Chapter 3  An Introduction to Organic Reactions: Acids and Bases
3.1 Reactions and Their Mechanisms
What kinds of reactions occur?

How reactions occur?
Substitutions (取代)

Substitution reactions occur when two reactants exchange parts to give two new products.

In a substitution, one replaces another.

\[
\text{A–B} + \text{C–D} \rightarrow \text{A–C} + \text{B–D}
\]

\[
\text{CH}_3\text{Cl} + \text{NaOH} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{OH} + \text{NaCl}
\]

\[
\text{H} \quad \text{H} \quad \text{H} + \text{Cl–Cl} \xrightarrow{\text{hv}} \text{H} \quad \text{H} \quad \text{C–Cl} + \text{H–Cl}
\]
Additions (加成)

- Addition reactions occur when two reactants add together to form a single new product with no atoms “left over”.

- In an addition all parts of the adding reagent appear in the product; two molecules become one.

\[
A + B \rightarrow C
\]

\[
\text{CH}_2=\text{CH}_2 + \text{Br}^-\text{Br} \rightarrow \text{Br} \quad \text{CH}_2=\text{CH}_2
\]

\[
\text{CH}_2=\text{CH}_2 + \text{H}^-\text{Br} \rightarrow \text{H} \quad \text{Br} \quad \text{CH}_2=\text{CH}_2
\]
Eliminations （消除）

Eliminations are the opposite of additions. Eliminations occur when a single reactant splits apart into two products.

In an eliminations one molecule loses the elements of another small molecule.

\[
\text{A} \quad \rightarrow \quad \text{B} + \text{C}
\]

\[
\text{H} \quad \text{Br} \quad \text{NaOH} \quad \text{CH}_2=\text{CH}_2 \quad + \quad \text{H}^-\text{Br}
\]
Rearrangement (重排)

Rearrangement reactions occur when a single reactant undergoes a reorganization of bonds and atoms to yield an isomeric product.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C}=\text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H}_3\text{C} & \quad \text{C} \quad \text{CH}_3 \\
\text{C} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

\[\begin{array}{cc}
\text{A} & \rightarrow \\
\text{B}
\end{array}\]
Mechanisms of Reactions

A reaction mechanism (反应机理)

- An overall description of how a specific reaction occur.
- A description of the events that take place on a molecular level as reactants become products.

(a) More than 1 step
(b) Intermediates
3.1A Homolysis and Heterolysis of Covalent Bonds (共价键的均裂和异裂)

Reactions of organic compounds always involve the making and breaking of covalent bonds.

A covalent bond may break in two fundamentally different ways.
Homolysis

A bond breaks in an electronically symmetrical way so that each fragment takes away one of the electrons of the bond.

\[ \text{Homolytic bond cleavage} \]

Free radicals or radicals
Heterolysis

A bond breaks in an electronically unsymmetrical way so that one fragment takes away both electrons of the bond, leaving the other fragment with an empty orbital.

\[
\text{A} \quad \text{B} \quad \rightarrow \quad \text{A}^+ \quad + \quad \text{:B}^- \\
\text{Heterolytic bond cleavage}
\]

Ions

- Cations
- Anions

Ions
Heterolysis of a bond normally requires that the bond be polarized.

\[ \delta^+ A \rightarrow \bigg\downarrow A^+ + \downarrow B^- \]

Heterolysis is assisted by a molecule with an unshared pair that can form a bond to one of the atom.

\[ Y^{-} + \delta^+ A \rightarrow \bigg\downarrow \ Y^{-} A^+ + \downarrow B^- \]

Formation of the new bond furnishes some of the energy required for the heterolysis.
Conversely, there are two ways that a covalent two-electron bond can form:

- A bond can form in an electronically symmetrical (homogenic) way when one electron is donated to the new bond by each reactant.

- A bond can be formed in an electronically unsymmetrical (heterogenic) way when both bonding electrons are donated to the new bond by one reactant.

\[ \text{A}^- + \text{B}^+ \rightarrow \text{A}^- \text{B}^+ \]

\[ \text{A}^- + \text{B}^- \rightarrow \text{A}^- \text{B}^- \]