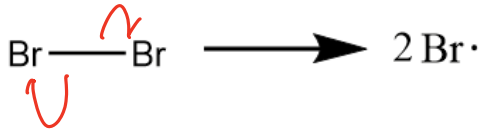
CHEM 223 (2024) SI Session #7

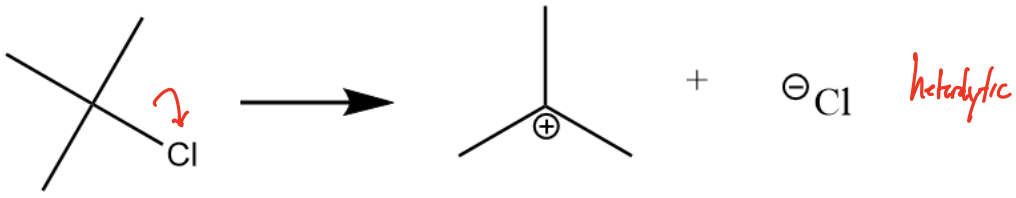
Learning Objectives: By the end of this session, students should be able to:

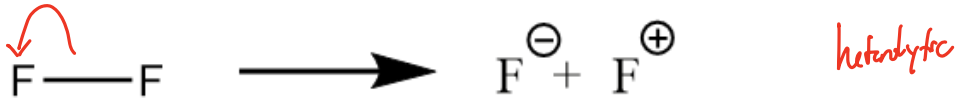
- Differentiate between homolytic and heterolytic cleavage
- Draw the 2(+1) steps in a halogenation reaction.
- Label and explain the different parts of a reaction-coordinate diagram.
- Explain the relationship between activation energy and reaction rate

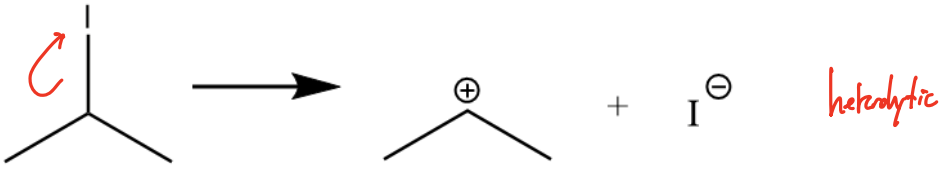
Section 1: Halogenation

1. Label each reaction as "homolytic" or "heterolytic" cleavage. Draw the appropriate mechanism arrows to support your answer.

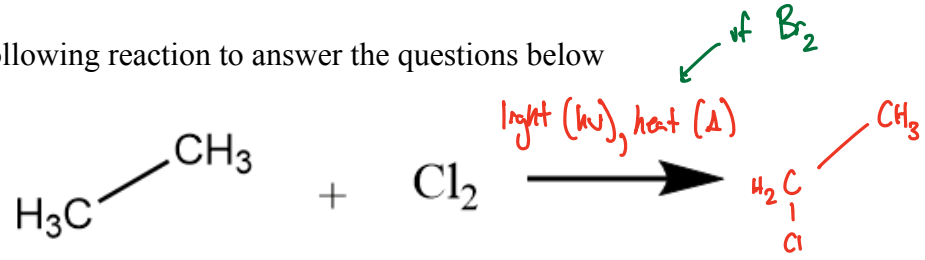
a. 

b. 

c. 

d. 

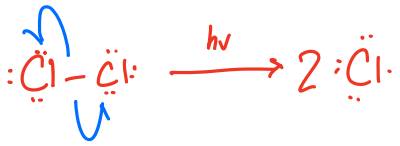
2. Use the following reaction to answer the questions below



   a. Draw the <u>major</u> product of the reaction and add in any missing reagents.

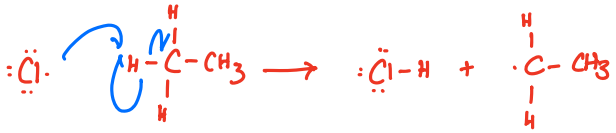
above

b. Draw the mechanism of the initiation step of the reaction.



c. Draw the mechanism of the two propagation steps that follow the initiation steps.

