

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

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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.

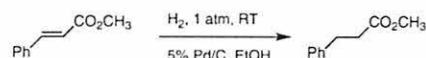
Given that typical laboratory sections usually contain 50 students, conducting a reaction that involves the generation of hydrogen gas is not practical. In addition, performing the reaction at elevated pressures or temperatures is not desirable. Development of an experiment satisfying the above criteria 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.

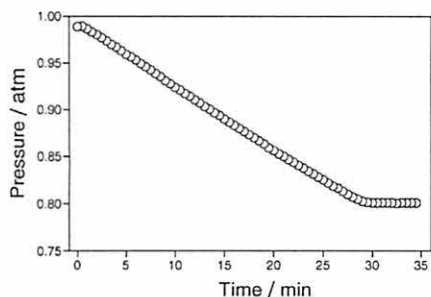


Figure 1. A graph of the hydrogen pressure versus time for the hydrogenation of methyl *trans*-cinnamate obtained by monitoring the reaction with a LabQuest.

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,

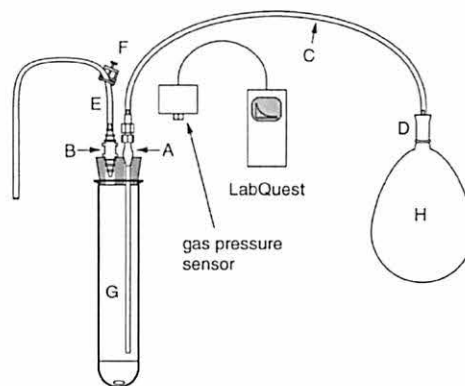


Figure 2. Apparatus used for the hydrogenation of methyl *trans*-cinnamate. The letters are described in the text.

$R = 0.0821$ atm L K^{-1} 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>.

The Solvent-less Hydrogenation of Unsaturated Esters using 0.5%Pd/Al(O)OH as a Catalyst

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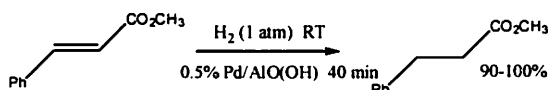
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Abstract: Catalytic hydrogenation is a common method used for the conversion of alkenes to alkanes. Typically these reactions are conducted in solution using a homogeneous or heterogeneous transition metal catalyst and a source of H₂. With the growing interest in green chemistry, it is desirable to provide students with the opportunity to conduct a green hydrogenation experiment. In this experiment, students use a 0.5%Pd/Al(O)OH catalyst to hydrogenate an alkene in the absence of solvent. This catalyst can be recovered without a loss in activity. The yield is virtually quantitative and the reaction is complete within 50 minutes at room temperature. This reaction exemplifies many of the principles of green chemistry and should be a nice addition to the experiments that undergraduates conduct in an organic chemistry lab (Scheme 1).

Introduction

Addition reactions are ubiquitous in organic chemistry. More specifically, the hydrogenation of alkenes to alkanes is a topic that is discussed in every organic chemistry textbook. The hydrogen source is usually from a balloon filled with hydrogen or catalytic transfer hydrogenation if the reaction is conducted at 1 atmosphere. One factor that these catalysts have in common is that they are typically used with a solvent. Our goal was to develop a green hydrogenation chemistry experiment for an undergraduate organic lab. By conducting a hydrogenation experiment in the absence of solvent, we would be one step closer to reaching this goal. Kim and coworkers reported that 2%Pd/Al(O)OH is a catalyst for solvent-less hydrogenation [1]. Methyl *trans*-cinnamate and dimethyl fumarate were two of the alkenes used in his experiments. We wanted to illustrate as many of the principles of green chemistry as possible in this hydrogenation reaction [2]. Several of these principles are:

1. The reaction between hydrogen and the alkene does not produce waste (by-products are not formed).
2. The hydrogenation reaction between hydrogen, alkene and catalyst is solvent-less.
3. A recyclable catalyst is used.
4. The reaction is conducted at room temperature and atmospheric pressure.
5. No derivatization is necessary.



