

# Propanol to Propane: An Advanced Laboratory Experiment Using Heterogeneous Catalysts for Two Successive Gas-Phase Reactions

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Examples of continuous-flow gas-phase reaction involving heterogeneous catalysts can be found in several popular books on chemical demonstrations as well as in this *Journal* (1–5). In this article, we describe a sequence of two organic reactions involving gas-phase heterogeneous catalysis suitable for use as a laboratory experiment. In the first reaction, 2-propanol is converted to propene using alumina beads as the catalyst. The product gas is purified with a mini-cold trap. In the second reaction, propene is hydrogenated to propane using a palladium catalyst in nearly 100% yield. Both propene and propane are characterized by proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) and both give elegant spectra that are ideally suited for interpretation by undergraduate students. This laboratory experiment is original in that gas-phase organic reactions are not usually experienced in chemistry laboratory programs. The experiment demonstrates continuous-flow, closed-system gas-phase reactions of fundamental importance in chemical industry. The experiment also demonstrates the power of NMR in the context for which it actually is used by organic and inorganic chemists: structural confirmation and analysis.

## Experimental Information

### Special Equipment

Each pair of students will need three unique pieces of equipment: an alumina-bead catalyst tube, a palladium catalyst tube and a U-shaped cold trap. All pieces should be constructed prior to the laboratory period. All three pieces can be used indefinitely. The alumina-bead catalyst tube (Figure 1) is constructed from a 20-cm length of 6-mm i.d. borosilicate glass tubing and is filled with 1.75 g of acidified alumina beads (100 mesh) held in place by two small plugs of steel wool.

The catalyst tube containing palladium-coated ceramic support (Figure 2) can be constructed from pieces of catalytic material obtained from an automotive exhaust catalyst: see the instructions in our previous article (5) or it can be purchased for about \$25 from Educational Innovations.<sup>1</sup>

The U-tube cold trap (Figure 3) is constructed from a 24-cm length of 6-mm i.d. borosilicate glass tubing using a hot flame (propane torch). The U-tube must fit into a 150-

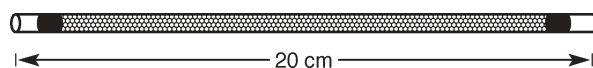


Figure 1. Alumina-bead catalyst tube.

mL beaker or 250-mL (9 ounce) plastic cup, which together will form the cold trap.

## Experimental Procedure

### Dehydration of 2-Propanol

The assembled apparatus is shown in Figure 4. Short pieces of tubing connect both the 1-mL syringe and the 60-mL syringe to the alumina-bead catalyst tube.<sup>2</sup> The 1-mL syringe is filled with 1 mL of anhydrous 2-propanol. Ring stands and clamps may be used to hold the two syringes in the appropriate position above the burner's flame with the 1-mL syringe slightly higher than the 60-mL syringe. The alumina-bead catalyst tube is heated gently while the liquid 2-propanol is slowly introduced to the catalyst tube. The liquid will flow downward through the tube until it hits the hot region. There it will vaporize, react with the hot alumina catalyst, and exit the catalyst tube as gaseous propene into the 60-mL receiver syringe. The following reaction has taken place:

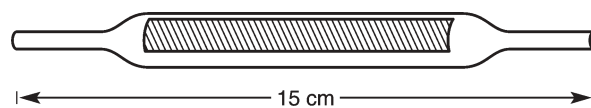


Figure 2. Catalyst tube containing palladium-coated ceramic support.

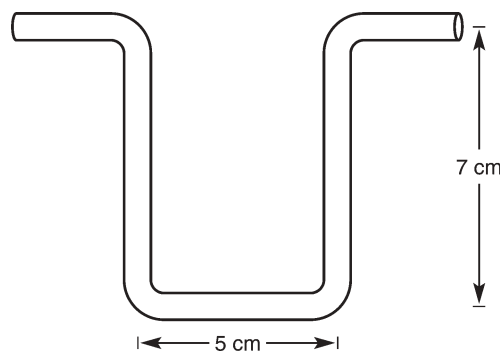
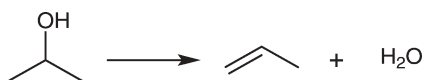


Figure 3. The U-tube cold trap.



### Purification of Propene

The propene collected is contaminated with water vapor and 2-propanol vapor. These are removed by slowly passing the product gas mixture through a cold trap. The assembled apparatus is shown in Figure 5. The cold trap is made by adding dry ice to rubbing alcohol (70% isopropanol) until the desired temperature range of  $-30$  to  $-40$  °C is attained. Water and 2-propanol will condense in the trap and the receiver syringe will fill with relatively pure propene (propene condenses at  $-47.4$  °C). Propene has a distinctive odor characteristic of alkenes. While it is not considered good lab practice to characterize products by inhaling their odors, propene is not toxic in small quantities so students may “sample” a few mL of the gas using a cupped hand. They probably will not like the odor, however!