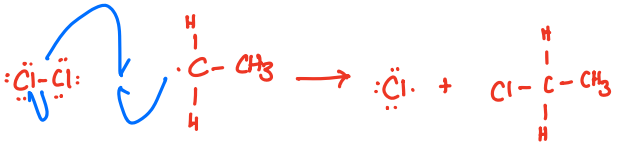
1st propagation



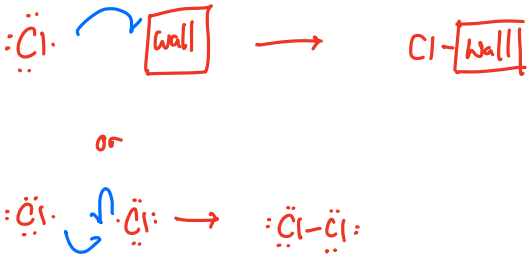
"abstracting" a proton

propagation steps always make radicals

2nd propagation



d. Give an example of one termination step for the reaction



termination steps consume radicals

Section 2: Thermodynamics, Kinetics and Reaction Coordinates

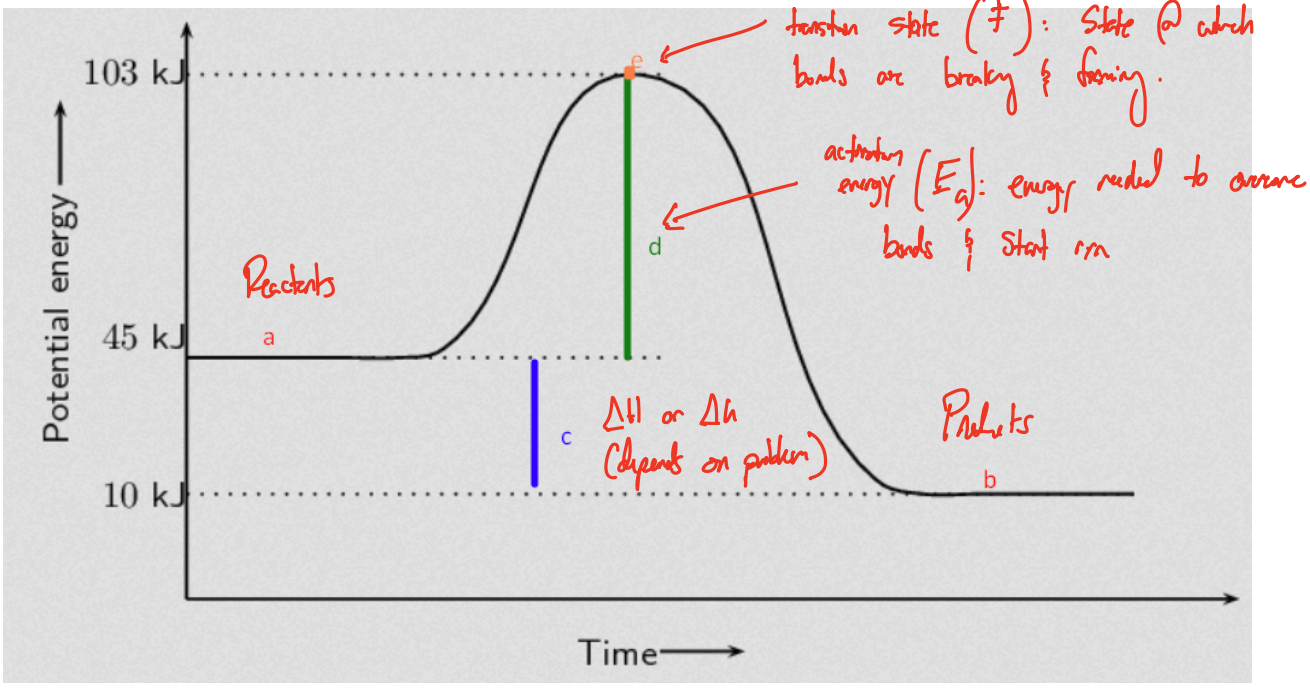
3. Briefly give a definition for each of the following Thermodynamic parameters.
   a. ΔH (enthalpy): heat released or absorbed during a chemical rxn.
      ↳ exothermic: ($\Delta H < 0$) heat is released
      ↳ endothermic: ($\Delta H > 0$) heat is absorbed
   b. ΔS (entropy): Change in randomness
      ↳ more molecules; more heat/volume; Gas >> Liquid > Solid
      $\Delta S > 0$: spontaneous; more entropy
      $\Delta S < 0$: non-spontaneous; less entropy.

c. ΔG (gibbs-free energy): amount of energy available to do work.

