RADICAL REACTIONS AND HALOGENATION

RADICAL HALOGATION OF ALKYL C-H BONDS:

General mechanism for radical halogenation of alkanes (i.e., sp³ C-H bonds):

\[ \text{initiation} \quad \text{X} \cdot + \text{X} \cdot \xrightarrow{\text{hv} \text{ or } \Delta} \text{2 X} \cdot \quad \text{[F₂ is too reactive I₂ is not reactive enough]} \]

\[ \text{propagation} \quad \text{R-CH}_2 + \text{X} \cdot \xrightarrow{\text{rate-determining step}} \text{R-CH}_2 + \text{H-X} \]

\[ \text{termination} \quad \text{2 X} \cdot \xrightarrow{\text{}} \text{X}_2 \]

Product distribution is dependent upon:

1. Ease of formation (stability) of the alkyl radical:

\[ \text{R-H} + \text{X} \cdot \xrightarrow{\text{}} \text{R} \cdot + \text{HX} \]

\[ \boxed{\text{benzylic ~ allyl > 3° > 2° > 1° > methyl}} \]

Helpful hint: Understanding the stability of radicals is key to predicting products in reaction.

2. Statistical (probability) factor

For propane it is 6:2 (1° : 2°) or 3:1. However, when the reaction is performed we get an equal mixture of 1-chloropropane and 2-chloropropane. This means that the energy of activation for abstracting a 2° hydrogen atom is lower than a 1° hydrogen atom. To help predict product ratios during radical chlorination or bromination, reactivity factors have been determined and are fairly consistent from alkane to alkane.
For **CHLORINATION** the product distribution is

\[ 3^\circ > 2^\circ > 1^\circ \quad \text{or} \quad 5.0 : 3.8 : 1.0 \]

For **BROMINATION** the product distribution is

\[ 3^\circ > 2^\circ > 1^\circ \quad \text{or} \quad 1600 : 82 : 1 \]

Remember, in class we discussed why bromination is so much more selective than chlorination using Hammond’s Postulate to understand the structure of the transition state. Make sure you understand the differences between an endothermic and exothermic reaction and the implication this has on the structure of the transition state.

**Helpful Hint:** Bromination is much more selective than chlorination

**ALLYLIC RADICAL HALOGENATION:**

Specialized reagent $N$-bromosuccinimide (NBS) is used for the selective bromination of allylic C-H bonds.

**Example:**

\[
\begin{align*}
\text{NBS} & \quad \text{ROOR} \\
& \quad \text{Br}
\end{align*}
\]

**RADICAL ADDITION OF H-X TO ALKENES:**

*Remember:* Under free-radical conditions (i.e., peroxides most commonly used) the addition of H-X occurs via **anti-Markovnikov** addition.

**Example:**

\[
\begin{align*}
\text{H-Br} & \quad \text{peroxides} \\
\text{H-Br} & \quad \text{no peroxides}
\end{align*}
\]

*Although we did not specifically discuss radical polymerization and synthetic polymers in class (section 15.14) you are responsible for this material.*

**Suggested problems from Ch. 15:** Normally, I would suggest some selected problems to focus on but for this chapter I **highly recommend** you work all of the problems (1-81) with a focus on the mechanism and synthesis questions (55-66) and spectroscopy and challenge problems (76-81).