### Preparing a Gas Sample for NMR spectroscopy

Propene is soluble in  $\text{CDCl}_3$  solvent, however the technique of dissolving a gas is different from that of a solid or liquid. Small portions (3 mL) of propene are repeatedly introduced to the  $\text{CDCl}_3$ -filled NMR tube via a long-stem pipet connected to the syringe of propene. After each portion is added, the NMR tube is capped and the contents shaken to dissolve the gas. Each 3-mL increment theoretically adds about 0.12 mmol (5.4 mg) of sample to the NMR tube. Increasing the size of the gas increment is not possible due to the capacity of the NMR tube.

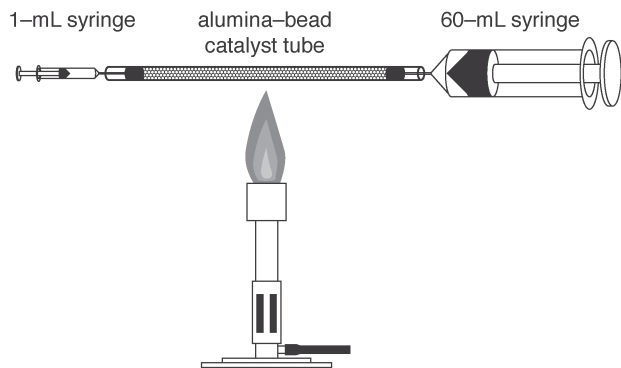


Figure 4. The assembled apparatus for the dehydration of 2-propanol.

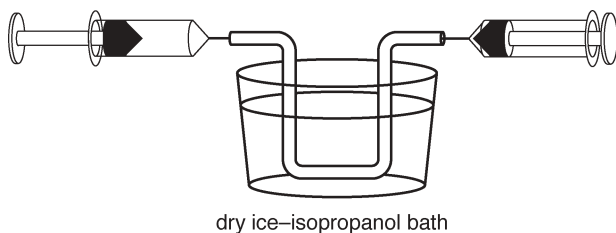
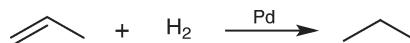


Figure 5. The assembled apparatus to remove the contaminants from propene.

### Hydrogenation of Propene

Two 60-mL syringes filled with hydrogen gas (combined volume 120 mL) are necessary for this portion of the experiment. Hydrogen can be prepared if necessary (6). The assembled apparatus is shown in Figure 6. In preparation for hydrogenation, the palladium catalyst is first purged of gases present from previous experiments by air over the catalyst while heating until the catalyst becomes tan in color. The catalyst is then activated by slowly passing 90 mL of  $\text{H}_2(\text{g})$  through the system while heating in a cool flame in a process similar to that just completed with air. The catalyst will turn black owing to the appearance of elemental palladium (catalyst tubes constructed from automotive catalysts will darken, but will not turn black).

The apparatus is now ready for the hydrogenation reaction. The reactant syringe (left) contains equal volumes of  $\text{H}_2(\text{g})$  and purified propene product gas. The gases are combined by transferring 30 mL of propene via a short length of tubing to a syringe containing 30 mL of  $\text{H}_2(\text{g})$ . The reactant syringe and receiver syringe are connected to the catalyst tube as shown in Figure 6. The catalyzed reaction can be conducted at room temperature because this reaction is exothermic. The hydrogen–propene mixture is slowly passed over the catalyst for 30–60 s. The glass catalyst tube becomes hot as the reaction proceeds.



The volume of the gases collected in the receiver syringe will be less than the original volume of gas mixture in the reagent syringe owing to the reaction stoichiometry. The NMR sample is prepared as described for propene.

### Hazards

Manipulating gases in syringes is generally safe and unintentional discharges are not common. Nevertheless, such discharges are possible and it is important to remember that all of the gases used are highly flammable and form explosive mixtures with air. 2-Propanol is a mild depressant similar to ethanol.

### Results and Discussion

#### $^1\text{H}$ NMR Spectrum of Propene

Characterization of the purified propene by  $^1\text{H}$  NMR spectroscopy (spectrum provided in Supplemental Material<sup>11</sup>) can be accomplished in a variety of ways. Simple comparison of the NMR spectrum obtained with available standard spectra (7–9) confirms the identity of the alkene (Figure 7). Alternatively, a first-order analysis of the spectrum can be performed and all resonances and respective couplings assigned with the assistance of selective proton-decoupling experiments. Referring to Table 1, the  $^1\text{H}$  NMR of propene is found to have four signals,  $\delta$  5.87, 5.06, 4.97, and 1.76 ppm.

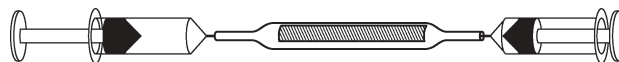


Figure 6. The assembled apparatus.

