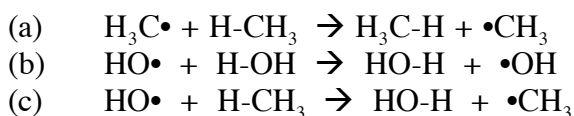


# CEM 888 Lab/Homework Assignment

## Due Wednesday, March 9, 2005

### Transition States and Reaction Paths

The purpose of this lab is to develop your abilities to easily locate and analyze transition state structures and their associated reaction paths. This time, we will use SPARTAN for the whole process, mainly because it's easy to build the inputs and Spartan makes it easy to visualize the vibrations of the molecules. We will begin by examining two symmetrical hydrogen atom transfer reactions, and then consider an unsymmetrical case. In the interests of time, the calculations should all be done at the UHF/3-21G level, but we'll have a chance in the homework to do more substantial things along this line. The three reactions are:



1. Use SPARTAN to input and optimize starting and ending species separately. Then put them together and optimize the van der Waals complexes of the incoming radical and its substrate. For reaction (c) you will also need to optimize the product vdW complex.

2. For reactions (a) and (b) you can make the very reasonable guess that the TSs will be symmetrical--i.e. that the C...H...C and O...H...O will have equal C-H and O-H bond lengths, respectively (but they don't have to be linear!). You can build them that way in Spartan by building  $\text{H}_3\text{C-Se-CH}_3$  where you have used the "expert" feature of the builder and chosen a linear, two-bonded "Se" atom to attach to your methyl groups. Same deal with the OH's, but be sure not to make your O linear! Go ahead and use the minimizer in the builder on your Se-containing structure. Check that it's symmetrical by querying the symmetry. Then, in expert mode still, change the Se to H *and that's it--don't reminimize*. Save it with a name and exit the builder. You might want to save a copy just in case something goes wrong (it often does).

3. Optimize your candidate TS structures, using just the "opt" (minimize) command in the ab initio window--not optimizing to a TS as far as the software can tell. The calculation shouldn't break the symmetry it recognized, and keeping that symmetry locks the reaction coordinate in place at the TS position, so you just want to minimize the energy within the symmetry. Calculate frequencies, and verify that you have only one imaginary frequency listed which, when visualized, corresponds to the H-transfer motion.

4. Return to the Spartan builder, and construct the inputs for the  $\text{HO}\cdot + \text{H-CH}_3$  reaction (you've already done the endpoints. Choose the various lengths of spectator C-H and O-H bonds based on what you found in (3). *Don't optimize yet!* Now run a single point calculation and request frequencies.

5. Optimize your  $\text{HO}\dots\text{H}\dots\text{CH}_3$  transition state structure by requesting a TS optimization and checking the "wavefunction" and "hessian" boxes at the bottom of the job setup dialogue box. This means your new submission will look back at the (stored) complete hessian and with that info will be more efficient in the TS search.

6. Write up a summary of your results, including potential energy diagrams with separated fragments, vdW complexes, and TSs. Include pictures of calculated TSs and minima. A useful reference for this assignment is: Basch, H.; Hoz, S. *J. Phys. Chem. A* **1997**, *101*, 4416-4431.

7. For extra credit, you can compute TSs and activation barriers for HO• abstracting H from ethane, the 2-position of propane, and the central C of isobutane to form, respectively, primary, secondary, and tertiary alkyl radicals. Then look at the C...H and O...H distances in the various TSs and see if they relate in an appropriate Hammond postulate manner to the calculated barriers and exothermicities of the reactions.