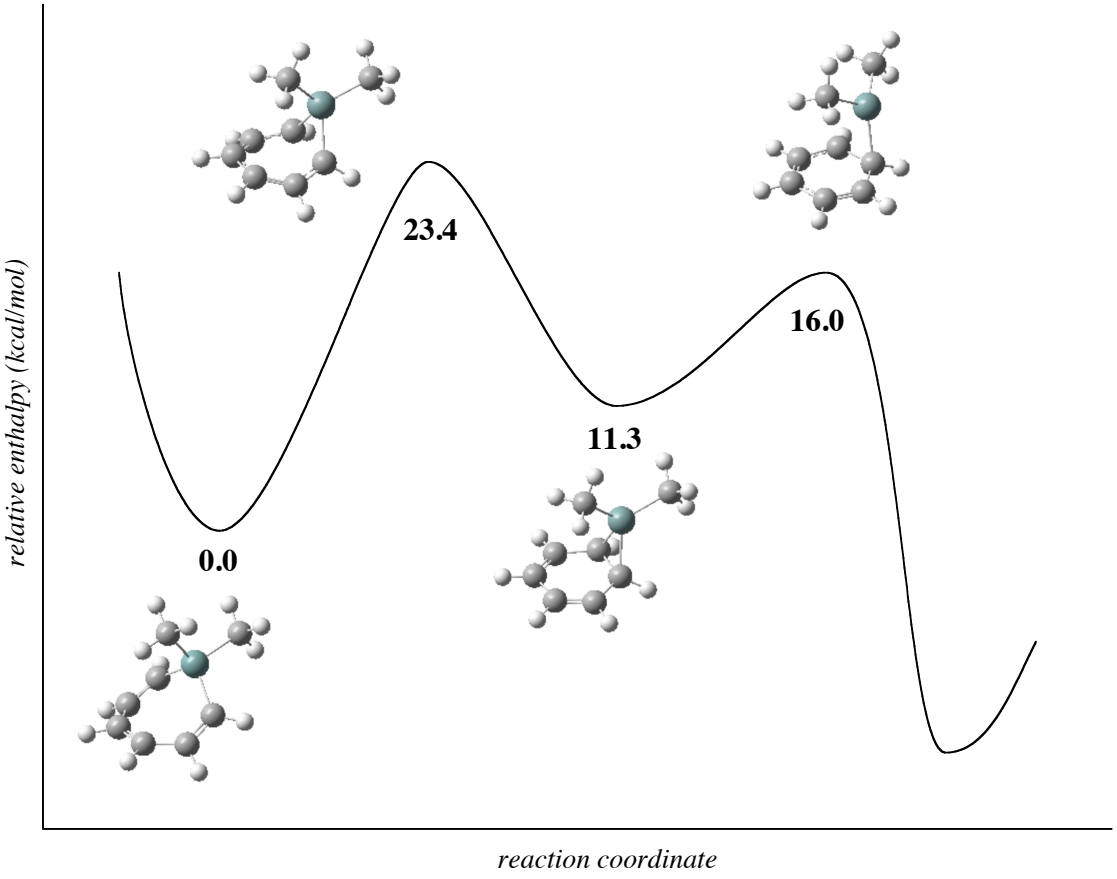
Chemistry 4021/8021 **Computational Chemistry** 3/4 Credits

Spring Semester 2010

Key

1. Consult Mochida, K.; Matsuhida, N.; Sato, R.; Nakadaira, Y. *Organometallics* **2006**, *25*, 4231.

   a. Scheme 2 (page 4232) shows the reaction for the thermolysis of **1** to benzene and singlet dimethylgermylene, $Ge(Me)_2$, and suggests a possible transition state (**3**). Determine whether **3** is really a transition state or whether it is a reactive intermediate (i.e., a high-energy minimum). Symmetry might prove useful in speeding up your calculations. Use M06-2X/6-31G(d) for your final assessment, although initial calculations at a lower level of theory and/or with a smaller basis set may prove useful at your discretion. Is **3** a TS or a minimum? If **3** *is* a minimum, find the transition-state structure between **1** and **3**, and the TS structure for dissociation. *Nota bene*: when imposing symmetry, one occasionally finds a TS structure associated with a molecular motion that breaks the symmetry, but that is *not* the reaction coordinate. *Visualize* your imaginary modes to decide if any TS structure is actually the one that you *want*.