Scheme 1. Hydrogenation of methyl *trans*-cinnamate.

It is important to note the difference between Kim's experimental conditions and our experimental conditions. Kim and coworkers reported that 2% Pd nanoparticles entrapped in an aluminum oxo hydroxy matrix (2% Pd /Al(O)OH) catalytically hydrogenated methyl *trans*-cinnamate in

essentially quantitative yield in 5 sec in the absence of solvent [1]. Since 2% Pd /Al(O)OH was not commercially available, it was decided to use commercially available 0.5% Pd/Al(O)OH and determine if similar results could be obtained. Our experimental results were essentially the same as Kim's, except the reaction times were approximately 40–50 minutes.

This experiment uses a hydrogen balloon as the hydrogen source [3]. Hexane is used to extract the product from the catalyst at the end of the reaction. By using thin layer chromatography of the filtrate, students can easily determine if the reaction has gone to completion. The product is obtained by rotary evaporation of the filtrate and the catalyst is recovered during filtration. Spectroscopic analysis by NMR and IR confirms that the alkene was hydrogenated.

After the reaction conditions were optimized, this lab was carried out by approximately 120 students working in pairs over a two year period. If the experimental procedure is followed, the reaction always goes to completion. Students have conducted this lab with yields ranging from 40–95%, with the average yield of 70–75%. Catalyst recovery is typically in the 50–75% range and the recovered catalyst has almost the same reactivity as the commercially prepared catalyst. The recovered catalyst can be recycled at least three times as determined by Kim, in addition to experiments conducted by my capstone student, Derek Fry.

One of the interesting features of this experiment is that initially this is a solid/solid/gas phase reaction. However, during the reaction, it was clear that an oil had formed and that this oil was coating the surface of the catalyst. In fact, the reaction became darker as the alkene was hydrogenated. Kim found a correlation between the melting point of the alkene and hydrogenation rates. Methyl *trans*-cinnamate, for example, has a melting point of 34°C and was one of the fastest alkenes to be hydrogenated. Kim has suggested that the heat released in the hydrogenation of the alkene enables the reaction to occur through a fused state [1].

In a hydrogenation experiment conducted earlier in the semester, students hydrogenated the same alkenes by using 5% Pd/C and therefore, readily observed the increase in waste that



Figure 1. The reaction mixture after purging with hydrogen.



Figure 2. Reaction mixture after 50 minutes.

the 5% Pd / C reaction produces. Not only can the catalyst not be recycled, but it also can produce additional waste since the reaction is filtered through Celite.

Hazards. Hydrogen gas is flammable and forms an explosive mixture with air. To minimize the possibility of an explosion, this reaction should be conducted in a well-ventilated hood. The hydrogen gas cylinder should be kept in a room different than the room in which the experiments are conducted. Methyl *trans*-cinnamate and 3-phenyl propionate are irritants. Hexane is flammable and must be kept away from flames. A MSDS for the catalyst has not been reported.

Experimental

This experiment uses microscale glassware. A piece of weighing paper (3"×3") is folded in half. One of the halves of the weighing paper is folded in half so a visible crease is seen in the middle of the weighing paper. The catalyst and alkene are placed carefully along the crease, and are well mixed using a pestle; this mixture is added to a 10 mL round bottom flask containing a stir bar. A rubber septum was inserted into the neck of the flask and a hydrogen balloon was used to purge the flask for 3 minutes [3]. After purging, the reaction was

stirred for approximately 40–50 minutes. Figures 1 and 2 illustrate the reaction at the beginning and after 50 minutes.

The septum was removed and three mL of hexane were added and stirred until most of the solids were suspended in the hexane. The heterogeneous solution was filtered using a Hirsch funnel, or preferably by using a propylene funnel with a polyethylene frit [4]. A TLC of the filtrate was taken to determine if the reaction has gone to completion; UV light and a solution of KMnO_4 are useful in this determination. A reaction that has gone to completion does not show a UV active spot or a yellow spot with the KMnO_4 staining solution. The hexane is removed using a rotary evaporator and the yield calculated. The catalyst is dried, weighed and the percent recovery calculated. The product is analyzed by NMR and IR. The atom economy, % atom economy and E factor are then calculated.

