

An Experimental and Computational Investigation of the Dehydration of 2-Butanol

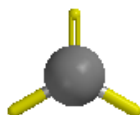
Summary. 2-Butanol will be dehydrated to a mixture of 1-butene and *cis*- and *trans*-2-butene using the method described in the lab text, Williamson, *et. al.* The product distribution will be determined by gas chromatography (GC). Steric energies of all possible product molecules will be calculated by Molecular Mechanics (MM) and heats of formation will be calculated using AM1 semi-empirical Molecular Orbital (MO) calculations. Calculated and experimental energies will be compared and an assessment of the calculations will be made. The SPARTAN '04 computer program will be used for the calculations, which will be done in the Chemistry Resource Center (CRC).

I. TUTORIAL ON THE USE OF THE SPARTAN COMPUTER PROGRAM.

This tutorial describes the use of SPARTAN. After logging onto the computer, launch the program by double-clicking (left mouse button) on the SPARTAN icon on your desktop, or in the Windows Programs menu. You will typically use the left mouse button to select items. The right button will be used to move the model around in the window and to manipulate its structure.

After launching SPARTAN, click on "File" in the menu bar, and then on "New" in the pull-down menu. A new "Builder" window will appear with a "fragment" window on its right. Click on the double-bonded carbon in the "fragment"

window, move the cursor into the "Builder" window, and click once to deposit the carbon double-bond fragment onto the "Builder" window. The fragment may have a different orientation than that shown here.



The screenshot shows the SPARTAN Builder window. At the top, there are tabs for 'Ent.', 'Exp.', 'Pep.', and 'Nuc.'. Below the tabs is a large grey area containing a carbon double bond fragment (>C=). Below this is a grid of chemical fragments: >C=, >N=, >O=, -H, -C≡, ≡N, =O, -F, -C≡, ≡N, =O, -Cl, >C-, >N-, \S-, -Br, >Si-, >N-, =S, -I. At the bottom, there are dropdown menus for 'Groups' (Alkene), 'Rings' (Benzene), and 'Custom' (cyclooctatetra). A 'Clipboard' button is also visible.

Moving the mouse with the left mouse button depressed rotates the fragment in the XY directions. <LEFT>

Moving the mouse with the left mouse button depressed while also holding down the <SHIFT> key rotates the fragment about the Z-axis (out of the screen).

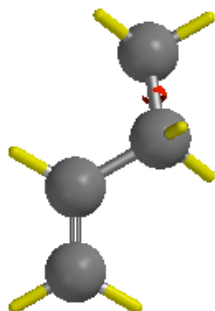
<LEFT><SHIFT>

Moving the mouse with the right mouse button depressed moves the molecule or fragment around the window. <RIGHT>

Rotate the fragment so that you can clearly see the double bond portion, make sure that you still have the >C= fragment selected from the builder menu, then position the cursor on the end of the double bond and left-click again. This should produce a carbon-carbon double bond.

Now select the tetrahedral sp^3 carbon from the fragment window, place the cursor on the end of one of the single bonds of the molecule in the Builder window and click once. This will add an sp^3 carbon to the molecule, making propene. Place the cursor on a single bond of the tetrahedral carbon and click

once to add another carbon, making 1-butene, which should look something like the following but probably with a different orientation.



Notice the little twisting arrow about the last bond that you made. This indicates that you can rotate about the single bond using the <ALT><LEFT> mouse sequence (hold down <ALT>, left click, and move the mouse to rotate the selected bond). You can select a bond by left clicking in the middle of that bond. This is a very useful sequence for setting up initial conformations in non-cyclic molecules. It is a simple way to choose a torsional angle about a bond. [Be careful: <ALT><RIGHT> changes the bond length!]

You now know how to build molecules in SPARTAN. Click on “Minimize” (the button that looks like an “E” with a down-pointing arrow above it) at the top of the Builder window to perform a preliminary geometry optimization/energy minimization. This gives a crude, local minimum geometry.

