Computational Chemistry
Problem Set 3
Due Monday, February 16, 2009 (at the start of class)

Total Possible Points = 69

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.

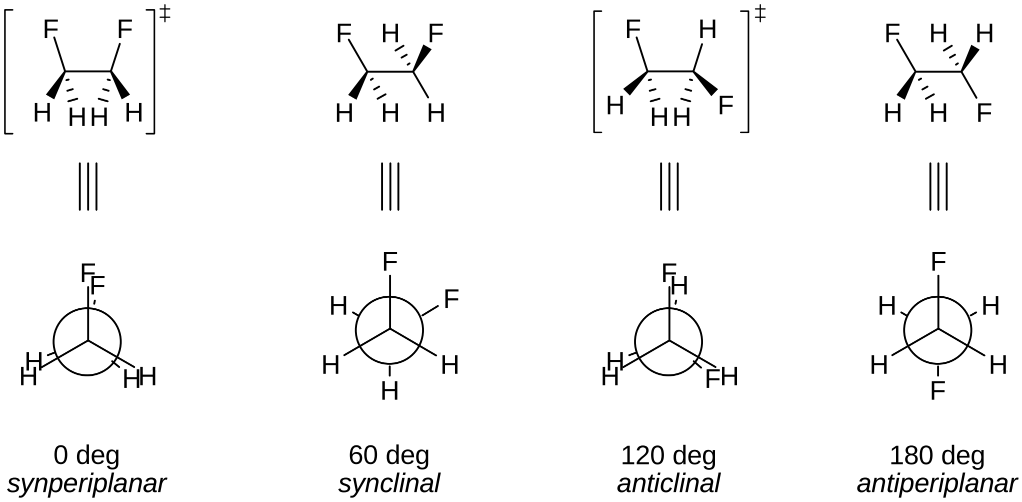
Material We Will Work on Together in Class

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?

Guessing Transition Structure Geometries Directly

We will locate each of the four stationary points below:



(Look at your handout from last week to see where the Klyne-Prelog conformational labels come from!)

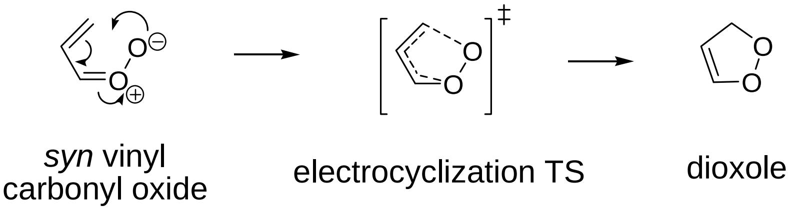
For the transition structures: Under Job Options, choose to do a Transition State Optimization Hartree-Fock 3-21G calculation. Before you submit the job, click on the Preview tab and click on the Generate button. At the end of the command line add `freq=noraman` (include at least one space between this key word and the other keywords in the command line). Then submit the job.

For the minima: Under Job Options, choose to do a Optimize + Vib Freq Hartree-Fock 3-21G calculation.

When these calculations are Complete, we will confirm the identities of the stationary points as minima or transition structures, measure optimized F-C-C-F dihedral angles, and compare and discuss relative energies.

Guessing Transition Structures by Interpolation

As I mentioned on the first day of class, one of my research students, Luke Valin '05, discovered a new atmospheric chemistry reaction. We will locate the transition structure for a simpler version of the molecule Luke worked on:



Start by doing an Optimize + Vib Freq Hartree-Fock 3-21G calculation on the reactant. (Note that you do not draw the electron-pushing arrows! I included them only to get your mechanistic organic juices flowing—to prove that you are already equipped to think about reactions not yet reported in the literature.) Write down the Number of the carbonyl oxide calculation as listed in the WebMO Job Manager. With the Calculated Output of the carbonyl oxide calculation on your screen, write down the numbers of each of the atoms. (We will do this together.)

Next, draw the dioxole by starting with a cyclopentane ring. (Go to Build: Fragment…, Category: Rings, and Fragment: Cyclopentane.) Again, do an Optimize + Vib Freq Hartree-Fock 3-21G calculation.

