# C343: Physical Chemistry Lab II

22 February 2021

1. Isotope Effects in Chemical Reactions

A direct consequence of the effect of isotoptic substitution in a molecule is that enthalpies of bond dissociation for isotopically substituted molecules (light to heavy) are larger than those for unsubstituted molecules.

1. Perform B3LYP/6-31G* calculations on HCl and on its dissociation products, chlorine atom and hydrogen atom. Following geometry optimization on HCl, calculate the vibrational frequency for both HCl and DCl and evaluate the zero point energy for each. In terms of a percentage of the total bond dissociation energy, what is the change noted in going from HCl to DCl?

2. d_1-Methylene chloride can react with chlorine atoms in either of two ways: by hydrogen abstraction (producing HCl) or by deuterium abstraction (producing DCl):
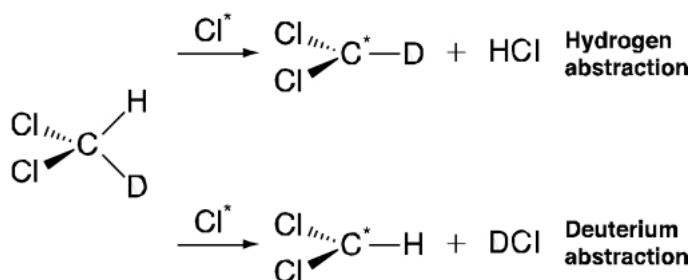

   (a) Which pathway is favored on the basis of thermodynamics? What would you expect the (thermodynamic) product ratio to be at room temperature?

Hint: Obtain the equilibrium geometry for dichloromethyl radical using the B3LYP/6-31G* model. Also obtain vibrational frequencies for both the unsubstituted and the deuterium-substituted radical and calculate zero point energies for the two abstraction pathways (you already have zero point energies for HCl and DCl).

(b) Which pathway is favored on the basis of kinetics? Is it the same or different from the thermodynamic pathway? What would you expect the (kinetic) product ratio to be at room temperature?

Hint: Obtain the transition state for hydrogen abstraction from methylene chloride using the B3LYP/6-31G* model. A reasonable guess is shown here:
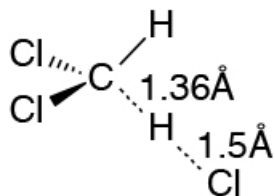
Calculate vibrational frequencies for the two possible structures with one deuterium and evaluate the zero point energies for these two structures. (For the purpose of zero point energy calculation, ignore the imaginary frequency corresponding to the reaction coordinate.)

(c) Compute the kinetic isotope effect for the reaction.