CHEM 321: AN E2 REACTION:  
DEHYDROHALOGENATION OF CYCLOHEXYL BROMIDE  

(A PARTNERS EXPERIMENT)

An important route to alkenes is that of dehydrohalogenation. The mechanism for this reaction is bimolecular, involving a collision between a strong base and an alkyl halide. Studies of the kinetics of the process show that the base attacks an electron-poor (acidic) hydrogen atom on the carbon adjacent to the one bearing the halogen (or other good leaving group). Meanwhile, the solvent tries to solvate the leaving group. In most cases, both the hydrogen and the halogen depart at the same time. Where a choice of acidic H atoms exists, the one whose removal leads to the most branched alkene is lost. Presumably this is because that alkene is thermodynamically most stable.

The purpose of this experiment is to illustrate an E2 reaction. The specific E2 reaction chosen is the dehydrohalogenation of cyclohexyl bromide using a strong base and ethanol, shown below. Other objectives include selecting a usable solvent given constraints imposed by reactants, working out a suitable product isolation scheme, and deciding on suitable chemical characterization tests.

\[
\begin{align*}
\text{Br} & \quad \text{Ethanol, boil} \\
\Theta \text{OH} & \quad \rightarrow \\
\text{Cyclohexene} & + \quad \text{Br}^\Theta + \text{H}_2\text{O}
\end{align*}
\]

Water would not dissolve the organic compound, and a nonpolar solvent would not dissolve KOH. Ethanol is chosen as a compromise solvent since both KOH and cyclohexyl bromide are at least somewhat soluble in it. But ethanol creates isolation problems. To recover a desired product, one must free it from unreacted reagents, solvent, and unwanted by-products. Ethanol’s boiling point is very close to that of cyclohexene, with which it is also infinitely miscible. However, cyclohexene is not soluble in water, whereas ethanol, KOH, and KBr are all water-soluble. The protocol is designed to exploit these properties – try to see how as you read it.

### EXPERIMENTAL SECTION 
(You will likely conduct this experiment in partners for sharing glassware.)

**CAUTION:** KOH is very corrosive. Clean up spills immediately and flush down the drain with lots of water. If any gets on your skin or clothing, wash with lots of water until the area doesn’t feel slippery any more.

Cyclohexyl bromide irritates moist membranes. Keep it out of your eyes and lungs.

**SYNTHESIS**

Add 25 mL of 95% ethanol, 10 mL of cyclohexyl bromide using a dispensette, and about 20 g of 85% KOH to a 100 mL boiling flask. Gently swirl the flask to get all of the KOH under the liquid surface. Add a medium sized stir bar to the reaction flask, and clamp it near the face of your hood. Bury the reaction flask in a shallow sand bath that is on top of a stirring hot plate. Attach a reflux condenser to the reaction flask and begin heating with vigorous stirring. Reflux gently (about 1 drop of condensate per sec) for 45 min. During this time the KOH will dissolve, and KBr will precipitate out as a fine powder.

**RECOVERY**

After 45 minutes remove the heat source and immerse the flask, still attached to the condenser, in a beaker of cold water. Put about 60 mL of tap water into a small separatory funnel. Pour the cooled contents of the boiling flask into the funnel. To assure complete transfer of the liquid product (solids should be avoided, but don’t worry if some transfer), add 10 mL of water to the boiling flask, swirl, and add the wash to the separatory funnel. Repeat wash with a fresh 10 mL of water. Shake the funnel hard to mix layers, venting as necessary. Allow the layers to separate. Discard the large lower aqueous layer. Add about 80 mL of fresh tap water into the funnel and shake again. Discard the new lower layer (leaving just the organic layer in the funnel). Decant the organic layer into a dry 50 mL Erlenmeyer flask (rid it of visible water as needed). Add a small layer of anhydrous calcium chloride, cork the opening and swirl for about 10 min to dry the product. The water washes should have removed essentially all the ethanol, so the crude product should now contain only cyclohexene and possibly cyclohexanol, which is a likely by-product via a substitution reaction. (Note: both cyclohexene, the desired product, and cyclohexanol, the possible side product, should be included in your pre-lab materials chart – with physical and chemical properties included!)
Use a Pasteur pipette to transfer the dry liquid into a dry 25 mL boiling flask. Drop in a boiling chip and distill through DRY glassware into a weighed receiving flask. Record the temperature when 1) the first drop drips into the receiving flask, 2) there is a constant drip rate into the receiving flask, and 3) the drip rate slows down. Stop heating when the drip rate slows (the vapor temperature will drop below the accepted boiling range). At the end of the distillation, note whether the residue in the boiling flask is a larger volume than you expect. If it is, you may have made some cyclohexanol (what is its boiling range?).