The relative enthalpies and structures of the two intermediates (**3** from Mochida et al. *is* a local minimum) and associated TS structures are illustrated in the preceding structure. At the M06-2X/6-31G(d) level, the electronic energies (E_h) of the structures from left to right are –2386.894 76, –2386.855 03, –2386.877 29, –2386.868 80.

b. Using whatever transition state you determine to be relevant, compare your calculated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to the experimental values given in the paper (assume the temperature difference between default 298 K in Gaussian and the experiment to have a negligible effect on the computed thermodynamic variables). Use your predicted $\Delta G^{\ddagger}$ to calculate the unimolecular rate constant, k, at 305.3 K (indicate the equation that you used to get the rate constant). Do your errors seem reasonable given the method and basis set used? Correct your electronic energies by doing *single point* calculations at the M06-2X/6-311+G(2df,p) level. Are things improved by comparison to experiment? While it is always possible that deviations between theory and experiment represent inaccuracy in the modeling, what *physical* effects might be responsible for differences between theory and experiment?

The relative enthalpy of the first TS structure (which corresponds to the rate determining step) is 23.4 kcal/mol, which compares reasonably with the experimental value of 20.5 kcal/mol. The computed entropies for **1** and the rate-determining TS structure are 101.794 and 101.905 cal/mol-K, respectively, which corresponds to an entropy of activation of +0.1 cal/mol-K. This compares poorly with the experimental value of –8.1 cal/mol-K. The experimental value may well reflect changes in the toluene solvation shell (the experimental values were determined in toluene solution) and our gas-phase calculations do not consider this possibility.

It is appropriate to use the transition-state theory equation from the text for a unimolecular reaction

$$k = \frac{k_B T}{h} e^{-\Delta G^{o\ddagger} / RT} \qquad (15.27)$$

The predicted free energy of activation for the rate determining step is 23.4 kcal/mol. At T = 305.3 K, eq. 15.27 predicts a unimolecular rate of 1.22 x 10^{-4} sec^{-1}. The experimental rate constant is reported as 2.23 x 10^{-4} sec^{-1}. This agreement of a factor of 2 is certainly quite good!

c. In the paper, the progress of the reaction is described as having been followed by proton NMR, but the shifts that were observed are not described. Could the reaction have been followed instead using UV/Vis spectroscopy? Based on TD DFT computed UV/Vis data (ask for 10 states in your calculations (do not use the default value of 3) and employ the PBE0 functional, which in G09 is invoked by the keyword

pbe1pbe), how would you expect the UV/Vis spectrum to evolve over the course of the reaction?

I chose to include diffuse functions in the basis set for the UV/Vis calculation, but this is not necessarily critical. In any case, at the PBE0/6-31+G(d) level, the reactant **1** is predicted to have a long-wavelength absorption with a significant oscillator strength at 283.7 nm. The product benzene has no allowed absorption at wavelengths beyond 174. So, following the disappearance of the 283.7 nm absorption might well have been an option. Note that the UV/Vis spectrum of **3** is not really relevant, since the low barrier to products means that the steady-state concentration of **3** will always be very low.

2. Here continues a problem that will carry over to the final exam. We add to the data at:

pollux.chem.umn.edu/8021/PES/

Your present task is to update your two structures on the potential energy surface (PES) with a calculation at the M06/6-31G(d) level (since there is no double slash, this implies re-optimizing the geometry). The most efficient way to do this will be to read in the force constants and geometry from your RHF frequency calculations (i.e., fopt=(readfc) geom=checkpoint, guess=read) as keywords. *Nota bene*: if you were using fopt=ts you will need to continue to use ts, of course. Once you have a reoptimized structure, do a new frequency calculation at the M06/6-31G(d) level and update your entry with those data.

Finally, compute the M06/6-31G(d) *aqueous* solvation free energy for your DFT structure using the SMD model in Gaussian09 (as a *single-point* calculation on the DFT optimized geometry). When the calculation completes, add the solvation free energy to the website data. Report only one position after the decimal place for the solvation free energy in units of kcal/mol (the solvation free energy is the difference between the M06 SCF energies in solution (found in the SMD output file) and in the gas phase (found in the M06 geometry optimization output file)).

As for Problem Set 2, full credit will be awarded for sensible PES data.