

Computational Chemistry
Problem Set 4

Due Monday, February 23, 2009 (at the start of class)

Total Number of Points = 82

Basic Technical Notes: (1) For security reasons, you are allowed to log into the Hope College computers only from a computer connected to the Macalester network. (2) On Macintosh computers, the WebMO software works with the Safari browser, but not with the (Macalester-endorsed!) Mozilla Firefox browser. On Windows computers, both Firefox and Internet Explorer should work.

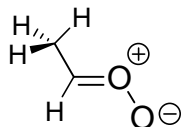
Material We Will Work on Together in Class

Getting started:

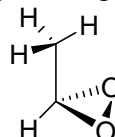
- Open the Safari web browser
- Go to mu3c.chem.hope.edu/~kuwata/cgi-bin/webmo/login.cgi
- Login—Do you remember your Username and Password?

Locating Transition Structures by Scanning the Reaction Coordinate

Start by performing Optimize + Vib Freq Hartree-Fock 3-21G calculations on *anti* acetaldehyde oxide (**I**) and methyl dioxirane (**II**). Please build the most stable conformers of **I** and **II** (as shown), and use the cyclopropane ring to start building **II**.



I



II

When each calculation is Complete, confirm that you have indeed converged to a minimum, and that you have obtained the conformers shown above. Measure the distance between the sp^2 -hybridized C and the terminal O (in **I**), and between the endocyclic C and either O (in **II**). Note the atom labels in **I**.

Next, with the results for **I** up on the screen, click on New Job Using This Geometry. In order to generate a reasonable initial geometry for the transition structure between **I** and **II**, we will come together to set up a Coordinate Scan Hartree-Fock 3-21G calculation.

When the Coordinate Scan job is complete, let's look for the C---O distance at which the energy is at a maximum. Now, we want to do a constrained optimization, with the C---O distance fixed at a slightly larger value, but with all other geometrical parameters minimized. (Why a slightly larger value? Note that the energy falls off rapidly as the C---O is further shortened. If the transition state optimization takes the molecule into this region of the potential energy surface, chances are you may end up with an undesired transition structure. Plus, the transformation of **I** into **II** is exothermic. The Hammond

Postulate tells us that the transition structure should therefore be early or reactant-like in structure.) We'll work together to alter the .com file.

When the constrained optimization is Complete, confirm that the C---O distance is at its desired value. Then click on New Job Using This Geometry and set up a Transition State Optimization Hartree-Fock 3-21G calculation. But before submitting the job, alter the .com file to have the keyword

```
opt=(ts,tight,calcall,noigentest)
```

Finally, we will verify that the transition structure we have located indeed connects minima **I** and **II**. With the transition structure up on the screen, click on New Job Using This Geometry. Under Job Options, choose to do an IRC Calculation (Forward) Hartree-Fock 3-21G calculation. Click on Preview and Generate. Alter the IRC keyword thus:

```
IRC=(CalcFC,Forward,maxpoints=100)
```

This tells Gaussian 03 to calculate 50 points down from the transition structure in the "forward" direction. (Note that the computer program may define "forward" differently from how we are defining it.) Also, whenever you run an IRC add the keyword

```
nosym
```

Often, a transition structure will possess an element of symmetry that the minima surrounding it lack. However, Gaussian 03 freaks out (crashes) if any symmetry element is lost during the course of a calculation. So, it is better to turn symmetry off (with the nosym keyword.) Finally, you are ready to submit the job.

While you are waiting for the IRC (Forward) calculation to finish, go ahead and set up and submit an IRC Calculation (Reverse).

Your Homework for the Week:

A valuable resource for finding all sorts of useful experimental and computational data, such as typical bond lengths, is the Computational Chemistry Database run by a friend of mine from graduate school, Dr. Karl Irikura of the National Institute of Standards and Technology:

<http://cccbdb.nist.gov>

1. (24 points total) Compute the potential energy curves for the hydrogen halide molecules HF, HCl, and HBr. In each case, do a Coordinate Scan Hartree-Fock Other calculation. A pop-up window should appear, into which you should type LANL2DZ Hit Preview and Generate. At the bottom of the .com file, choose to scan the bond length from 0.5 Å to 5.0 Å by 0.05 Å increments with the command

```
1 2 0.5 S 90 0.05
```

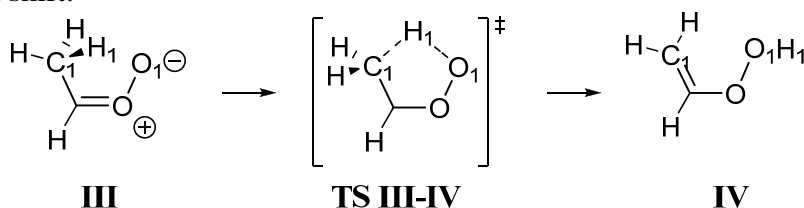
Then submit each job.

