubber septum and take the whole assembly to the hood at Desk 3 at the south end of Rm 215, where you will find a tank of H₂ with a pressure regulator attached as shown:
Check that the small needle valve on the \( \text{H}_2 \) regulator is closed (clockwise) and make sure the top main tank valve is open (counterclockwise). The low pressure gauge should not be reading over 10 pounds/in\(^2\). Attach the hose from the \( \text{H}_2 \) needle valve to the needle via a cut off syringe barrel, and slowly open the needle valve and blow up the balloon to a small diameter of 7-10 cm (3-4 in).

Close the needle valve, pull the needle out of the rubber septum and observe the size of the balloon over a period of 3 to 5 minutes. If there are no major leaks, the balloon should stay the same size for this time period. If it does not, try to locate the leak by immersing the seals in a pan of water and noting bubbling. If the rubber septum is leaking, replace it. If a connector is leaking, try another or wrap it with a rubber band or a few turns of copper wire tightened by twisting with a pair of pliers (available at the stockroom). A small amount of stopcock grease may also help. Once you are satisfied that your apparatus is "hydrogen-tight", proceed as described below.

**Synthesis:**

Remove the 5-mL flask from the apparatus. Blow out any residual hydrogen with nitrogen gas. Add 20 mg of 10% Pd on activated carbon (if you are doing 22.4, use 10% Pd on activated carbon) using your small plastic column funnel from your red kit. Weigh out 1 mmol of methyl oleate and dissolve it in 2 mL of methanol. Pour this solution into the flask containing the Pd/C making sure that you wash the Pd/C adhering to the plastic funnel and the sides of the flask into the bottom of the flask. Reattach the flask to the hydrogenation apparatus and take it back to the hydrogen tank. Purge air from the system by inflating the balloon with \( \text{H}_2 \) as described above, but instead of pulling the needle out of the septum, detach the hose from the needle so that the \( \text{H}_2 \) can leak out through the needle. Hold the apparatus inside the hood when you do this so the \( \text{H}_2 \) goes up the hood. Reattach the \( \text{H}_2 \) hose, reinflate the balloon, and then detach the hose again so the gas can escape. Repeat this purging a third time. By this time, the air should be fairly well purged from the apparatus. Re-inflate the balloon with \( \text{H}_2 \) one more time, but now pull the needle out of the septum so that the apparatus remains under the pressurized \( \text{H}_2 \) atmosphere. Back at your desk hood, stir the solution over a magnetic stirrer for 30 min. You may notice the balloon growing smaller as the \( \text{H}_2 \) is absorbed.
Isolation and Purification:

After 30 min, remove the flask from the apparatus and filter off the catalyst through a filter pipet as follows: Push a piece of cotton firmly into a Pasteur pipet that is clamped above a reaction tube or micro test tube. With a second pipet, transfer the reaction mixture into the filter pipet and allow the solution to filter through the cotton to remove the charcoal. If necessary, force the solution through the filter pipet with a rubber bulb. Rinse the reaction flask, stirring bar, and transfer pipet with a few drops of methanol and filter this solution also.

Allow the methanol to evaporate from the collection tube by leaving it open in your desk until the next lab period or blow off the methanol with a stream of nitrogen while warming the tube. The residue should be pure solid methyl stearate, which has a mp so low (40-42°C) that it will melt if held in a warm hand. Analyze your product by mp and as directed in your experimental assignment sheet.

Cleaning Up:

A freshly filtered catalyst is pyrophoric (spontaneously flammable in air), so do not dispose of the filter pipet immediately. Since the amount of catalyst used is so small, the chances of fire inside the pipet are quite remote, but care is warranted. Wet the catalyst with water, remove it from the pipet (this may require breaking the pipet) and place it in the recycled Pd/C container in the Hooded shelf. If oily, run liquid IR & also run methyl oleate for comparison.

Answer the following questions at the end of your report:

1. Predict the products from the Pd-catalyzed hydrogenation of the following. Show stereochemistry where important.

   ![Chemical Structures](image)

2. With respect to the volume of hydrogen that is consumed during complete hydrogenation, how could you distinguish between oleic acid, linoleic acid, and linolenic acid? (Use Aldrich to determine the structure of these naturally-occurring fatty acids.)

# Synthetic Experiment PreLab Grading Sheet

Name(s): ____________________________  
TA: ________________________________  
Date: ________________________________  

PreLab For Exp't #: 133  
Title: Reduction: Brown Hydrogenation of Methyl Oleate

<table>
<thead>
<tr>
<th>Date, Name, Desk #, Experiment # &amp; Title(abbreviated after 1st pg), Section &amp; TA Name</th>
<th>Possible Points</th>
<th>Missed Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
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<tr>
<td>Goals</td>
<td>8</td>
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<tr>
<td>Reactions, structures, conditions, diagrams</td>
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<td></td>
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<tr>
<td>Completeness of Chemical Data Table(s)</td>
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<tr>
<td>Chromatographic Behavior Comparison</td>
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<tr>
<td>Spectral Features Comparison</td>
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<td>Work-up - Explanation of the product isolation and purification process</td>
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<tr>
<td>PreLab Exercise</td>
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**TOTAL FOR PRELAB**: 100

Date Handed in: ________________

General Comments: ________________  

Total Points: ________________
Synthetic Experiment Final Report Grading Sheet

Name: ________________________________

TA: ________________________________

Date: ________________________________

Final Report For Exp't #: 133

Title: Reduction: Brown Hydrogenation of Methyl Oleate

<table>
<thead>
<tr>
<th>Name, Date, Experiment Title (abbreviated after 1st page) and every page numbered</th>
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<td>4</td>
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</tbody>
</table>

**OBSERVATIONS and DATA** - Overall organization, readability, completeness

| Data: Weighing data, molecular weights, moles, density, volumes, Rf’s. | 8               |              |
| Product analysis conditions i.e. weight of sample and KBr for IR; solvent and field strength for NMR; ionization mode for MS; solvent and wavelength range for UV/Vis, | 12              |              |

| Yield: Show % yield calculations with limiting reagent clearly stated. | 12              |              |
| Purity: Record melting points, color, TLC analyses or other indicators of purity. |                |              |

**RESULTS AND DISCUSSION** - Overall organization, readability, completeness

| Results; Achievement of goals | 8               |              |
| Product Analysis Data: Quality and Interpretation – Structure(s) drawn and interpreted on the product spectrum. | 16              |              |
| Interprett all NMR peaks (including impurities) or major IR or MS peaks. Explain how spectra confirm product identity. Discuss all UV/Vis λ_max in terms of conjugation. | 24              |              |

*See Lab Guide Chapter 3, Section 3.4 for guidelines in annotating spectra and Ch 11 for help with interpretation.*

**POSTLAB QUESTIONS**

| 16              |              |

**TOTAL POINTS**

| 100              |              |

Date Handed in: ________________________________

General Comments: ________________________________

Total Points: ________________________________