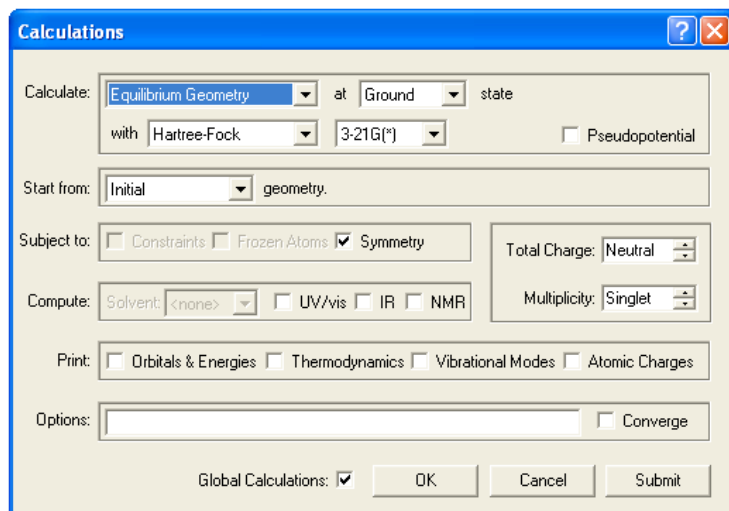
Under “File” choose “Save As” and in the new dialog box that appears type in “1-butene” and click on Save. *If a file already exists with that name you will need to overwrite it or change the name.* (Under “Model” in the Menu bar, you may choose different types of models with which to view the molecule and you may rotate and move them as before.) You may now set up and carry out calculations on this molecule.

A note about conformer searching. You should have read about global vs local minima in Williamson. If only one minimization is carried out on a molecule, which can assume more than one conformation, the conformation that results may represent a local minimum-energy conformation and not a global minimum-energy conformation. Thus the result may lead to a conformation that is not the lowest energy conformation. For example in butane two staggered minimum energy states exist but only one of those is a lowest energy minimum or global minimum. The other is a local minimum. SPARTAN has the capability to examine the energies of various conformations of a molecule and decide upon which represents the lowest energy conformation. Using this option is known as running a “conformer search”. What happens is that the energy for one conformation is calculated, a bond is rotated to produce another conformation, the energy of which is then calculated, and so on.

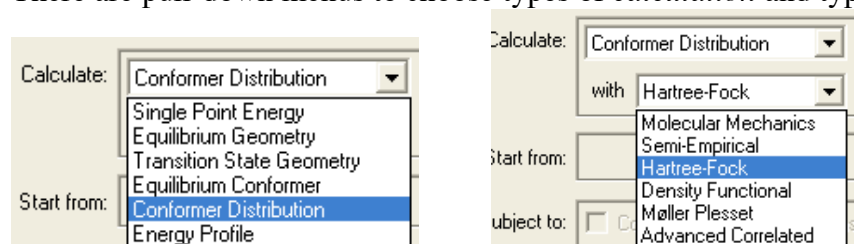
SPARTAN can calculate energies for a whole set of conformers. The more flexible the molecule (more single bonds, few rings), the more conformers. For the butenes calculations in this experiment, you will use conformer searching. Please note that it takes a LOT of computer power for larger molecules and/or more precise computational methods than those used in this lab exercise. Often it will be sufficient to run a calculation without doing a conformer search. Because conformer searching can be very computer and time intensive it is important to know when and when not to use conformer searching.

