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

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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 nanoparticles entrapped in an aluminum oxo hydroxy matrix (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
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.

Results and Discussion

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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.

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

**References and Notes**

4. A propylene filter funnel, 18mL, 10 micron polyethylene frit (OP-6602–10) can be purchased from Chem Glass.
6. Dimethyl fumarate works equally well in this experiment.