

1. We saw in class how a small difference in activation energies, $\Delta(\Delta G^\ddagger)$, leads to a large difference in rate constants, k_1/k_2 .
 - a. What value of $\Delta(\Delta G^\ddagger)$ makes $k_1/k_2 = 2$ at -78°C , 20°C , and 100°C ?
 - b. How could you make a reaction more selective, by raising or lowering the reaction temperature? Assume $\Delta(\Delta G^\ddagger)$ is temperature-independent.
 - c. What, if any, is the downside of adjusting the temperature to enhance selectivity?
2. Calculate and compare HF/3-21G energy curves for internal rotation about the CC single bonds in 1,3-butadiene and acrolein, $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$. Procedural tips:
 - a. Build model.
 - b. Define dynamic constraint by 1) define **Dihedral constraint**, 2) select constraint by clicking on purple symbol, 3) select **Display: Properties**, 4) check **Dynamic**, 5) enter angle range ($0^\circ \rightarrow 180^\circ$) and number of steps (13).
 - c. Submit **Energy Profile** calculation using **Hartree-Fock** with **3-21G**.
 - d. After calculation is complete, close model (**modelname.spartan**) and open "list" model (**modelname.M001.spartan**).
 - e. Add relative energies (in kcal/mol) and dihedral angles to spreadsheet. Copy data to Excel and print plots
 - f. Why are the curves so different at *small* dihedral angles?
3. A **structural motif** is a recognizable arrangement of atoms, such as a *half chair* cyclohexane or DNA *double helix*. In many cases, we can infer some molecular properties from the motif, for example, a nonplanar alkene is more strained than a planar one. Carefully and thoroughly examine the *Spartan* transition state models (HF/3-21G) for one of the two reactions in problem #1 of HW #2. (I have provided models¹ for both reactions so you can choose the one that interests you more.) 1) Identify as many structural motifs as you can in each transition state.² 2) Try to rationalize the relative energies of the transition states for each reaction.
 - **hw2q1a.sxf** – 4 transition states for problem 1a, HW #2
 - **hw2q1b.sxf** – 4 transition states for problem 1b, HW #2

¹ The original *Spartan* models occupied a great deal of memory (> 1 Mbyte). The models provided here have been saved in a different format called *Spartan Exchange*. This format saves space by discarding the model wave function, but you can still open these models from inside Spartan (do not double-click on the model file; that won't work) and examine them in the usual way. Use **Display Properties** to get the model energies.

² List a motif even if it appears in the same way in all of the transition states.

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HW #3, Due W, Feb 20 (**REVISED DATE #2**)