Results and Discussion

The application of the twelve principles of green chemistry to chemical reactions continues to grow exponentially. Over the last decade, significant progress in green chemistry research has been made. Given the fact that students will benefit by being exposed to green chemistry, the development of a green hydrogenation experiment was undertaken. Several of the twelve principles of green chemistry are illustrated in this hydrogenation reaction. One of the most important principles of green chemistry is to avoid the production of waste. Due to the fact that this reaction proceeds in quantitative yield, this principle is easily attained. Additional principles such as the use of a recyclable catalyst, running a reaction at ambient temperature and using no solvent are illustrated in this experiment.

$$\text{Atom Economy} = \left(\frac{MW_{\text{product}}}{\sum \text{mass}_{\text{reagent}}} \right) * 100\%$$

$$\% \text{ atom economy} = \left(\frac{\sum \text{mass}_{\text{reagent in products}}}{\sum \text{mass}_{\text{reagent}}} \right) * 100\%$$

$$\text{E factor} = \left(\frac{\sum \text{mass}_{\text{waste and byproducts}}}{\sum \text{mass}_{\text{product}}} \right) * 100\%$$

Scheme 2. Green chemistry metrics calculated by students.

This lab also provides students the opportunity to calculate atom economy, % atom economy and the E-factor (Scheme 2) [5]. The atom economy and % atom economy are 100% for this reaction. In terms of the mass of the waste, this would be mainly determined by the % recovery of the hexane. It is important to point out to students that a solvent-less reaction does not necessarily imply that no solvent is used in the synthesis of a molecule. In this case, solvent is used to separate the product from the catalyst. Therefore, efficiency of hexane recovery has a direct effect on the E-factor.

The set-up of this reaction is simple to assemble. If proper precautions are taken, the use of a hydrogen balloon as a hydrogen source for the reaction is not a problem. Students can discuss the other sources of hydrogen supply that one would consider for the hydrogenation of an alkene at an industrial scale such as catalytic transfer hydrogenation or the conversion of methane into hydrogen and carbon monoxide.

This experiment may be the first opportunity that students have to learn about green chemistry. Since many catalysts used in organic chemistry often become part of the waste, this experiment demonstrates to students this does not need to be

the case. All of the recovered catalyst is placed in a container so that it can be recycled.

Conclusion

Although the synthesis of organic molecules without a solvent may seem counter-intuitive to students, it is in complete agreement with many of the twelve principles of green chemistry. The hydrogenation of the two esters described in this experiment nicely illustrates several of the twelve principles proposed by Andraos and Warner [2]. This experiment promotes waste reduction, the use of a recyclable catalyst, conducting a reaction at ambient temperature and not using a solvent (solvent-less). The product is isolated from the catalyst using hexane and the % atom economy is 100%. The major source of waste in this experiment is inefficient recovery of hexane which has a deleterious effect on the E-factor.

Integrating one or two green experiments into the organic lab curriculum is not difficult to accomplish. The hydrogenation of unsaturated aldehydes and ketones is presently being studied for the purpose of assessing the full potential of Pd/Al(O)OH. Hydrogenation of additional alkenes [6], as well as the development of critical thinking labs using Pd/Al(O)OH, is currently under investigation. We are confident that this experiment will be a useful addition to the

already published greener hydrogenation experiments in the literature.

Acknowledgements. We thank Marshall University for financial support.

Supporting Materials. Student handout, instructor handout and NMR and IR of the products are available (<http://dx.doi.org/10.1333/s00897132487a>).