CHARACTERIZATION
After weighing it, test your product to see if it is an alkene, and interpret the test results in the discussion section of your report:

CAUTION: Bromine causes severe skin burns. If any gets on your skin, immediately wash the affected area with sodium thiosulfate solution or glycerol. Rub the solution in to be sure all bromine has reacted. Then rinse with water.

CAUTION: Carbon tetrachloride (solvent for the bromine) is toxic to the liver and is a carcinogen. Avoid skin contact and vapors.

Bromine absorption test: Label three test tubes "(+ control)," "(-) control," and "sample". Put 0.5 - 1 mL of hexane or similar alkane and one or more drops of 1 M bromine in carbon tetrachloride into each of the tubes so that after mixing there is a persistent reddish-brown color. At this point these tubes amount to negative controls since they contain hexane (no double bonds) and have a persistent Br₂ color. To the appropriate tube, add one drop of authentic cyclohexene (this becomes the positive control), one drop of an alkane compound (this becomes the negative control), or one drop of your product (sample), and mix. See tabular format of instructions below. A positive result is a change to a clear, colorless solution.

<table>
<thead>
<tr>
<th>To this test tube:</th>
<th>add: Hexane or similar alkane (solvent)</th>
<th>1M bromine in carbon tetrachloride (test reagent)</th>
<th>Control substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+) control</td>
<td>add: 0.5-1.0 mL</td>
<td>One or more drops</td>
<td>Add one drop hexene</td>
</tr>
<tr>
<td>(-) control</td>
<td>add: 0.5-1.0 mL</td>
<td>One or more drops</td>
<td>Add one drop hexane*</td>
</tr>
<tr>
<td>sample</td>
<td>add: 0.5-1.0 mL</td>
<td>One or more drops</td>
<td>Add one drop product</td>
</tr>
</tbody>
</table>

*In this case, it is ok if you do not add anything else to the (-) control besides the solvent and the test reagent (amounting to a negative control without addition of a third substance).

Permanganate test: Label three test tubes "(+ control)," "(-) control" and "sample". Mix about 1 mL of water and one drop of aqueous permanganate solution in each test tube. The color should be a reasonably dark purple and persistent. Now to the appropriate tubes add one drop of a positive control, one drop of a negative control or one drop of your product. Decide what to use for each control, and record the names of the chemicals you choose. Mix each vigorously until no further change occurs. See tabular format of instructions below. A positive result is a change to reddish-brownish solution.

<table>
<thead>
<tr>
<th>To test tube below</th>
<th>add: Water (solvent)</th>
<th>Aqueous permanganate solution (test reagent)</th>
<th>Control substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+) control</td>
<td>add: ~1 mL</td>
<td>One or more drops</td>
<td>Add one drop hexene</td>
</tr>
<tr>
<td>(-) control</td>
<td>add: ~1 mL</td>
<td>One or more drops</td>
<td>Add one drop hexane*</td>
</tr>
<tr>
<td>sample</td>
<td>add: ~1 mL</td>
<td>One or more drops</td>
<td>Add one drop product</td>
</tr>
</tbody>
</table>

*In this case, it is ok if you do not add anything else to the (-) control besides the solvent and the test reagent (amounting to a negative control without addition of a third substance).

IR spectrum: Obtain an IR spectrum of your product using the ATR accessory of the IR instrument. Work carefully, but rapidly since the expected product evaporates fast. Annotate as needed to show that you made the alkene and that little or no reactant, solvent, or side product is present. (Consider the workup history of your product. What are possible contaminants? Keep in mind their pertinent physical properties, compared to physical operations you performed to recover the product).
CLEAN UP

Pour the cyclohexene into the “Student Prep Cyclohexene” bottle in hood. Pot residue if any should go into the bottle for mixed organic compounds. Spent CaCl$_2$ goes onto a paper towel in the hood (controls stench).