- (a) (12 points) Download each coordinate scan file, open in Excel, and find the location (in Å) of the minimum energy. Set the energy of the minimum equal to zero, re-calculate the energies at all other points relative to that zero, and convert the energies to kcal/mol. Plot the relative energy (in kcal/mol) vs. bond length.

- Turn in a printout of the final plots for all three molecules. Label the bond length (in Å, to two decimal places) and bond dissociation energy (in kcal/mol to two decimal places) on each plot.
- (b) (12 points) Find in the chemical literature (*e.g.* in the database mentioned above) experimental values for the bond length and bond dissociation energy for HF, HCl, and HBr. Tabulate these values and compute the relative error in each computed value.

Are you thoroughly unimpressed with the accuracy of these calculations? You should be! Quantum chemistry can do a lot better job in predicting bond dissociation energies—even more accurately than experiment in some cases—but these require more sophisticated methods. We will talk about these methods in a couple of weeks.

2. (19 points total) Yet another possible reaction of *syn* acetaldehyde oxide is the 1,4-hydrogen shift:



Follow the same scanning procedure we did together in class to find the transition structure (labeled **TS III-IV**) between *syn* acetaldehyde oxide (**III**) and a molecule called vinyl hydroperoxide (**IV**). Please note the following:

- Do all of your calculations with the B3LYP 6-31G(d) method. While this will require substantial computer time, this will make your results directly comparable to results you calculated on the previous problem set.
 - When you search for **TS III-IV**, scan the distance between atoms C₁ and H₁.
 - Confirm that **IV** has all real frequencies. If this is not true, alter your initial geometry and repeat the optimization.
- (a) (3 points) Write down the imaginary (negative) frequency (in cm⁻¹) of transition structure **TS III-IV**, and briefly describe the motion associated with this vibrational frequency. (Hint: This imaginary frequency should be significantly higher in magnitude than other imaginary frequencies we have computed so far this semester. This reflects the fact that the reduced mass of the vibration is largely determined by the very light hydrogen atom.)
- (b) (2 points) Calculate the activation energy (in kcal/mol, to two decimal places) for the reaction.
- (c) (2 points) Calculate the reaction energy (in kcal/mol, to two decimal places) for the reaction.
- (d) (12 points) Tabulate the optimized values for $r(\text{C}_1\text{-H}_1)$ and $r(\text{H}_1\text{-O}_1)$ in **III**, **TS III-IV**, and **IV**. Also tabulate the values for $r(\text{C}_1\text{-H}_1)$ and $r(\text{H}_1\text{-O}_1)$ in the final geometries of your IRC (Forward) and IRC (Reverse) calculations. Are the final IRC geometries consistent with your having found the correct transition structure? Briefly discuss.

3. (4 points total) Using your results from the previous question, as well as from Question 3 on Problem Set 3, answer the following:
- (a) (2 points) At 298 K, how much faster does *syn* acetaldehyde oxide react *via* the 1,4-hydrogen shift than *via* dioxirane formation? Assume the pre-exponential factors for both reactions are identical, and report your answer to two significant figures.
- (b) (2 points) At 2000 K, how much faster does *syn* acetaldehyde oxide react *via* the 1,4-hydrogen shift than *via* dioxirane formation? Assume the pre-exponential factors for both reactions are identical, and report your answer to two significant figures.

The vinyl hydroperoxide formed in the 1,4-hydrogen shift is a very important source of hydroxyl radical (OH) in the troposphere. Your results provide evidence that (i) the 1,4-H shift is very favorable kinetically and (ii) the kinetic preference for the 1,4-H shift decreases as the *syn* acetaldehyde oxide has more internal energy.

4. (35 points total) To get you geared up to tackle your final project at the end of the semester, let's consider a question where I don't spell out the chemical background or procedure in detail. First, read about characterizing S_N2 reactions on pp. 208-210 in the *Exploring Chemistry with Electronic Structure Methods* book. Next, using HF theory and the 6-31+G(d) basis set, locate all the stationary points (reactants, ion-dipole complex I, transition structure, ion-dipole complex II, and products) for three S_N2 reactions of substituted methanes:
- Your nucleophile will be SeH^- , and your leaving group (generically referred to as X^-) will be F^- , Cl^- , and Br^- .
 - Don't worry about the zero-point energies (ZPEs) discussed by your textbook yet—we'll talk about them in class next week.
 - You are free to use whatever transition structure location method(s) you want.
- (a) (18 points) For each reaction, set the combined energies of the reactants to zero, and report the energies (in kcal/mol to two decimal places) of ion-dipole complex I, the transition structure, ion-dipole complex II, and the products relative to that zero.
- (b) (9 points) For each reaction, tabulate the $Se\cdots C$ and $C\cdots X$ bond lengths for ion-dipole complex I, the transition structure, and ion-dipole complex II
- (c) (8 points) Report, and rationalize, any periodic trends you see in the results summarized in your answer to parts (a) and (b).