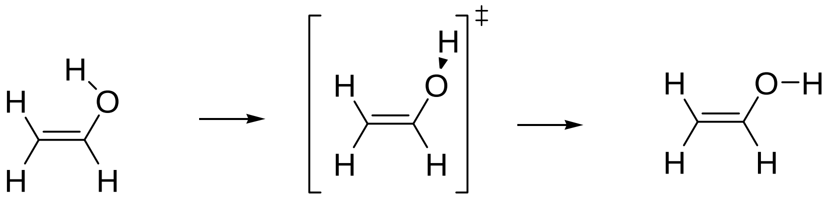
Next, we will as a class open the Calculated Output for the dioxole. Click on New Job Using This Geometry. For our interpolation scheme to work, the atoms must be numbered the same way in the reactant and in the product. To do this, first rotate the dioxole so its orientation matches that of the vinyl carbonyl oxide. Then go to Tools: Z-Matrix… in the Build window. In the **Order** column, renumber any atoms in the dioxole that do not match their numbers in the carbonyl oxide. (We will do this together.) When you are done renumbering, click on the ReOrder and OK buttons. Then submit the job using the same commands (Optimize + Vib Freq Hartree-Fock 3-21G) as before, but with a new job name.

Finally, we will as a class open the Calculated Output for the re-numbered dioxole. Confirm that the numbering scheme is correct. Click on New Job Using This Geometry. Then click on Job options. Choose to do a Saddle Calculation Hartree Fock 3-21G. Click on the Advanced tab, and type in the box next to "Second Geometry (job number)" the number of the carbonyl oxide job. Click on the Preview tab and the Generate button. Alter the keyword `OPT=(QST2)` to `OPT=(QST2,TIGHT,CALCALL)`. (QST2 is Gaussian 03's geometry interpolation algorithm.) Finally, submit the job.

We will work together on characterizing each stationary point, and how the energy and geometry of the system change along the reaction coordinate.

Your Homework for the Week

1. (14 points total) Locate the transition structure for the interconversion of the two stable conformers of vinyl alcohol. (You optimized the geometries of the minima in Problem Set 2.)



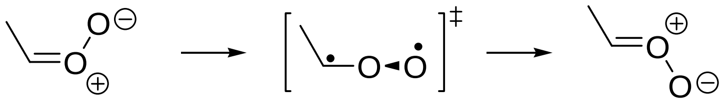
vinyl alcohol-0 vinyl alcohol-TS vinyl alcohol-180

(0 and 180 refer to the H-O-C=C dihedral angle)

In the Job Manager, open one of your successful vinyl alcohol calculations and click on the New Job Using This Geometry. Then click on Open Editor and adjust the H-O-C=C dihedral angle to 90°. (Be sure to select the H atom first, since this is the atom we wish to move!) Then follow the same procedure we used for 1,2-difluoroethane transition structures in class.

(a) Tabulate the absolute energies (in hartree to five decimal places), and the relative energies (in hartrees, and in kcal/mol to two decimal places) for vinyl alcohol-0, vinyl alcohol-TS, and vinyl alcohol-180. (You are free to use, or not use, the Spreadsheet function in WebMO to do this.)
(b) Write down the optimized value for the H-O-C=C dihedral angle in the transition structure (in deg, to one decimal place). Is this value consistent with the Hammond Postulate? Briefly explain.
(c) Write down the imaginary (negative) frequency (in cm^{-1}) of the transition structure, and briefly describe the motion associated with this vibrational frequency.

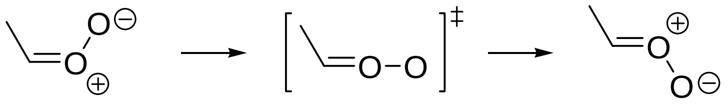
2. (12 points total) There are two mechanisms for the interconversion of *syn* and *anti* acetaldehyde oxide. One, as discussed in class, is rotation about the C=O double bond (Reaction 1):



[1]

syn rotation TS *anti*

The other mechanism involves inversion at the central oxygen (Reaction 2):

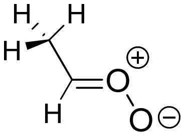


[2]

syn inversion TS *anti*

Location of the rotation transition structure is very difficult, and we will not tackle it until later in the semester. However, it will be straightforward (if time consuming) to locate the inversion transition structure. Here's how you would do this:

- Recall that we did calculations on both the *syn* and *anti* conformations of acetaldehyde oxide during class on February 2. Make sure that your *anti* acetaldehyde oxide has precisely this conformation and B3LYP/6-31G(d) energy:

  anti

  -228.90545 Hartree

  If this is not the case, rotate the methyl group and repeat a Geometry Optimization B3LYP 6-31G(d) calculation.