LABORATORY REPORT: Minor (skeleton) report

Complete the electronic form for this experiment. Guidelines for this report:

- **Title**
- **Source reference**
- **Introduction** containing:
  - experiment objective(s) (what was the purpose of performing the experiment?);
  - context (the experiment that was performed as a means through which the purpose could be met – pertinent concepts and techniques included);
  - rationale (why is this objective worthwhile?); and
  - Figure 1 should include the experimental E2 reaction above (add in the mechanism arrows) AND the competing SN2 side reaction (mechanism arrows), with an appropriate caption. Use ChemDraw.
- **Experimental methods** (refer to previous experiment handouts for examples)
- **Results** presenting actual data/observations that support whether the goal was met or not (e.g., mp/bp range, IR spectra, chemical tests, appearance, percent yield, etc.)
  - Sentences stating/introducing results / tables / figures
  - % yield
  - observed boiling range (report temperature of fastest drip rate to the end of the slow drip rate as your boiling range)
  - tables for chemical test results
  - IR spectra for your product and appropriate comparison compounds, and
  - IR peak assignment table for your product and appropriate comparison compounds
- **Discussion** containing:
  - a reiteration of the objective,
  - comments on how these data compare to published values and what conclusions can be drawn*,
  - plausible reasons for percent yield deviations from 100 percent,
  - chemistry concepts supporting results/interpretations (including figures when appropriate, such as reactions for chemical tests), and
  - a summary sentence indicating whether or not objectives were met

- **References** (additional to source reference, and provide appropriate citations throughout the report)

- **Appendix** containing:
  - calculations with work (including % yield), brief protocols for chemical tests, and/or additional supporting figures (chemical test reactions)

PRE-LAB QUESTIONS

1. If you spill any potassium hydroxide as you measure or handle it, how should you dispose of it?
2. Draw a setup of your liquid-liquid extraction for this experiment. Label the organic and aqueous layers (use the product’s density if you are unsure if it will be the top or bottom layer), and indicate which layer each of the following will “prefer” and thus migrate to: cyclohexene, ethanol, potassium hydroxide, and potassium bromide.
3. If the side product is formed, what might be observed on the experimental product’s IR spectrum?
REMEMBER THESE GUIDELINES FOR ALL IR SPECTRA:

Label and attach the IR spectra to your lab report, or insert them into the report document. Your RESULTS section should direct the reader to IR spectra (labeled as FIGURES):

How do I label an IR spectrum?
- With an appropriate figure caption (see example) and figure number under the figure
- The correct name of the chemical, spelled out, is in the caption
- The molecular structure of the chemical (so the reader may see what functional groups are present – include on experimental product as well, with the structure of the expected product)
- Circle individual peaks you choose to discuss in your report, and tell what vibration is the likely cause of each peak. You need to assign enough significant peaks to allow the reader to see that the product is what it is claimed to be and is pure (or contaminated) as claimed in the report. Label each chosen peak explicitly with the name of the responsible molecular vibration. Examples: O-H stretch, sp² C-H stretch, C=O stretch. These assignments should be chosen to confirm that the molecule is of the class you claim it to be. You should not use the sp³ C-H stretch unless it is a main significant signature peak.
- Figure caption includes a citation to a bibliographic citation in your REFERENCES section

What are the IR spectra that I should include in my report?
- IR spectrum of experimental product
- Published IR spectrum of expected major product, citation included
- Published IR spectra of any potential contaminants or side products that would show characteristic IR peaks, citation(s) included
- To decide whether contamination from specific compounds is significant, evaluate the relative intensities of pertinent peaks in the product spectrum along with intensities of those peaks in the spectra of the starting materials and/or plausible side products.

Where can I find published IR spectra? (These resources are on the course webpage under “Useful Links” as well.)
- Spectral Database for Organic Compounds, SDBS. URL: http://sdb.db.aist.go.jp