Radical Halogenation

1) Synthetic utility
2) Cl₂ or Br₂ → reagents
3) conditions
4) mechanism
5) stereochemistry
6) regiochemistry

alkane → alkyl halide

hv (light, usually UV)

abstraction - removal of a hydrogen

chain reaction - a mechanism that repeats continuously (until reagents run out) since one of the products produced is itself a reactant.

propagation

termination

(no radicals)

(disproportionation)
Hammond Postulate - The structure of the transition state (‡) more closely matches the structure of the product/reactant/intermediate that is closer to the transition state in energy.

In this case, the ‡ more closely resembles the reactant, so there is not a huge difference in the Ea for forming a 1° vs 2° vs 3° carbon radical.

Relative reactivity of Cl⁻ to 1°: 2°: 3°

1H x 5 = 5  6H x 1 = 6  3H x 1 = 3

Regiochemistry - Every possible monohalogenated product would form, and the most likely product depends on both the reactivity of the hydrogen involved along with the number of hydrogens.
Relative reactivity of Br₂ 1°: 2°: 3° 1: 80: 1,600

\[ \text{Br}_2 + R-H \rightarrow \text{Br}-H + R' \]

\[ \Delta H > 0 \text{ (endothemic)} \]

Since the transition state in this step more closely resembles the product, there is a greater difference in the activation energies for the formation of a 1° vs 2° vs 3° radical.

\[ \text{RC} \rightarrow \text{Br}_2 \rightarrow \text{Br} \rightarrow \text{Br} \rightarrow \text{RC} \]

\[ \begin{align*}
1H \times 1,600 & \quad 2H \times 80 & \quad 3H \times 1 \\
= 1,600 & \quad 160 & \quad 3
\end{align*} \]

- When possible, bromine is used instead of chlorine due to bromine's greater selectivity.
- Chlorination is more frequently used when only one major product forms,

\[ \text{Ex: } \text{C}_6\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_6\text{H}_5\text{Cl} \]
\[ |\Delta H_F| \gg |\Delta H_{Cl}| > |\Delta H_{Br}| \leq \text{all are} \quad \Delta H < 0 \]

The reaction with \( \text{F}_2 \) is so exothermic that there is almost no difference in the \( \text{Ea} \) for forming different radicals, \( 1^0 : 2^0 : 3^0 \rightarrow 1^1 : 1.2 : 1.4 \)

\[ \Delta H_{I^2} > 0 \]

Halogenation using \( \text{I}_2 \) is not possible since the reaction is endothermic (alkyl iodides would decompose under light).