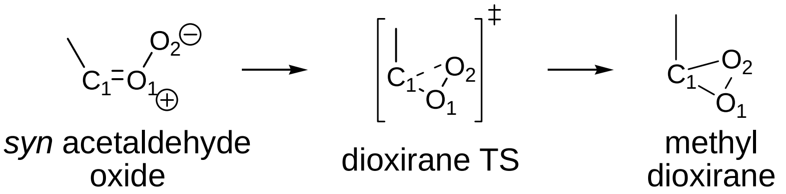
- In the Job Manager, open one of your successful acetaldehyde oxide calculations and click on the New Job Using This Geometry. Adjust the O-O=C angle to 180º. (Be sure to click on the terminal O first.) Under Job Options, choose to do a Transition State Optimization B3LYP 6-31G(d) calculation. Click the Advanced tab and click the box next to Cartesian Coordinates. (We always have to do this whenever we set an angle to 180º.) Click on the Preview tab and click on the Generate button. You should see in the command line the keyword `OPT=(TS,CalcFC,NoEigentest)`. This keyword should be altered thus: `OPT=(TS,tight,calcall,NoEigentest)`

  (By the way, Gaussian 03 is not case-sensitive. If you are doing computational chemistry under the influence of e. e. cummings and type `opt=(ts,tight,calcall,noeigentest)` it would be equally valid.)

  Then submit the job. (Note: It took me ~30 min for this job to complete. These non-trivial calculations are typical of what is published in the chemical literature.)

(a) Write down the O-O=C bond angle (in deg, to one decimal place) in the optimized transition structure for Reaction 2.
(b) Write down the imaginary (negative) frequency (in cm^{-1}) of the transition structure, and briefly describe the motion associated with this vibrational frequency.
(c) For Reaction 2, calculate the activation energy (in kcal/mol, to two decimal places) for the forward reaction (*syn* → *anti*) and the reverse reaction (*anti* → *syn*). (You will need to refer to the B3LYP 6-31G(d) results for *syn* and *anti* acetaldehyde oxide that we obtained in class last week.)

3. (19 points total) *Syn* acetaldehyde oxide can undergo other unimolecular processes besides Reactions 1 and 2, as discussed in the previous problem. Another process is formation of a three-membered ring known as a dioxirane (Reaction 3):



[3]

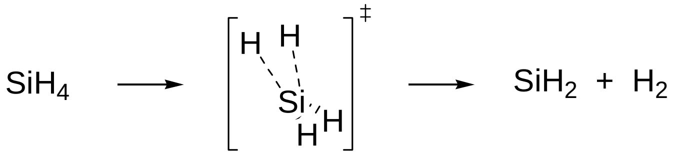
- Note the Job Number of your *syn* acetaldehyde oxide calculation from last week.

- Build methyl dioxirane by going to `Build:Fragment` and adding the cyclopropane ring to your workspace. Delete hydrogens and add non-hydrogen atoms as needed to make methyl dioxirane. Use the `Clean-Up:Add Hydrogens` function to put the hydrogens of the methyl group in reasonable locations. Do an Optimize + Vib Freq B3LYP 6-31G(d) Calculation. Confirm that methyl dioxirane has all real frequencies. If not, alter your initial geometry and repeat the optimization.

- Finally, locate the transition structure using the same method demonstrated in class for the *syn*-vinyl carbonyl oxide → dioxole reaction. Be sure that your atoms are labeled in the same order in the reactant and in the product. Also note that you should repeat the methyl dioxirane calculation at the B3LYP/6-31G(d) level (not the Hartree-Fock 3-21G level) before starting your transition structure search.

(a) Write down the imaginary (negative) frequency (in cm^{-1}) of the transition structure, and briefly describe the motion associated with this vibrational frequency.
(b) Write down the C_1-O_1, O_1-O_2, and C_1-O_2 bond lengths (in Å, to three decimal places) for the reactant, the transition structure, and the product, even if the atoms are not bonded. Relate the trends in these bond lengths to the changes in bonding that happens along the reaction coordinate.
(c) Calculate the activation energy (in kcal/mol, to two decimal places) for the reaction.
(d) Calculate the reaction energy (in kcal/mol, to two decimal places) for the reaction.

4. (10 points total) An active area of materials science research involves computer modeling of the semiconductor preparation process. One key reaction in this process involves the loss of molecular hydrogen from Group 14 hydrides such as silane:



(Prof. Jim Doyle in Physics and I have talked about collaborating on a project that would include modeling the analogous reaction of germane, GeH_4.)

Start by doing Optimize + Vib Freq B3LYP 6-31G(d) Calculations on the reactant and each of the products of the above reaction. Confirm that SiH_4, SiH_2, and H_2 all have all real frequencies.

