

An Undergraduate Organic Chemistry Laboratory: The Facile Hydrogenation of Methyl *trans*-Cinnamate

Kenneth J. O'Connor,* Kimberly Zuspan, and Lonnie Berry

Department of Chemistry, Marshall University, Huntington, West Virginia 25755, United States

*oconnor9@marshall.edu

Handheld, portable data-collection devices allow the real-time monitoring of chemical reactions by students in teaching laboratories. These devices are primarily marketed for high school and college-level general chemistry experiments, but developing labs for organic chemistry would greatly expand their usefulness at the college level. Many organic chemistry laboratory experiments could employ this technology, one of which is described here.

Hydrogenation of alkenes is an important reaction in the synthesis of organic molecules. There have been many reports in this *Journal* on the topic of catalytic hydrogenation experiments (1–23). Despite these reports, a hydrogenation experiment that meets the following criteria has yet to be developed for an undergraduate organic chemistry lab:

- A high-yield, microscale reaction that takes place at one atmosphere pressure.
- A reaction that takes place at room temperature and can be easily conducted within a 2 to 3 h lab period.
- A safe, convenient, inexpensive H₂ delivery system is used.
- A gas pressure sensor and a portable data-collection device are used to plot the hydrogen pressure versus time as the reaction progresses.
- Verification of the 1:1 relationship between the amount of hydrogen consumed and the amount of alkene hydrogenated.

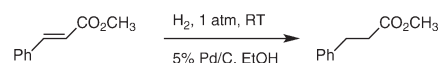
Given that typical laboratory sections usually contain 50 students, conducting a reaction that involves the generation of hydrogen gas is not practical. In addition, performing the reaction at elevated pressures or temperatures is not desirable. Development of an experiment satisfying the above criteria would provide students with an excellent opportunity to hydrogenate an alkene, coupled with an appropriate use of technology.

After experimenting with several alkenes, methyl *trans*-cinnamate was chosen for this experiment because it can be hydrogenated at room temperature in less than 1 h under an initial hydrogen pressure of approximately 1 atm (Scheme 1). This reaction was monitored using a gas pressure sensor connected to a Vernier LabQuest.¹ When the hydrogen pressure remains constant, one can conclude that the reaction has gone to completion (Figure 1). By using the ideal gas equation, the theoretical decrease in hydrogen pressure can be calculated and then compared to the experimental results.

Preparation of Hydrogenation Apparatus

The purchase of a gas pressure accessory kit (\$10) from Vernier facilitates assembly of the apparatus shown in Figure 2.

Scheme 1. Hydrogenation of Methyl *trans*-Cinnamate



Letter designations A through H are used in the following paragraph to refer to different parts of the apparatus depicted in Figure 2. A test tube (25 mm × 200 mm) is equipped with a #5 two-hole rubber stopper that contains a Luer-lock adapter (A) (adapter A, Tygon tubing C and the two-hole rubber stopper are included in the gas pressure accessory kit). A small spinning bar, 10 mg of 5% Pd/C, and 100 mg of methyl *trans*-cinnamate are added to the test tube. A small volume, 3 mL, of absolute ethanol is used to rinse any catalyst or alkene on the sides of the test tube to the bottom of the test tube. Hose-to-hose connector B is inserted in the stopper's second hole.² Luer-lock adapter A is attached to Tygon tubing C, which is equipped with Luer-lock fittings on both ends. The other Luer-lock fitting of Tygon tubing C is inserted into a short piece of rubber vacuum tubing D. A 20–30 cm piece of Tygon tubing E (3/16 in. i.d. × 5/16 in. o.d.) is attached to the hose-to-hose connector B.

Hose clamp F is placed on Tygon tubing E approximately 2 cm from hose-to-hose connector B. The hose clamp is tightened all the way. An 18 cm piece of Tygon tubing G (1/8 in. i.d. × 1/32 in. o.d.) is inserted into the two-hole rubber stopper so that it makes contact with Luer-lock adapter A. Note that Tygon tubing G does not make any contact with the ethanol solution. A balloon (H) filled with hydrogen gas from a hydrogen cylinder is placed on the other end of the rubber vacuum tubing.

Experimental Procedure

By opening the hose clamp slightly, the rate at which the test tube is purged with hydrogen can be controlled. If the end of Tygon tubing E is placed in a beaker of water, the hydrogen purge rate can be monitored and adjusted so that a constant stream of H₂ bubbles is observed. After purging the test tube for 3 min, the hose clamp (F) is closed completely. The gas pressure sensor is then connected to the LabQuest. The LabQuest is turned on and programmed by the students to collect data for 45 min. The Luer-lock connector of C is removed from the rubber vacuum tubing and is quickly connected to the gas pressure sensor. The test tube contents are stirred using a magnetic stirrer and data collection is immediately initiated. When there is no longer an appreciable change in hydrogen pressure, the alkene has been completely hydrogenated, as shown in Figure 1. Typical reaction times are between 30 and 45 min.

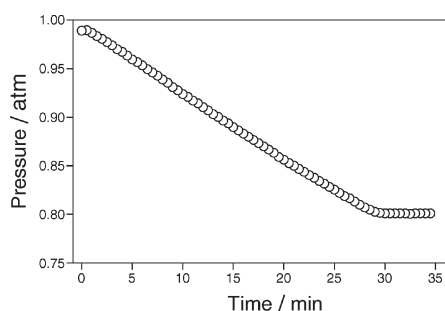


Figure 1. A graph of the hydrogen pressure versus time for the hydrogenation of methyl *trans*-cinnamate obtained by monitoring the reaction with a LabQuest.

