Chapter 5
Alkene: Introduction
Thermodynamics and Kinetics

Each Family of Organic Compounds Can Be Placed in One of Four Groups

Group I
- R—CH=CH—R
- R=C=C=R
- R—CH=CH—CH=CH—R

Group II
- RCH2—X (X = F, Cl, Br, or I)
- RCH2—OH
- RCH2—OR
- R—OH

Group III
- R—Z—R
- Z = an atom more electronegative than C
- Z = C or H

Group IV
- ""`
- ""`
- Z = N, O, or S

The families in a group react in similar ways.
**Electrophiles**

An electrophile has
- a **positive charge,**
- a **partial positive charge,**
- or an **incomplete octet.**

**Nucleophiles**

A nucleophile has
- a **negative charge,**
- a **lone pair,**
- or a **π bond.**
A Nucleophile Reacts with an Electrophile

Your first organic reaction is a two-step reaction.

The Mechanism of the Reaction

The mechanism of a reaction is the step-by-step description of the process by which reactants are converted into products.

Curved arrows show where the electrons start from and where they end up.
The Mechanism of the Reaction (step 2)

the mechanism for the second step of the reaction

\[
\text{CH}_3\text{CH}^-\text{CHCH}_3 + \cdot\text{Br}^- \rightarrow \text{CH}_3\text{CH}^-\text{CHCH}_3 \\
\text{H} \quad \text{new } \sigma \text{ bond} \quad \text{H}
\]

How to Draw Curved Arrows

\[
\text{CH}_3\text{C}^-\text{Br}^- \rightarrow \text{CH}_3\text{C}^=\text{Br}^- + \cdot\text{Br}^- \\
\text{CH}_3\text{C}^-\text{H} \rightarrow \text{CH}_3\text{C}^-\text{H} + \text{H}_3\text{O}^+ \\
\text{H}_2\text{O}^- \rightarrow \text{H}_2\text{O}^- \quad \text{correct} \\
\text{H} \quad \text{correct} \\
\text{H} \quad \text{correct} \\
\text{H} \quad \text{correct}
\]
How to Draw Curved Arrows

\[
\text{correct: } \quad \text{not correct: }
\]

How to Draw Curved Arrows

\[
\text{correct: } \quad \text{incorrect: }
\]
How to Draw Curved Arrows

Molecular Formula and the Degree of Unsaturation

\[ \text{molecular formula} = C_nH_{2n+2} - 2 \text{ hydrogens for every } \pi \text{ bond or ring} \]

\[ \text{degree of unsaturation} = \text{the total numbers of } \pi \text{ bonds and rings} \]
Saturated and Unsaturated Hydrocarbons

Saturated hydrocarbons have no double bonds. Unsaturated hydrocarbons have one or more double bonds.

Nomenclature of Alkenes

Replace “ane” of alkane with “ene.”

The functional group gets the lowest possible number.

1-butene
2-butene
2-hexene
2-propyl-1-hexene

the longest continuous chain has 8 carbons, but the longest continuous chain containing the functional group has 6 carbons, so the parent name of the compound is hexene
Stereoisomers are Named Using a *cis* or *trans* (or *E* or *Z*) Prefix

![Stereoisomers Diagram](image)

Nomenclature of Dienes

two double bonds = diene

![Dienes Diagram](image)
Nomenclature of Alkenes

Number the chain in the direction that gives the double bond the lowest number.

Substituents are stated in alphabetical order.
Nomenclature of Alkenes

If both directions give the same number for the double bond, the correct name has the lowest substituent number.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} &= \text{CHCH}_2\text{CHCH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{2,5-dimethyl-4-octene} & \text{not} \\
\text{4,7-dimethyl-4-octene} & \text{because } 2 < 4 \\
\text{CH}_3\text{CHCH} &= \text{CCH}_2\text{CH}_3 \\
\text{Br} & \quad \text{CH}_3 \\
\text{2-bromo-4-methyl-3-hexene} & \text{not} \\
\text{5-bromo-3-methyl-3-hexene} & \text{because } 2 < 3
\end{align*}
\]

Nomenclature of Cyclic Alkenes

In a cyclic compound, a number is not needed to denote the position of the double bond: because it is always between C1 and C2.

\[
\begin{align*}
\text{3-ethylcyclopentene} & \\
\text{4,5-dimethylcyclohexene} & \\
\text{4-ethyl-3-methylcyclohexene} & 
\end{align*}
\]
Nomenclature of Alkenes

1,6-dichlorocyclohexene
not
2,3-dichlorocyclohexene because 1 < 2

5-ethyl-1-methylcyclohexene
not
4-ethyl-2-methylcyclohexene because 1 < 2

Nomenclature of Alkenes

2-bromo-4-ethyl-7-methyl-4-octene
not
7-bromo-5-ethyl-2-methyl-4-octene because 4 < 5

6-bromo-3-chloro-4-methylcyclohexene
not
3-bromo-6-chloro-5-methylcyclohexene because 4 < 5
Vinylic and Allylic Carbons

vinyllic carbon: the $sp^2$ carbon of an alkene
allylic carbon: a carbon adjacent to a vinyllic carbon

Vinyl and Allyl Groups

A vinyl group is the smallest group that contains a vinyllic carbon.

An allyl group is the smallest group that contains an allylic carbon.