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An Undergraduate Organic Chemistry Laboratory Experiment: The Use of Thin Layer Chromatography to Monitor the Hydrogenation of Unsaturated Esters

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Abstract: Thin layer chromatography (TLC) represents a simple yet valuable technique employed by chemists for monitoring the progress of a chemical reaction. In most undergraduate organic lab courses, students conduct an experiment using TLC. For example, the reduction of benzophenone with NaBH₄ can be easily monitored by TLC in order to determine when the reaction has gone to completion. Unfortunately, virtually all of the experiments published in organic chemistry laboratory textbooks that incorporate TLC involve reactions that are conducted in an open atmosphere. Consequently, students do not learn how to use TLC to determine when a reaction has gone to completion for reactions that take place under an inert or gaseous atmosphere. A micro-scale hydrogenation experiment of unsaturated esters using 5% Pd/C has been developed to address this void in organic chemistry lab courses. This experiment enables students to master the use of thin layer chromatography to monitor the progress of a reaction conducted under a gaseous atmosphere. During pre-lab, a guided inquiry approach was used to teach students how to sample the reaction by using a 16 gauge (G) needle and a 30 μ L micropipette. Methyl *trans*-cinnamate and dimethyl fumarate were chosen as representative alkenes. Student yields were between 50–90% with an average yield of approximately 70–75%.

Introduction

The use of TLC to monitor a chemical reaction that is open to the atmosphere is often found in organic laboratory textbooks. However, if you ask most students how to use TLC to monitor a reaction in a closed system, it is quite likely that they will be unable to provide you with a plausible answer. In order to introduce students to TLC at the beginning of the semester, students reduced benzophenone to diphenyl methanol and monitored the reduction by TLC. Later in the semester, students hydrogenated methyl *trans*-cinnamate and monitored the progress of the reaction by using TLC (Figure 1).

One of the main challenges that students first encounter when monitoring a hydrogenation reaction is how to use a micropipette to sample reactions that are not open to the atmosphere? In other words, how is the micropipette able to pass through the rubber septum? Unfortunately, organic laboratory textbooks from publishers do not contain experiments that teach students how to monitor a chemical reaction of a closed system [1]. Over the past one and one-half years, our students have conducted the hydrogenation of methyl *trans*-cinnamate and dimethyl fumarate, successfully employing closed-system TLC monitoring techniques.

At the beginning of the pre-lab lecture, each pair of students assembled the hydrogenation apparatus for the reaction with limited guidance from the instructor (Figure 2). One of the goals of this experiment was to have students use critical thinking skills to a) provide a reasonable approach to taking a TLC of the reaction (a closed system) and b) to determine when the reaction has gone to completion by using TLC. It is important to remember that at this point in the semester,

students have only used 10 μ L micropipettes to sample a reaction for TLC (i.e., the reduction of benzophenone). In other words, students are not aware that sampling reactions under a gaseous atmosphere is easily accomplished by using a longer micropipette and an appropriately sized gauge needle.

Once the students have assembled their apparatus, a series of questions was asked by the instructor. The purpose of this guided inquiry part of the experiment was to provide students with an opportunity to use their critical thinking skills in order to propose a method to use TLC to monitor their hydrogenation reaction. An overview of their written responses follows:

- (a) Instructor: In the beginning of the semester you conducted a reaction in which benzophenone was reduced with sodium borohydride. How did you use TLC to monitor the reduction of benzophenone with NaBH₄?

We placed a 10 μ L micropipette into the solution and then spotted the TLC plate. The plate was developed using 20% ethyl acetate: 80% hexane. The TLC plate was analyzed by using UV light and a KMnO₄ stain.

- (b) Instructor: Look at the apparatus that you have assembled and determine how you would use TLC to monitor this reaction. Assume 3 mL of ethanol are in the RBF. The following were the most common responses:

a) "Use a syringe with an 18G needle to remove a sample of the reaction mixture for TLC and then spot the mixture using with a micropipette on the TLC plate."

b) "Stick the 10 μ L micropipette through the 18G needle and sample the solution."

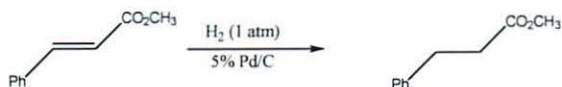


Figure 1. The hydrogenation of trans-methyl cinnamate using 5% Pd/C.



