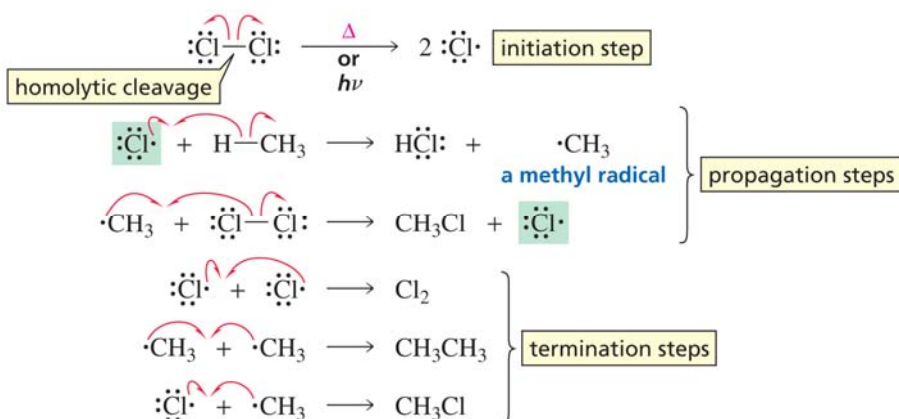


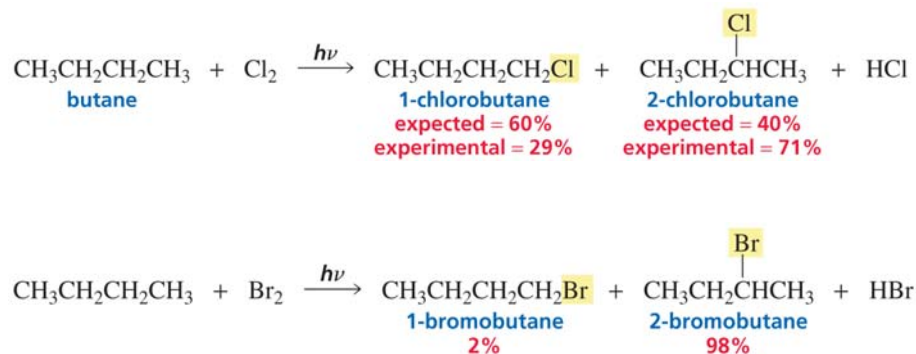
Outline

- Free-radical chlor/bromination
 - Heterolytic vs homolytic cleavage
 - Mechanism of free-radical halogenation
- Probability and reactivity in product distributions
 - Chlorine: 3d 5.0, 2d 3.8, 1d 1.0
 - Bromine: 3d 1600, 2d 82, 1d 1
- Radical stability with substitution
 - MO interaction diagram; discuss stabilization

Mechanism of free-radical halogenation



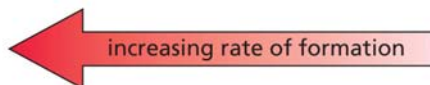
Probability and reactivity in product distributions



Reactivity and selectivity

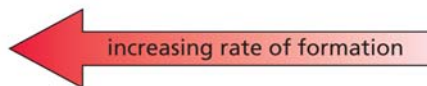
relative rates of alkyl radical formation by a chlorine radical at room temperature

tertiary > secondary > primary
 5.0 3.8 1.0



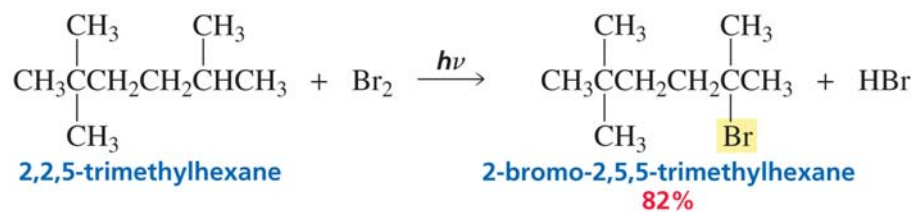
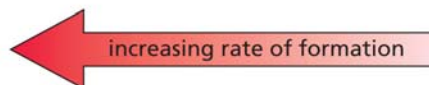
relative rates of radical formation by a bromine radical at 125 °C

tertiary > secondary > primary
 1600 82 1

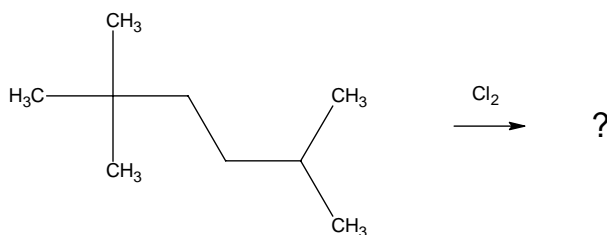


What products do we expect?

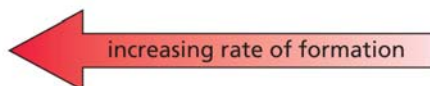
tertiary > secondary > primary
1600 82 1



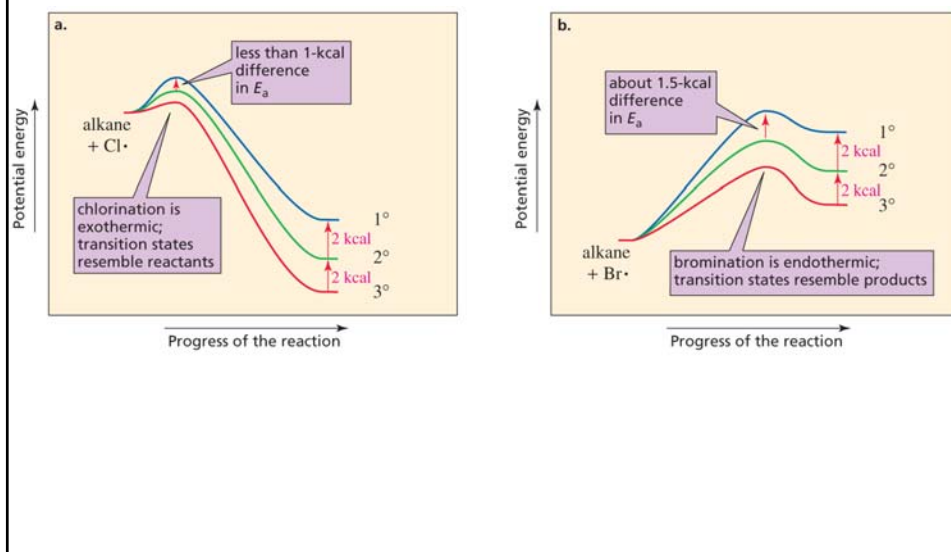
What products do we expect?



tertiary > secondary > primary
5.0 3.8 1.0



Reason for the product distribution



Stability of alkyl radicals