II. RUNNING A MOLECULAR MECHANICS (MM) CALCULATION FOR 1-BUTENE USING THE CONFORMER SEARCH CAPABILITY.

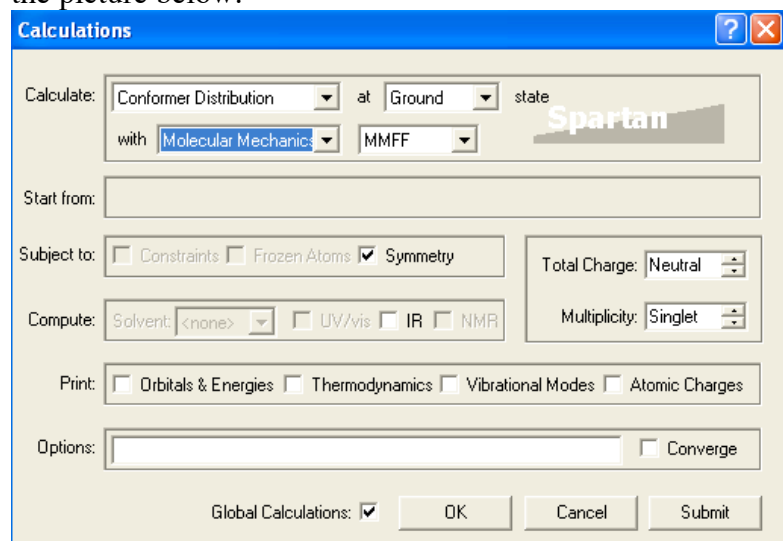
Once **1-butene** is built and present in the main window, under the “Setup” menu, choose “Calculations”. You will see the following menu box.



There are pull-down menus to choose types of *calculation* and types of methods (*with*), as shown below:



For your first calculation, you should “Calculate” a **Conformer Distribution** “with” **Molecular Mechanics**. When you have finished making selections for this run, your calculation box should like the picture below:



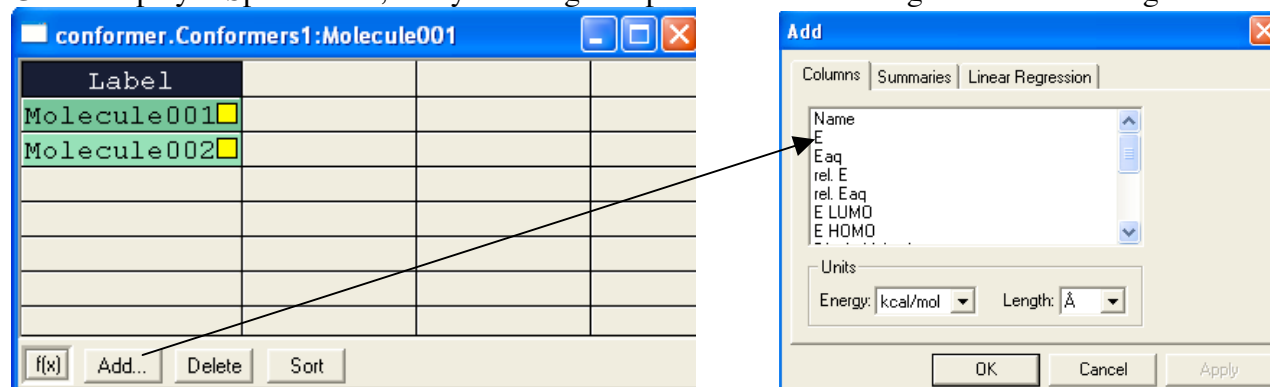
Molecular mechanics is a basic, ball-and-spring classical type of method for computing. The conformer distribution calculation will search automatically for unique conformations of your structure. The more single bonds you have in the structure, the longer such a calculation gets. It is always best to start a conformer search using molecular mechanics, to find the best conformations quickly (molecular mechanics is the fastest method to search conformer space).

Once you have the calculation set up as described above, click on the “Submit” button.

The job will be submitted, and should finish quickly. The program will tell you when it is done.

Now, File > Close your original structure (no structures in the builder screen). Click on File > Open and select the file with a name like “yourfilename.Conformers1.spartan”, where *yourfilename* is the name you gave to the run. IT IS VERY IMPORTANT TO SELECT THIS FILE, NOT “yourfilename.spartan”; it contains the conformations that are found.

Go to Display > Spreadsheet, and you will get a spreadsheet something like the following.



Left-click on the “Add...” button, and select “E” for energy from the choices you will get. Click the “OK” button in the “Add” box. The result will be a spreadsheet that shows energies (in the units selected from the “Add” box) and the conformations found by the computation.

