Acid-Catalyzed Hydration Reactions

Overview: This experiment will allow you to examine the product distribution for alkene hydration reactions. Using Spartan, you will calculate the energies of all reasonable carbocations resulting from the protonation of a given alkene. From your Spartan results, you can make predictions about the expected product ratio based on relative stabilities of the carbocation intermediates. You will then perform the hydration experiment in the laboratory and compare your actual results to the theoretical predictions that you made. You should review the mechanism for acid-catalyzed hydration given in sections 8.4-8.5 of Ege.

Each student will be assigned one of three possible alkenes. Your "balanced reactions" section in your notebook should consist of the acid-catalyzed reaction of your assigned alkene, including all possible carbocation intermediates and alcohol products. Your table of reagents should include those relevant to your assigned alkene; it is not necessary to include the other two alkenes and their corresponding products.

Procedure:

Part A. Spartan Modeling of Acid-Catalyzed Hydration

Building Molecules. *We will begin our study by using Spartan to build a carbocation.*

1. From the Desktop menu choose Spartan '04.

2. Before performing a calculation, you must build a molecule then save it. Click on **File** and choose **New**. This opens the building tools so can construct the molecule. The basic building tools are shown on the right side of the screen.

3. Build the carbocation. The following example for building a carbocation formed from 1-hexene will make this easier. Use the instructions as a guide for constructing the carbocations corresponding to your assigned alkene;

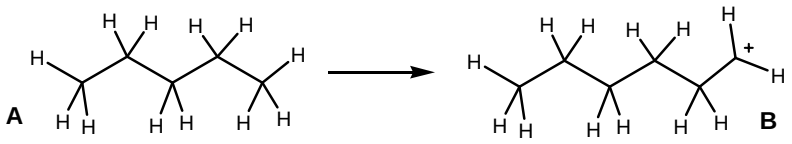
   Example building of 1-hexyl carbocation from 1-hexene:

   Start building the carbocation by choosing the sp^3 carbon from the model kit. Click the left mouse button in the work area to add the sp^3 carbon to the screen.

   Next, click on a yellow hydrogen of the molecule on the screen. This will add a second sp^3 carbon to the molecule you are building, giving you the molecule ethane (CH_3CH_3) on the screen. Gray = C. Yellow or white = H.

   Add three more sp^3 carbons to the molecule to generate pentane (see **A** below).

   Now you need to add an sp^2 carbon that has only 3 valences (e.g. a carbocation). To do this, you need to go to the expert tool kit. Click the **Exp** tab at the top-right. Highlight C. Highlight the three valence button. Now click on a terminal hydrogen of the pentane. You have now built the 1-hexyl cation (see **B** below).



   The following mouse commands are useful as you are building in Spartan:
   Left mouse: rotate molecule
   Right mouse: translate molecule
   Shift-left mouse: rotate molecule in plane of screen
   Shift-right mouse: enlarge/shrink molecule
   Alt-left mouse (when bond is highlighted): rotate torsion angle
   Alt-right mouse (when bond is highlighted): stretch/shrink bond length

4. Before performing a semi-empirical calculation (time intensive), you will "clean-up" the carbocation you built using a quick minimization. Click the **Minimize** button at the top of the screen. (*E with down arrow*).

5. Save the molecule. Under the **File** menu, choose **Save As** and save the file with an appropriate name.

Semiempirical Calculations. *You will set up a semi-empirical calculation that will allow you to obtain an optimized geometry and energy for the carbocation.*

6. Choose **Semi-Empirical** under the **Setup**-**Calculations** menu. The Setup Semi-Empirical Dialog box appears; set the tasks as follows:

   Calculate: Equilibrium Geometry (pull down menu)
   with: Semiempirical AM1
   Start from: initial geometry
   Options: leave this box blank

   Total Charge: +1
   Multiplicity: singlet

7. Click the submit button. When the job is finished and you click OK, the molecule's structure is updated.

8. The calculated energy can be found under **Display**, then **Properties**. Record this energy in your notebook.

Visualization of the carbocation LUMO. *The charge distribution in this charged ion will be displayed.*

9. Choose **Setup**, then **Surfaces**. In the surfaces dialog box choose **Add**. Select **density** from the **Surface** menu, select **LUMO** from the **Property** menu, and **low** from the **Resolution** menu.

10. Select **Submit** from **Setup** menu. A dialog appears telling you that your calculation has been submitted. Click on **OK** to remove it from the screen.

11. When the calculation has completed you will be notified. Click on **OK** to remove the dialog from the screen.

12. Select **Surfaces** from the **Display** menu. Check the yellow box next to the word density. You can click on the colorful surface of the molecule. A **Style** dialog box at the bottom right corner will appear; it allows you to manipulate the appearance of the surface. The surface represents the LUMO, Lowest Unoccupied Molecular Orbital, the orbital where it is easiest to put the next pair of electrons. As such, it locates positive charge and identifies where a nucleophile will approach. Red represents regions of high electron density. Blue represents regions of low electron density.

13. Sketch the LUMO surface in your notebook. Note that the carbocation has two faces, indicated by having a blue spot on either side. This indicates that attack by nucleophiles can occur on either face. Is the blue color significantly different on the two faces of the carbocation?

14. To finish, choose **Close** from the menu.

15. Repeat the necessary steps for all reasonable carbocations formed by protonation of your assigned alkene.

16. Report your results to the instructor so that a table of class data can be organized. Obtain data for all of the compounds from the class.

Part B. Experimental Acid-Catalyzed Hydration

Synthesis.

1. To a 5 mL round bottom flask equipped with a magnetic stir bar, add 1 mL of sulfuric acid of appropriate concentration (see below), followed by 0.5 mL of alkene to the vigorously stirred acid.

Alkene	Acid Concentration
1-hexene	85% w/w
3,3-dimethyl-1-butene	85% w/w
2-ethyl-1-butene	65% w/w

2. An air condenser should be connected to prevent splattering and to minimize loss due to evaporation.
3. Stir the solution as vigorously as possible for ten minutes.
4. Add a second 0.5 mL portion of alkene and stir for an additional ten minutes.
5. Add 2 mL of water to the reaction and stir for ten minutes.

Work-up.

6. Extract the resulting mixture with 3 mL of diethyl ether.
7. Dry the ether layer with sodium sulfate.
8. Transfer the solution to a dry conical vial.

Analysis.

9. Obtain a gas chromatographic trace of your product mixture, comparing the retention times of your product(s) to those of the standards that are provided.

10. Calculate the percent composition of the alcohol products based on the GC trace (compute out of 100% ignoring any remaining starting material). Report your results to the instructor so that a table of class data can be organized. Obtain data for all of the compounds from the class.

Post-lab.

1. Make a table that includes the energies for the carbocation intermediates. Predict which isomer is most likely to be formed for each of the alkenes.
2. Compare the predicted results from the Spartan exercise to the laboratory results.