

## Problem Set 5

1. In accord with the Hammond postulate, 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. 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 ( $\Delta H^\circ$ ). (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.) Finally, state what the rate-determining step's transition state resembles. Use the Hammond postulate to explain your reasoning.

2. In accord with the Hammond postulate, 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, the intermediate, or the product. Use the Hammond postulate to explain your reasoning. Repeat the exercise for a two-step reaction with a late first transition state and an early second transition state.
3. The photochemical reaction of 2,6-dimethylheptane 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. Show your calculations. (Note: For these reaction conditions, the relative rates of hydrogen atom abstraction are 5.5:4.5:1.0 for 3°:2°:1° alkyl carbons.)