9.1: Overview

Learning Objectives

- Students will build understanding of radical reactions.
- Students will build knowledge of what drives selectivity in radical halogenation reactions.
- Students will be able to use Orca to calculate the bond dissociation enthalpy of $C-H$ bonds and the stability of carbon-based radicals.
- Students will be able to use calculated BDE values, and radical stability calculations to interpret the experimental halogenation of norbornane.

Overview: This exercise seeks to help you understand how the concept of bond dissociation enthalpy (BDE) can serve help predict reactivity of $C-H$ bonds in a radical reaction. Halogenation of aliphatic $C-H$ bonds proceeds via a hydrogen atom abstraction from the hydrocarbon by a radical halogen atom. The identity/reactivity of the radical halogen species and the stability of the carbon-based radical formed upon hydrogen atom abstraction play a large role in what $C-H$ bond of a molecule is halogenated. In this exercise we will calculate the bond dissociation enthalpy of $C-H$ bonds of norbornane using Orca and Avogadro.[1–5] By comparing these values to the experimental results of a radical chlorination of norbornane, we can gain insight into the surprising selectivity of this reaction.

Faculty Notes: This exercise is designed to help students understand what bond dissociation enthalpies are and how they relate to the regioselectivity of radical $C-H$ halogenation. Before assigning this exercise, students should have learned the mechanism of radical $C-H$ halogenation and how to use the relative reactivity of halogen radicals to predict the distribution of halogenated products.

There are a total of 4 calculations that students will need to perform with Orca in this exercise. Each of these calculations can take 30-40 minutes if run on a single processor. To minimize the amount of time that this exercise takes, students should be advised that they can run more than one calculation at the same time. Moreover, if working in groups, students can distribute these calculations over several computers. Alternatively, the output files for all calculations are provided in the faculty resources for this exercise. These files can be given to students to analyze and answer the questions at the end of the exercise. Overall, this exercise should take students about 2 hours to complete.