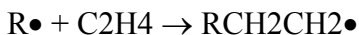


GAUSSIAN HOMEWORK PROBLEM

Addition reactions of the type



And their reverse “ β -scission” reactions play a crucial role in polymerization, pyrolysis, and combustion. These exothermic reactions have significant barriers, and run in the forward direction at low temperatures. This is the key reaction in free radical polymerization to form polyethylene, the highest volume chemical process in the world. Above their “ceiling temperature” the equilibrium constant favors the reactants over the products, and the reactions run backwards. These back reactions are the key steps in the breakdown of polymers or other high molecular weight organics, e.g. to make ethylene in a naphtha cracker, or to make the gases that burn from the paraffin wax in a candle. The details of how the reverse reactions depend on R are thought to control the cetane and octane numbers of diesel and gasoline.

Despite their importance in kinetics, only a small number of these reactions have been measured experimentally, due to technical difficulties. At present, several researchers are attempting to calculate these reaction rates using quantum chemical techniques.

Your assignment is to use GAUSSIAN and the transition state theory equation to compute both the forward and the reverse reaction rates at the B3LYP level of theory for the simplest member of this reaction family: $R = CH_3$. Compare the ratio of the rates you calculate with the literature value of the equilibrium constant.

To help you out, we have provided the geometry of the transition state (see the Web page) and will arrange a help session in the computer lab for those unfamiliar with Gaussian.