7.1: Overview

Learning Objectives

- Students will demonstrate the ability to estimate the sign of the ΔG° of a chemical reaction.
- Students will be able to calculate the ΔG°, ΔS°, and ΔH° of a reaction using density functional theory with Orca.
- Students will be able to search for a transition state of a simple one step reaction using Orca.
- Students will be able to relate the magnitude of $\Delta G^\ddagger$ to the rate of a reaction.

Overview: The energy changes involved in reagents reacting to make products are extremely informative to chemists. Specifically, this information can give us insight into how much product can be formed and how fast the reactants can be converted into products. Organic chemists will often use simple methods to estimate the direction of a chemical reaction based on thermodynamic principles. While such tools are useful as a first approximation, more accurate information can be very useful for chemists seeking to make a compound in the highest yield possible or to understand a chemical process. In the exercise that follows we will learn how to calculate both the thermodynamic equilibrium as well as the activation barrier of a simple chemical reaction using Orca.[1–3]

Faculty Notes: This exercise is designed to help students relate fast and simple thermodynamic approximations of a reaction to more accurate computations done using density functional theory. Before assigning this exercise, students should have been exposed to basic reaction thermodynamics. Specifically, students should have seen how Gibbs free energy can be related to entropy and enthalpy. Additionally, students should have a basic understanding of microscopic entropy, such as being able to predict whether a dissociation reaction will be entropically positive or negative. A standard desktop computer takes about 15 minutes to run the computation in this exercise. Overall, the exercise should take students about 1.5 hours to complete.

A note on reaction coordinate diagrams: in a typical reaction coordinate diagram as seen in organic chemistry textbooks, the x-axis is the reaction coordinate, and the y-axis is energy. This diagram describes the potential energy surface for a single molecule undergoing the reaction, and so energy is a reasonable choice of axis. This activity utilizes transition state theory which assumes an ensemble of molecules in quasi-equilibrium between the starting material and transition state. Entropic and energetic factors affect this ensemble, and the reaction coordinate diagrams address this by using Gibbs energy instead of energy. Based on this statistical treatment, showing structures, and using reaction coordinate is somewhat misleading, though it is still common practice. For pedagogical reasons, in the figures below we have chosen to include structures to indicate the reactants, products, and transition state on these diagrams.