Experiment 3 —

Mystery Reaction of Cyclohexene

Pre-lab preparation (1) As an introduction to IR spectroscopy, read Hornback sections 13.4 - part of 13.6, pp 505 - 511. (2) Look up the relevant physical data for cyclohexene and draw its structure. (What data are relevant, you ask? Read the experiment. For example, are you going to boil it, freeze it, or set fire to it? So do you need the boiling point, the melting point, or the flash point?) (3) Also as a fun reminder of some gen-chem principles, calculate the number of molecules of cyclohexene that you will be starting with. (4) Refer to the data table at the end of this handout, and determine what IR absorptions you should see in your spectrum of cyclohexene.

In this experiment, you will become a combination of detective and mad scientist. (Please practice your maniacal laughter before lab.) You will reflux cyclohexene over a palladium on carbon catalyst and then use gas chromatography and IR spectroscopy to determine a plausible structure for the product (or products).

Reflux is a common method for maintaining a constant reaction temperature by boiling the solvent and returning the vapors to the reaction flask. For example, a reaction could be run at 110°C in refluxing toluene as the solvent. Application of heat raises the temperature until the toluene boils. At that point additional heat input affects the *rate* of vaporization; the temperature can't rise above the boiling point of the solvent, 110°C. No thermostat or temperature adjustment is needed. Condensing the vapors prevents loss of the solvent as the reaction proceeds.

Experimental procedure. Work with a partner. Place 3.0 ml of cyclohexene and 100 mg (*n.b.* that's *miligrams*, not grams) of Pd/C catalyst into your dry 50-ml r.b. flask. Although the solid catalyst will probably provide enough nucleation sites to ensure smooth boiling, toss in a boiling chip just to be on the safe side. Clamp the flask by its neck to the monkey bars above an IR lamp, and attach a dry condensor. That's the setup. Simple, eh? Don't forget to use a little

grease so the joints don't become permanently locked together. Remember which way the water flows? Also, keep in mind that all you're trying to do is keep the condensor cool — you don't need the water running full blast.

Turn on the lamp. Once the mixture starts boiling, you can ease off on the heat to keep it boiling gently. (Applying more heat is just going to vaporize the cyclohexene faster, it's not going to raise the temperature, right?). After about an hour, let the mixture cool to room temperature.

Add one drop of water to coagulate the catalyst. This will make it easier to filter (see below). Then add a few pieces of anhydrous calcium chloride ($CaCl_2$), and give it 5 or 10 min to do its job. $CaCl_2$ is a drying agent — it has a high affinity for water, and is therefore very effective at removing traces of water from organic solvents. Drying agents will generally clump when they interact with water. So think about this — if *all* of your $CaCl_2$ has clumped, have you gotten rid of all the water? If all or some of your $CaCl_2$ has *not* clumped, have you gotten rid of all the water? In either case, would it make sense to add more? Here's one more thing to think about — atmospheric humidity. The drying agent is busily glomming onto the water, but more water is rushing in because you left the flask open to the air. Sort of defeats the purpose, doesn't it? Plus, your goodies will be escaping out of the opening! Here's one more bit of advice — it's easier to stopper an Erlenmeyer flask than a beaker. Plus, stuff doesn't slosh out of flasks as easily. In general, use flasks for anything you care about, rather than beakers. Once the sample is dry, filter it into a clean, dry test tube (provided). Use a piece of fluted filter paper and a short-stemmed funnel.

Obtain a gas chromatogram of the sample. As we did in the distillation experiment, we'll assume that the peak areas are proportional to moles. That's not really true, but it's not a bad approximation here. Compare this chromatogram to that of cyclohexene.

Obtain an IR spectrum and compare this with the spectrum of cyclohexene provided. The table below may help you to identify some key features of the spectra and determine what happened.

Bond type	Typical ν range	Intensity
C_{sp}–H stretch	3310 - 3320 cm^{-1}	Strong
C_{sp2}–H stretch	3000 - 3100 cm^{-1}	Moderate
C_{sp3}–H stretch	2850 - 2950 cm^{-1}	Moderate
C≡C stretch	2100 - 2200 cm^{-1}	Weak-Moderate
C=C=C stretch	1900 - 2000 cm^{-1}	Moderate
C=C stretch	1640 - 1670 cm^{-1}	Weak-Moderate
C=C stretch (conjugated)	1600 - 1630 cm^{-1}	Moderate
CC combo stretch (aromatic ring)	1450 - 1500 cm^{-1}	Moderate
CH_2 bend	1420 - 1480 cm^{-1}	Strong
=C–H bend	650 - 1000 cm^{-1}	Weak-Moderate
=C–H bend (aromatic ring)	700 - 800 cm^{-1}	Moderate-Strong

Post-lab write-up. You can do this before you leave, then there's no separate report required. (1) Write a balanced equation for the reaction that you believe occurred. Draw all structures clearly (skeletal structures are fine). (2) Briefly explain how the GC and IR data support your proposal. (3) Explain, in terms of structures, what makes this reaction favorable. That is (assuming the reaction went to product(s)), why are the products thermodynamically more favorable than the reactants. (4) Predict what would happen if you were to repeat this experiment starting with (a) 1,4-cyclohexadiene, (b) cyclopentene, (c) cyclobutene. For each case, write a balanced equation, and predict what compound(s) would be present at equilibrium. (5) Attach your spectra and chromatograms to your duplicate notebook pages, and you're done. (6) Go home. Eat a nutritious dinner. Get some rest.