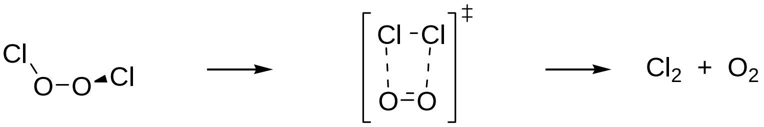
Next, as in Problem 3, we will locate the transition structure of interest by performing a "Saddle" (QST2) calculation. The interpolation procedure is slightly different here, however, since there are two products:

> Write down the number of the completed SiH_4 job in the Job Manager. View the Calculated Output of the SiH_4 job. Click on New Job Using This Geometry. Alter the geometry as follows: Adjust two of the Si-H bond lengths to 3.0 Å. Adjust the angles between these two lengthened Si-H bonds to 15°. Check that the distance between the H's on the two lengthened bonds is around 0.78 Å. Then click on Job options. Choose to do a Saddle Calculation B3LYP 6-31G(d). Click on the Advanced tab, and type in the box next to "Second Geometry (job number)" the number of the silane calculation. Click on the Preview tab and the Generate button. Alter the keyword `OPT=(QST2)` to `OPT=(QST2,TIGHT,CALCALL)`. Finally, submit the job.

(Note that since we created the initial geometry of the transition state by perturbing the reactant geometry, we are assured that the atoms will be labeled consistently. So that's one plus.)

(a) Write down the imaginary (negative) frequency (in cm^{-1}) of the transition structure, and briefly describe the motion associated with this vibrational frequency.
(b) Calculate the activation energy (in kcal/mol, to two decimal places) for the reaction.
(c) Calculate the reaction energy (in kcal/mol, to two decimal places) for the reaction.

5. (14 points total) As you all know from Analytical Chemistry, one of the key molecules in the ozone depletion mechanism is chlorine peroxide, ClOOCl. One possible way for this molecule to decompose is shown below:



Molecular chlorine is very light-sensitive, and will decompose readily in sunlight to give two chlorine atoms. The other product, molecular oxygen, is formed in an electronically excited state. Unlike ground state O_2, which has two unpaired electrons, electronically excited O_2 has no unpaired electrons. The O_2 product is therefore a singlet, like most of the molecules we have considered so far. However, there is some quantum mechanical funny business: the highest energy electron pair has an equal probability of occupying the π_x^* molecular orbital and the π_y^* molecular orbital. There are special commands we use to describe this degeneracy effect, as I mention below.

Start by doing Optimize + Vib Freq B3LYP 6-31G(d) Calculations on the reactant and each of the products. Some hints:

- Make sure that the ClOOCl structure you locate is a minimum! If it is a transition structure, alter the geometry and repeat the Optimize + Vib Freq Calculation.

- For O_2, before you submit the job, click on the Preview tab and the Generate button, and change `B3LYP` to `UB3LYP`. Add the keyword `guess=mix` The last two alterations enable Gaussian 03 to treat the delocalization of electron density into the π_x^* and π_y^* orbitals.

View the Calculated Output of the ClOOCl job. Click on New Job Using This Geometry. Alter the geometry as follows: Adjust the Cl-O-O-Cl dihedral angle to 0.0°. Set the O-O bond length to 1.21 Å. Set each of the Cl-O bond lengths to 3.0 Å. Finally, set each Cl-O-O bond angle to 97°. (It is important that you click the atoms in the order given.) Then click on Job options. Choose to do a Saddle Calculation B3LYP 6-31G(d). Click on the Advanced tab, and type in the box next to "Second Geometry (job number)" the number of the ClOOCl calculation. Click on the Preview tab and the Generate button. Alter the keyword `OPT=(QST2)` to `OPT=(QST2,TIGHT,CALCALL)`. Change `B3LYP` to `UB3LYP` and add the keyword `guess=mix`

(a) Write down the optimized value of the dihedral angle of ClOOCl (in deg, to one decimal place) and briefly rationalize its value.
(b) Write down the imaginary (negative) frequency (in cm^{-1}) of the transition structure, and briefly describe the motion associated with this vibrational frequency. (The motion is kind of ambiguous, at least to my eyes! Later this semester, we will learn a rigorous technique for predicting more precisely the geometries of the minima surrounding a transition structure.)
(c) Calculate the activation energy (in kcal/mol, to two decimal places) for the reaction.
(d) Calculate the energy change (in kcal/mol, to two decimal places) for the reaction.