Figure 2. Hydrogenation apparatus assembled by students during pre-lab.

c) "I would insert an 18G needle through the septum to get a small sample of the reaction mixture. Then I would spot it on the TLC plate using a micropipette."

Although choice a) is an option, it is not the best option since the yield will continue to decrease due to repeatedly removing solution from the round bottom flask. Choices b) and c) are not plausible because neither the micropipette nor the syringe needle is long enough to reach the solution. (Figure 3).

At this point in the pre-lab lecture, each pair of students was given a 16G needle.

1. Instructor: After giving each pair of students a 16G needle, the following question was asked: Does having a 16G needle change your approach to using TLC to monitor this reaction?

No.

2. Instructor: A 30 μ L micropipette was then given to each pair of students. The last question asked was: How would you use TLC to monitor the reaction?

"After pushing the 16G needle through the rubber septum, insert the 30 μ L micropipette into the 16G needle until the tip of the micropipette touches the solution in the round bottom flask (RBF). Remove the 30 μ L micropipette and the 16G needle. Spot the TLC plate with the 30 μ L micropipette." The responses to this question were essentially identical for the class. (Figure 4).

It was clear that after the students were given the 30 μ L micropipette and the 16G needle, students were confident in their ability to monitor a hydrogenation reaction. The students were instructed to set up their reactions in the hood. As one student filled up the balloon with nitrogen, another student placed 100 mg of methyl *trans*-cinnamate, 3 mL of ethanol, 10 mg of 5% Pd/C and a stir bar in a 10 mL RBF. A septum was inserted in the flask and the flask was purged with nitrogen for 3 minutes, followed by purging with hydrogen for three minutes. (Figure 5) After purging the flask with hydrogen, the heterogeneous mixture was stirred.

Students typically used 3–5 TLC plates to monitor the progress of the reaction by using TLC. In their notebook, they drew pictures of their TLC plates after they were visualized by UV light and then stained using a solution of KMnO_4 ,

(Figure 6). By using UV light, students could readily determine if the alkene was completely hydrogenated since a UV active spot for the alkene would no longer be visible. In addition, when the TLC plate was dipped into a dilute solution of KMnO_4 , a yellow spot would be visible only for the unsaturated ester. Hence, the absence of a yellow spot after staining with KMnO_4 indicates the reaction has gone to completion.

Once the reaction has gone to completion as determined by TLC, the solution was filtered through Celite by using either a Hirsch funnel or preferably a polyethylene filter containing a 10 micron polypropylene frit [2]. The round bottom flask was rinsed using 3 X 1 mL of hexane. The filtrate was evaporated using a rotary evaporator. An IR spectrum and a NMR spectrum of the product were taken (see supporting information).

Hazards. Hydrogen gas is flammable and forms an explosive mixture with air. To minimize the possibility of an explosion, this reaction should be conducted in a well-ventilated hood. The hydrogen gas cylinder should be kept in a separate room. After filtering the solution and removing the filtrate, the Pd/Celite mixture is rinsed with 3 mL of water and the mixture placed in a hazardous waste container. Methyl *trans*-cinnamate and 3-phenyl propionate are irritants. Hexane, ethanol and ethyl acetate are flammable and must be kept away from flames. Celite is a lung irritant and harmful if inhaled; it should be used only in a well-ventilated hood.

Experimental

To a 10 mL round bottom flask (RBF) were added 100 mg of alkene, 10 mg of 5% Pd/C, and a stir bar. Three milliliters of ethanol were added to the RBF and a rubber septum was inserted into the neck of the flask. The RBF was purged with nitrogen using a nitrogen filled balloon (Figure 5). After purging for three minutes with nitrogen, the RBF was purged using a hydrogen filled balloon. By inserting a 30 μ L micropipette into a 16G needle, the reaction was monitored by TLC. The elution solvent was ethyl acetate (20%): hexane (80%).