As all hydrogen nuclei of the molecule couple with each other, the multiplicities of the resonances are very complex. Integration and the relatively upfield position immediately allows the assignment of the methyl H(a) resonance at  $\delta$  1.76, and of the vinylic resonances, the most complex at  $\delta$  5.87 can be assigned as H(b). Unambiguously distinguishing between the geminal vinylic H(c) and H(d) requires a closer examination of the coupling pattern, using the assistance of selective decoupling. The vicinal coupling of H(a) and H(b) can be determined from the NMR spectrum to be 6.8 Hz. Decoupling of H(a) collapses the geminal vinylic H(c) and H(d) resonances into two doublets of doublets,  $\delta$  5.06 ( $J = 2.4, 17.4$  Hz) and  $\delta$  4.97 ( $J = 2.2, 10.0$  Hz). H(c) and H(d) must then have an average geminal coupling constant of  $J = 2.3$  Hz; the larger vicinal trans coupling constant of  $J = 17.4$  Hz and smaller vicinal cis coupling constant of  $J = 10.0$  Hz assign H(c) to be at  $\delta$  5.06 and H(d) to be at  $\delta$  4.97. It remains to determine the long-range, four-bond couplings between H(a) and H(c), and H(a) and H(d). To that end, decoupling of H(d) results in a doublet of doublets for the H(a) methyl resonance,  $\delta$  1.76 ( $J = 1.4, 6.8$  Hz), whereas decoupling of H(c) results in a doublet of quartets for the H(d) resonance,  $\delta$  4.97 ( $J = 1.0, 10.0$  Hz). Decoupled spectra are provided in the Supplemental Material.<sup>W</sup>

Homonuclear correlation spectroscopy (COSY) can be used to check that chemical-shift assignments are correct (Table 2). The relative intensities of the crosspeaks can be used as a guide to distinguish between the large vicinal couplings and the weaker geminal and long-range couplings.

As an additional check, the now fully elucidated spin system of propene can be used to simulate its NMR spectrum (10); that simulation compared with values (11, 12) and spectra (13) calculated by others as well as with the actual spectrum itself.

A first-order analysis allows for the unambiguous assignment of the propene <sup>1</sup>H NMR spectrum and determination of the magnitudes of its coupling constants, but does not provide for the *signs* of those coupling constants. In <sup>1</sup>H NMR, coupling is dominated by the Fermi contact term, used to describe the electron–nuclear interaction (14, 15). Although the vector model of this interaction predicts negative gemi-

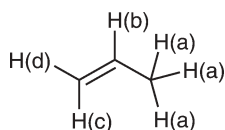


Figure 7. Proton assignment in propene.

**Table 1. <sup>1</sup>H NMR Chemical Shifts and Coupling Constants**

Nucleus	Chemical Shift, (ppm)	Coupling Constant/Hz		
		H(a)	H(b)	H(c)
H(a)	1.76	–	–	–
H(b)	5.87	6.8	–	–
H(c)	5.06	1.4	17.4	–
H(d)	4.97	1.0	10.0	2.3

nal coupling constants, compensatory bond-angle dependence and  $\pi$ -orbital mixing result in a positive value for H(c)–H(d) coupling. Similarly, the long-range four-bond H(a)–H(c) and H(a)–H(d) couplings are predicted to be negative. These predictions are most simply confirmed using COSY-45 (16, 17) (see Supplemental Material<sup>W</sup>).

### <sup>1</sup>H NMR Spectrum of Propane

The propane produced provides a clear, first-order spectrum: the methyl groups appear at  $\delta$  0.93 ppm as a triplet with coupling constant  $J = 7.3$  Hz and the methylene group appears as a distinct septuplet with identical coupling constant at  $\delta$  1.36 ppm. Minor contaminants also are apparent. A small quantity (about 3% by integration) of the starting isopropyl alcohol, the methyl groups of which can be seen as a doublet with  $J = 6.0$  Hz at  $\delta$  1.65 ppm, remains. Water ( $\delta$  1.58 ppm), principally from the solvent (CDCl<sub>3</sub>), also can be identified. Two unknown contaminants, possibly ethane and methane, appear as singlets at  $\delta$  0.89 ppm and 0.25 ppm, respectively (spectrum provided in Supplemental Material<sup>W</sup>).

### Acknowledgments

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### Supplemental Material

Instructions for the students, notes for the instructor, and NMR spectra are available in this issue of *JCE Online*.

### Notes

1. The Gas Reaction Catalyst Tube Kit (includes syringes and tubing) can be ordered from Educational Innovations (sells worldwide); part number #GAS-100, email: info@teachersource.com, website: <http://www.teachersource.com> (accessed Dec 2005).

2. Syringes and related equipment can be ordered from a variety of vendors including Educational Innovations, Flinn Scientific (United States sales only), Micromole, and Fisher Scientific. Part numbers and links to their Web sites are provided at our microscale gas Web site, [http://mattson.creighton.edu/Microscale\\_Gas\\_Chemistry.html](http://mattson.creighton.edu/Microscale_Gas_Chemistry.html) (accessed Dec 2005).

**Table 2. Crosspeak Locations and Assignments, Homonuclear COSY of Propene**

Location, $\delta(f1), \delta(f2)$	Assignment
1.76, 5.86	H(a)–H(b)
1.75, 5.09	H(a)–H(c)
1.75, 4.95	H(a)–H(d)
4.98, 5.89	H(d)–H(b)
4.99, 5.04	H(d)–H(c)
5.07, 5.88	H(c)–H(b)

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