You can look at the molecular geometry of the conformations by checking the yellow boxes, one at a time (left-click). In this way, you can see the geometries of the conformations and their steric energies (NOT the heat of formation when a molecular mechanics computation is done).

Label	E (kcal/mol)		
Molecule001	5.43313676		
Molecule002	5.69303857		

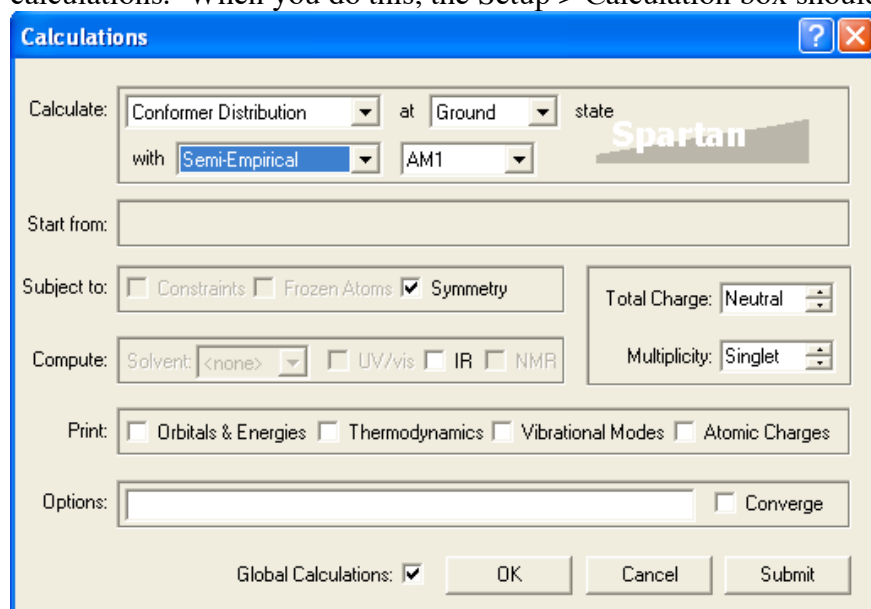
Record the energies (remember units) and a brief description of each conformational geometry. You can save an individual checked conformation as a picture (JPEG) or as a PDB structure file by using File >

Save and selecting the appropriate filetype. PDB files are particularly good, since they can be visualized using the Mercury freeware program.

Repeat the above procedure for (*E*)-2-butene and (*Z*)-2-butene. Record conformation energies and conformer descriptions.

III. RUNNING AN AM1 SEMI-EMPIRICAL MOLECULAR ORBITAL (MO) CALCULATION ON 1-BUTENE USING THE CONFORMER SEARCH CAPABILITY.

Repeat the same set of calculations described above for **1-butene, (*E*)-2-butene and (*Z*)-2-butene**, except that you should choose the Semiempirical AM1 molecular orbital method for doing the calculations. When you do this, the Setup > Calculation box should look as follows:



The AM1 method will actually give you estimated heats of formation (ΔH_f) for your conformations, instead of more arbitrary, relative steric “energy” units given by the Molecular Mechanics MMFM methods. Note that the more complex AM1 calculations take a little longer to run.

Record conformation energies and conformer descriptions for this new set of computations.

In your final report, compare the energy differences between the isomers to the energy differences that are given your textbooks. You can also compare the AM1 heats of formation to those given by NIST. You can find the actual heats of formation for 1-butene, (*E*)-2-butene and (*Z*)-2-butene at the NIST WebBook site, <http://webbook.nist.gov/chemistry/>. Set your WWW browser to this site, then choose to search by either “Name” or “Formula”. You should set units to cal/mol, or be ready to convert your computed energies from cal/mol to SI units (1 cal = 4.18 J). Report the NIST heats of formation, which can be found as “**gas phase thermochemistry data**” or “**gas phase thermodynamic data**” through <http://webbook.nist.gov/chemistry/name-ser.html>. Your report should cite the source as “NIST WebBook”, with the WWW address.

This exercise was developed by Paul Lahti and Peter Samal, Dept of Chemistry, UMass, Amherst.

(rev 7/23/08)