Acid-Catalyzed Hydration Reactions

Objective: Two alkenes will be subjected to acid-catalyzed hydration, and the distribution of the product alcohols will be determined by gas chromatography. Spartan will then be used to calculate the energies of all reasonable carbocations resulting from the protonation of the two alkenes. Analysis of the relative stabilities of the carbocation intermediates and the alcohol product distribution will allow you to determine whether a relationship between carbocation stability and alcohol product distribution exists.

Background Information:

You should review the mechanism for acid-catalyzed hydration given in sections 8.4-8.5 of Solomons.

You will be assigned one of two 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 alkene and its corresponding products.

Procedure:

Part A. Experimental Acid-Catalyzed Hydration

To a 25 mL round bottom flask equipped with a magnetic stir bar, add 2 mL of 85% sulfuric acid followed by 1 mL of alkene to the vigorously stirred acid. Stopper the flask to prevent splattering and to minimize loss due to evaporation. Stir the solution as vigorously as possible for ten minutes. Add a second 1 mL portion of alkene and stir until the mixture becomes homogeneous; this generally requires an additional 30 minutes. Add 4 mL of water to the reaction mixture and stir for ten minutes. Extract the resulting mixture with 4 mL of diethyl ether; then wash the organic layer with aqueous NaCl solution, and dry the organic layer with sodium sulfate. Transfer the organic layer to an eppi tube. 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. 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.

Part B. Spartan Modeling of Acid-Catalyzed Hydration

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.

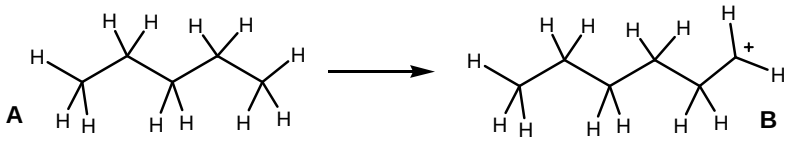
Example building of 1-hexyl carbocation from 1-hexene:

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.

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.

9. Repeat the necessary steps for all reasonable carbocations formed by protonation of your assigned alkene. Report your results to the instructor so that a table of class data can be organized.

Analysis:

Obtain a copy of class data. Make a table that includes the energies for the carbocation intermediates and the corresponding alcohol product distribution. Compare the predicted results from the Spartan exercise to the laboratory results.