Students typically sampled the reaction every 10–15 minutes until they determined that the reaction had gone to completion; the reaction time is typically 40–50 minutes. UV light and an aqueous solution of KMnO_4 were used to determine the absence of methyl *trans*-cinnamate. At the end of the reaction, the RBF was purged with nitrogen. The heterogeneous solution was filtered using a Hirsch funnel or a 10 micron propylene filter funnel containing a thin layer of Celite [2]. The RBF was rinsed with 3 X 1 mL of hexane and also filtered. The filtrate was concentrated by using a rotary evaporator and the product, an oil, was analyzed by NMR and IR. The percent yield is typically between 50–90 %. The Pd/C/Celite mixture was rinsed with 2 mL of water and placed in a hazardous waste container.

Results and Discussion

TLC is often used by organic chemists to monitor a chemical reaction. After examining several organic chemistry laboratory text books, it became clear that TLC was used as an analytical technique only for reactions that were open to the atmosphere. Even textbooks that were specifically written to teach organic chemistry laboratory techniques do not discuss

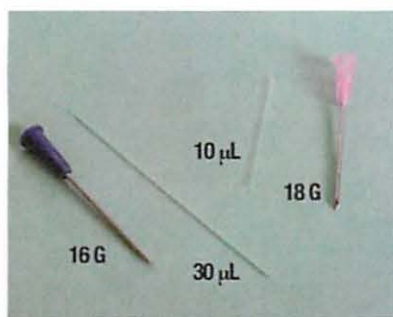


Figure 3. A comparison of the length of a 30 μL micropipette and a 10 μL micropipette.



Figure 4. The use of a 30 μL micropipette and a 16G needle to sample the reaction by TLC.



Figure 5. Purging of 10 mL RBF with N_2 followed by H_2 .

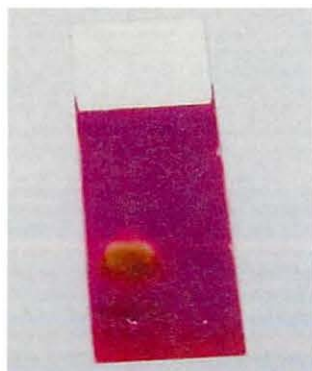


Figure 6. A TLC plate stained with KMnO_4 . Lane 1 was spotted at $t = 0$ min and lane 2 was spotted at $t = 40$ min. Methyl *trans*-cinnamate, in the left lane, is easy to visualize (yellow spot). The product, methyl-3-phenyl propionate, is in the right lane and does not react with KMnO_4 .

the use of TLC to monitor the progress of a reaction that is not open to the atmosphere [1]. Based on previous research conducted with my capstone students on the hydrogenation of unsaturated esters, I decided to develop an experiment that would teach students how to monitor a chemical reaction in a closed system [3].

One of the benefits of TLC is that it provides the researcher with the ability to determine when the reaction has gone to completion. Most experiments in undergraduate laboratory textbooks provide students with a detailed procedure and therefore, the use of TLC to monitor the reaction is not necessary. Experiments with detailed reaction procedures are often referred to as “cookbook” labs and greatly minimize the need for students to use critical thinking skills during the experiment. As Pickering stated in 1988, “Organic labs have degenerated into cooking. There is some sort of cosmic futility in most organic labs. Make a white powder, prove that it is what you expect, donate it to chemical waste, again, and again, and again” [4].

In the experiment presented in the student handout, students understood that they would be hydrogenating an unsaturated ester. However, they did not know how to monitor the progress of the reaction using TLC or the reaction time. Hence, this experiment is not your classic “cookbook” experiment. Students had to use critical thinking skills to determine how to sample a reaction under a hydrogen atmosphere and how to use that knowledge to monitor the progress of the reaction. Having students experience the value of thin layer chromatography to a chemist cannot be overstated, and this experiment achieves this objective.

The execution of this experiment could have been much simpler for the students and the instructor if the instructor had informed the students on how to monitor a hydrogenation reaction by TLC during the pre-lab part of this experiment. Unfortunately, the educational value of this experiment would have been minimized and they would have simply followed a “cookbook” experimental procedure. At the end of pre-lab, students were asked for their overall opinion of the experiment. Student feedback was very positive. A representative sampling of their responses is given in Table 1.