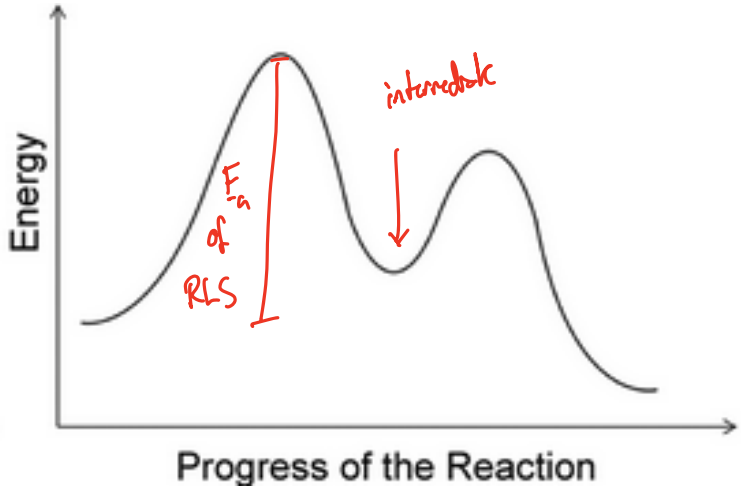
↳ ΔG < 0: spontaneous, endergonic

↳ ΔG > 0: non-spontaneous, exergonic

4. Label the following reaction coordinate diagram.



5. In the following reaction coordinate diagram, label the intermediate and activation energy of the rate limiting step.



6. Explain the effects of activation energy and temperature on reaction rate.

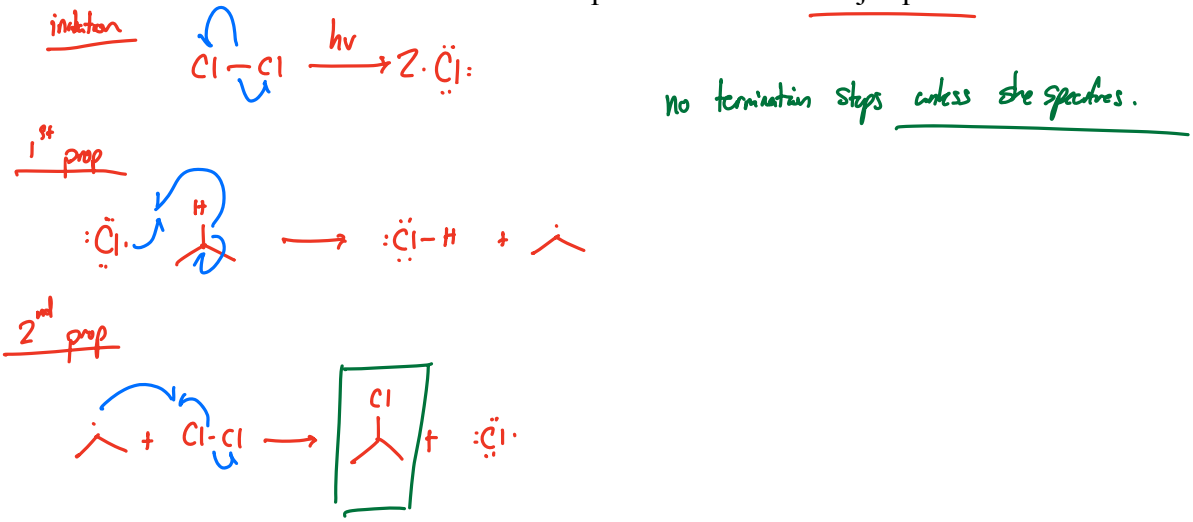
↓ E_a = faster rxn: lower energy barrier means that the rxn can occur more often.

↑ Temp = faster rxn: more average energy per molecule means that E_a has a higher likelihood of being overcome.

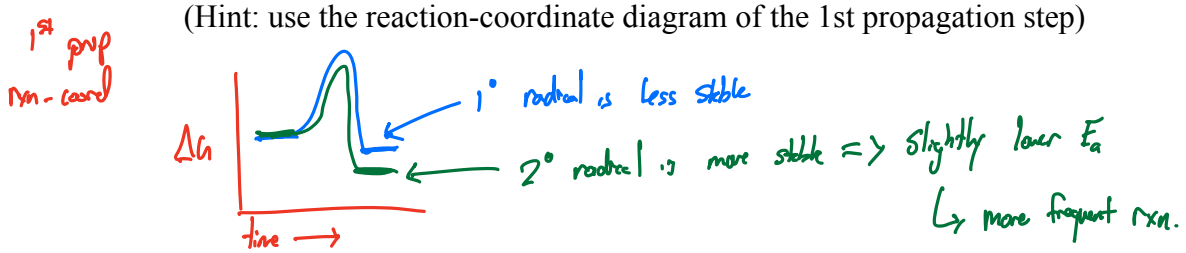
Section 3: Combining Sections 1 and 2; Selectivity and Hammond's Postulate

7. Propane undergoes free-radical chlorination.
   a. Draw the two possible products of this reaction.

   b. Draw the mechanism of the production of the major product.

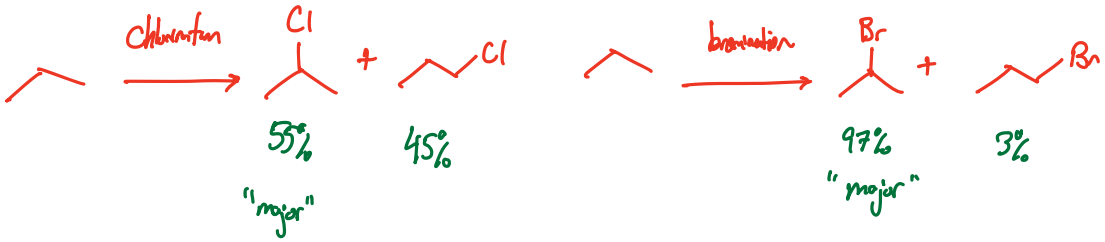


   c. Explain, using a reaction-coordinate diagram, which product is the major product. (Hint: use the reaction-coordinate diagram of the 1st propagation step)



8. Propane undergoes free-radical bromination.
   a. Compare the abundance of the major product in the chlorination and bromination cases.

more abundant (relative to other products)



b. Explain the difference in abundance using a reaction-coordinate diagram and the transition state of the chlorination and bromination (Hint: use the reaction-coordinate diagram of the 1st propagation step)