Chemistry 333 Discussion

Problem Set 5

1. Use homolytic bond-dissociation enthalpies (kJ/mol) in Table 4-2 (p. 167 of Wade, Organic Chemistry, 9th edition) to calculate the standard heats of reaction for the following two (2) reactions.

A.

\[(\text{H}_3\text{C})_3\text{COH} + \text{HBr} \rightarrow (\text{H}_3\text{C})_3\text{CBr} + \text{H}_2\text{O}\]

B.

\[\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow 2\text{H}_2\text{O}\]

2. Draw a labeled reaction-energy diagram (graph of potential energy versus reaction coordinate) for a three-step overall exothermic reaction with the:
   A. first step being the rate-determining step
   B. second step being the rate-determining step
   C. third step being the rate-determining step

Label each graph with the following: reactants (r), transition states (ts\(x\)), intermediates (int\(x\)), products (p), activation energies (Ea\(x\)), and overall standard heat of reaction (\(\Delta H^o\)). (Note: Each subscript, \(x\), needs to be a number that refers to the appropriate primary mechanistic step. For example, Ea\(1\) is the label for the activation energy of the first step.)

3. Draw a labeled reaction-energy diagram for a two-step reaction with an early first transition state and a late second transition state. State whether the transition states resemble the starting material, intermediate, or product. Repeat the exercise for a two-step reaction with a late first transition state and an early second transition state.

4. The photochemical reaction of 2,4-dimethylpentane with molecular chlorine affords a mixture of monochlorinated alkyl halides. Draw the structures of these products and predict the molar ratio when the reaction is run at 25 °C. (Note: For these conditions, the relative rates of hydrogen atom abstraction are 5.5:4.5:1.0 for 3°:2 °:1° alkane carbons.)