Conclusion

The application of TLC as an analytical tool for monitoring chemical reactions in an open atmosphere is usually mastered in most undergraduate organic chemistry lab courses. However, students are rarely given the opportunity to learn how to use TLC to monitor the progress of a chemical reaction under a gaseous atmosphere such as an inert gas or hydrogen gas. By using a guided inquiry approach, students came to the conclusion that by inserting a 30 μL micropipette into a 16G needle, the hydrogenation of methyl *trans*-cinnamate could be monitored by TLC (Figures 4 and 6). Students hydrogenated methyl *trans*-cinnamate in 50–95% yield with an average yield of approximately 70–75% [5]. This experiment has been conducted for the past one and one-half years. Student feedback for this experiment was very favorable and many students enjoyed the break from performing “cookbook” experiments. Ideally, this experiment will be adopted by other instructors for the development of critical thinking laboratory skills of undergraduates enrolled in an organic chemistry laboratory course.

Table 1. Students' comments of the lab experiment after pre-lab lecture

Response #	Student's Comments
1	Better than a pre-lab lecture and better than following the directions from the book.
2	It was empowering to know that I have a functioning chemistry-focused, problem solving brain.
3	Super awesome, it made me think; it frustrated me at first because I was confused but it then clicked.
4	Figuring out procedures by exercise increases understanding of the procedure and retention of the concepts covered rather than the simple "trained monkey" procedure of doing what is told in a lab manual.
5	It is much more interactive than the traditional method of using a lab-manual. I found it much more valuable to think and discuss the lab than the traditional method which is akin to following a recipe in a cookbook.
6	I think this is a useful experiment to know how to conduct a gas related experiment.
7	This is an A+ lecture & experiment!
8	It's a lot more interesting figuring out parts of the procedure on our own instead of following a written procedure specifically.
9	Majestically. Like I could conquer all of Organic Chemistry.
10	I feel that I just had a learning experience. I feel better that I was able to learn from our trial and errors, in order to create an apparatus suitable for this reaction to occur appropriately.
11	I feel like this was the first time I have understood an experiment BEFORE doing it.

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Supporting Materials. The proton NMR and IR spectra of methyl 3-phenyl propionate, a student handout and instructor notes are included in the supporting materials (<http://dx.doi.org/10.1333/s00897132509a>).

References and Notes

- These are just a few laboratory textbooks reviewed for experiments in which the reaction was not open to the atmosphere: (a) Zubrick, J. *The Organic Chem Lab Survival Manual: A Student's Guide to Techniques*, 8th ed.; Wiley: New York, 2012. (b) Padias, A. *Making the Connections 2: A How-To Guide for Organic Chemistry Lab Techniques*, 2nd ed.; Hayden-McNeil: 2011. (c) Pavia, D.; Kriz, G.; Lampman, G.; Engel, R. *A microscale approach to organic laboratory techniques*, 5th ed.; Brooks/Cole: 2012. (d) Lehman, J. *The Student's Lab Companion: Laboratory Techniques for Organic Chemistry*, 2nd ed., Prentice Hall: 2008. (e) Lehman, J. *The Student's Lab Companion: Laboratory Techniques for Organic Chemistry*, 2nd ed., Prentice Hall: 2008. (f) Williamson, K. *Macroscale and Microscale Organic Experiments*, 2nd ed., Heath: 1994. (g) Mayo, D.; Pike, R.; Forbes, D. *Microscale organic laboratory*, 5th ed., Wiley: 2011.
- A propylene filter funnel, 18mL, 10 micron polyethylene frit (OP-6602-6610) can be purchased from Chem Glass. (https://acs.expoplanner.com/files/acsfall12/ExhibFiles/1043_1892_OP_Displ_FilterFunnel_Flyer.pdf last accessed June 1, 2013)
- O'Connor, K.; Zuspan, K.; Berry, L. *J. Chem Ed.* **2011**, *88*, 325-327.
- Horowitz, D. *J. Chem. Ed.* **2007**, *84*, 346-353.
- Dimethyl fumarate has also been used and the results are similar to those obtained with methyl *trans*-cinnamate.