At the end of the reaction, the catalyst is removed using a filtering pipet containing glass wool, sand, and Celite or by vacuum filtration using a Hirsch funnel containing Celite; vacuum filtration is the preferred method of filtration because it requires less time. The Celite is moistened with 2 mL of ethanol, followed by filtration of the test tube contents. The Celite is rinsed with 5 mL of ethanol and the filtrate is analyzed by thin-layer chromatography (TLC) by using Whatman silica gel TLC plates containing a fluorescent indicator, using a solvent mixture of 5% ethyl acetate/95% hexane.

The product is isolated by removing the solvent using a hot plate and a gentle stream of air supplied by an air hose connected to a glass pipet. After obtaining the mass of the product, have students obtain a ^1H NMR of the product in CDCl_3 . The ^1H NMR confirms that the product, methyl-3-phenylpropionate, was formed exclusively owing to the presence of the two new methylene resonances for the product; the vinyl proton resonances of the reactant are not present in the ^1H NMR of the product.³ Student yields are typically between 80 and 95%.

Hazards

Hydrogen gas is flammable and forms an explosive mixture with air. To minimize the possibility of an explosion, this experiment is conducted in a well-ventilated hood. In addition, the hydrogen cylinder used to fill the balloon is not kept near the students performing this experiment. After filtering the solution containing the 5% Pd/C catalyst, 2 mL of water is used to wash the filter pipet or the Hirsch funnel; the filter pipet or the Celite from the Hirsch funnel is then placed in a hazardous waste container. The 5% Pd/C is a flammable solid, therefore, sparks and open flames are not allowed to be used or generated during this lab. Ethyl acetate, hexane, and ethanol are volatile and flammable. Methyl *trans*-cinnamate and methyl-3-phenylpropionate are irritants. Celite is an irritant and harmful if inhaled, so it should only be used in a well-ventilated hood. Sand is not considered hazardous.

Results and Discussion

Most students obtain graphs similar to the graph in Figure 1. By using the initial and final pressure and the ideal gas equation, students determine whether the amount of alkene equals the amount of hydrogen consumed in this reaction. Using the ideal gas equation, the theoretical decrease in hydrogen pressure is 0.200 atm ($n = 0.000617$ mol alkene, $T = 293$ K, $V = 0.074$ L,

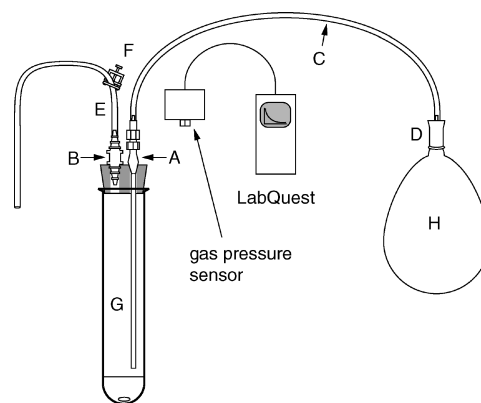


Figure 2. Apparatus used for the hydrogenation of methyl *trans*-cinnamate. The letters are described in the text.

$R = 0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}$).⁴ Students typically obtain a decrease in hydrogen pressure of 0.180–0.200 atm and, therefore, demonstrate that there is a good correlation between the decrease in hydrogen pressure and the amount of alkene used in this reaction.

It is interesting to note that if one performs several control reactions in which the test tube only contains hydrogen to test the hydrogen pressure maintenance, after 35 min, there is at most a 1.0% decrease in the initial hydrogen pressure. Therefore, the decrease in hydrogen pressure during the reaction with methyl *trans*-cinnamate is almost entirely due to the reaction of hydrogen with the alkene.

Conclusions

One of the advantages of this experiment is that students are able to perform a catalytic hydrogenation reaction using experimental conditions that are similar to those discussed in a first-semester organic chemistry course, namely, 5% Pd/C as a catalyst, H_2 initially at 1 atm, and the reaction is conducted at room temperature (24). Students are also able to learn a practical application of the ideal gas law in addition to determining the stoichiometry of the amount of alkene to amount of hydrogen in a classic hydrogenation reaction of a molecule containing a double bond. Comments from students after they completed this experiment are very favorable. Given that LabQuests are becoming more commonly used in chemistry departments, this experiment will serve as a nice addition to the labs that are currently being conducted in organic chemistry teaching labs.

Notes

1. The LabQuest (\$323), gas pressure sensor (\$83), and gas pressure accessory kit (\$10) can be purchased from Vernier. By using a TI84 calculator, Vernier Easy Link software (\$59), and the gas pressure sensor (\$83), this experiment can be conducted at a lower cost (prices from Jun 2010).
2. The 3/16 in. to 5/16 in. hose-to-hose connector can be purchased online from U.S. Plastics for \$1.28, part number 64110 (prices from Jun 2010).
3. The ^1H NMR of the alkene and the product of this reaction are in the supporting information.
4. Explanation of how these values were obtained is in the supporting information.

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Supporting Information Available

Student handout including pre- and postlab questions; instructor notes; ^1H NMR of the alkene and the product. This material is available via the Internet at <http://pubs.acs.org>.