6.4
Electrophilic Addition of Hydrogen Halides to Alkenes
General equation for electrophilic addition

\[ \text{C} = \text{C} + \text{E}^- \text{Y} \rightarrow \text{E} - \text{C} - \text{C} - \text{Y} \]
When $EY$ is a hydrogen halide

$$\text{C} = \text{C} + \delta^+ \delta^- \text{H} - \text{X} \rightarrow \text{H} - \text{C} - \text{C} - \text{X}$$
Example

\[
\text{CH}_3\text{CH}_2\text{C} = \text{CCHCH}_2\text{CH}_2\text{CH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_3 \quad \text{CHCl}_3, \ -30^\circ \text{C}
\]

(76%)
Electrophilic addition of hydrogen halides to alkenes proceeds by rate-determining formation of a carbocation intermediate.
Electrons flow from the $\pi$ system of the alkene (electron rich) toward the positively polarized proton of the hydrogen halide.
Mechanism

\[ \text{Mechanism} \]

\[ +\text{C} - \text{C} - \text{H} \]

\[ \text{H} - \text{X}^\text{-} \]

\[ \text{C} = \text{C} \]
6.5
Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule
When an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogen substituents, and the halogen adds to the carbon that has the fewer hydrogen substituents.
Markovnikov's Rule

\[ \text{CH}_3\text{CH}_2\text{CH}═\text{CH}_2 + \text{HBr} \xrightarrow{\text{acetic acid}} \text{CH}_3\text{CH}_2\text{CHCHCH}_3 \]

(80%)
Markovnikov's Rule

Example 2

\[ \text{CH}_3\text{C} = \text{C} \text{H} \xrightarrow{\text{HBr}} \text{CH}_3\text{C} = \text{CH}_3 \text{Br} \]

(acetic acid)

(90%)
Markovnikov's Rule

Example 3

\[
\text{HCl at } 0^\circ C \rightarrow \text{Cl}\]

(100%)
6.6
Mechanistic Basis
for
Markovnikov's Rule

Protonation of double bond occurs in direction that gives more stable of two possible carbocations.
Mechanistic Basis for Markovnikov's Rule:
Example 1

\[
\text{CH}_3\text{CH}_2\text{CH}\equiv\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CHCHCH}_3 \quad \text{acetic acid}
\]
Mechanistic Basis for Markovnikov's Rule: Example 1

\[ \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_3 + \text{Br}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 + \text{CH}_3\text{CH}_2\text{CHCH}_3\text{Br} \]
Mechanistic Basis for Markovnikov's Rule:

Example 1

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 & \quad \text{primary carbocation is less stable: not formed} \\
\text{CH}_3\text{CH}_2\text{CH}^-\text{CH}_3 \quad \text{+ Br}^- \\
\text{HBr} \\
\text{CH}_3\text{CH}_2\text{CH}^-\text{CH}_2 & \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCHCH}_3 \quad \text{Br}
\end{align*}
\]
Mechanistic Basis for Markovnikov's Rule:

Example 3

H

\[ \text{HCl at 0°C} \]

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_3
\end{align*}
\]
Mechanistic Basis for Markovnikov's Rule: Example 3

HCl

H

H

H

+CH₃

Cl⁻

H

H

CH₃

Cl

CH₃
Mechanistic Basis for Markovnikov's Rule: Example 3

Secondary carbocation is less stable: not formed
6.7
Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes
H$_2$C$\equiv$CHCH(CH$_3$)$_2$

\[ \rightarrow \] HCl, 0°C

\[ \downarrow \]

CH$_3$CHCH(CH$_3$)$_2$ $^+$

\[ \rightarrow \] CH$_3$CHC(CH$_3$)$_2$

H

\[ \downarrow \]

CH$_3$CHCH(CH$_3$)$_2$

\[ \rightarrow \] CH$_3$CH$_2$C(CH$_3$)$_2$

Cl (40%)

(60%)

Cl