<table>
<thead>
<tr>
<th>Vinyl Group</th>
<th>Allyl Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CH—</td>
<td>CH₂=CHCH₂—</td>
</tr>
<tr>
<td>vinyl group</td>
<td>allyl group</td>
</tr>
<tr>
<td>CH₂=CHCl</td>
<td>CH₂=CHCH₂Br</td>
</tr>
<tr>
<td>common name: vinyl chloride</td>
<td>allyl bromide</td>
</tr>
<tr>
<td>systematic name: chloroethene</td>
<td>3-bromopropene</td>
</tr>
</tbody>
</table>

The substituent is on the vinyllic or allylic carbon.
Substituent Names

The Structure of an Alkene

ρ orbitals overlap to form a π bond
Six Atoms of an Alkene are in the Same Plane

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

the six carbon atoms are in the same plane

---

Stereoisomers for Compounds with Two Double Bonds

\[
\begin{align*}
  \text{ClCH}_2 & \quad \text{C} \quad \text{H}_2\text{C} \quad \text{H} \\
  \text{C} \quad \text{C} & \quad \text{H} \\
  \text{ClCH}_2 & \quad \text{C} \quad \text{CH}_2\text{H}_3
\end{align*}
\]

(2Z,4Z)-1-chloro-2,4-heptadiene

\[
\begin{align*}
  \text{H} & \quad \text{C} \quad \text{H} \\
  \text{C} & \quad \text{C} \quad \text{H}_2\text{C} \\
  \text{ClCH}_2 & \quad \text{C} \quad \text{H}
\end{align*}
\]

(2Z,4E)-1-chloro-2,4-heptadiene

\[
\begin{align*}
  \text{ClCH}_2 & \quad \text{C} \quad \text{H}_2\text{C} \quad \text{H} \\
  \text{H} & \quad \text{C} \quad \text{C} \\
  \text{ClCH}_2 & \quad \text{C} \quad \text{CH}_2\text{H}_3
\end{align*}
\]

(2E,4Z)-1-chloro-2,4-heptadiene

\[
\begin{align*}
  \text{H} & \quad \text{C} \quad \text{H} \\
  \text{C} & \quad \text{C} \quad \text{H}_2\text{C} \\
  \text{ClCH}_2 & \quad \text{C} \quad \text{H}
\end{align*}
\]

(2E,4E)-1-chloro-2,4-heptadiene
Reactions of Organic Compounds

Organic compounds can be divided into **families**. All members of a family react in the **same way**. The **family** a compound belongs to depends on its **functional group**.

A Reaction Coordinate Diagram

A reaction coordinate diagram shows the **energy changes** that take place in each step of a reaction.
Thermodynamics and Kinetics

The equilibrium constant gives the relative concentration of reactants and products at equilibrium.

\[
A + B \rightleftharpoons C + D
\]

\[
K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[C][D]}{[A][B]}
\]
Exergonic and Endergonic Reactions

$\Delta G^\circ = \text{free energy of the products} - \text{free energy of the reactants}$

the relationship between $\Delta G^\circ$ and $K_{eq}$

$$\Delta G^\circ = -RT \ln K_{eq}$$

Gibbs Free-Energy Change ($\Delta G^\circ$)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\Delta G^\circ = \text{(free energy of the products)} - \text{(free energy of the reactants)}$

$\Delta H^\circ = \text{(heat required to break bonds)} - \text{(heat released from breaking bonds)}$

$\Delta S^\circ = \text{(freedom of motion of the products)} - \text{(freedom of motion of the reactants)}$
Increasing the Amount of a Product Formed in a Reaction

Le Chatelier’s Principle: if an equilibrium is disturbed, the system will adjust to offset the disturbance

\[
A + B \rightleftharpoons C + D
\]

\[
K_{eq} = \frac{[C][D]}{[A][B]}
\]

Coupled Reactions: an endergonic reaction followed by an exergonic reaction

Calculating $\Delta H^\circ$

\[
\text{HC} = \text{C} \quad \text{H} + \text{H--Br} \rightarrow \text{H} \quad \text{H-C-C-H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{Br}
\]

$\pi$ bond of ethene $DH = 62$ kcal/mol  
$H-\text{Br} \quad DH = 88$ kcal/mol  
$DH_{\text{total}} = 150$ kcal/mol

$C-H \quad DH = 101$ kcal/mol  
$C-\text{Br} \quad DH = 71$ kcal/mol  
$DH_{\text{total}} = 172$ kcal/mol

$\Delta H^\circ$ for the reaction = $DH$ for bonds being broken − $DH$ for bonds being formed

= 150 kcal/mol − 172 kcal/mol

= −22 kcal/mol
Catalytic Hydrogenation

\[
\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{H}_2 \xrightarrow{\text{Pd/C}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

\[
\text{alkene} + \text{H}_2 \xrightarrow{\text{Pd/C}} \text{alkane}
\]

*reduction reactions*

(the number of C-H bonds increases)
Catalytic Hydrogenation

hydrogen molecules settle on the surface of the catalyst and interact with the metal atoms

the alkene approaches the surface of the catalyst

the π bond between the two carbons is replaced by two C-H bonds

CH₂CH=CHCH₃ → CH₃CH—CHCH₃ → CH₃CH—CHCH₃

H—H H· ·H H H

Using $\Delta H^\circ$ Values to Determine the Relative Stabilities of Alkenes

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Pd/C</th>
<th>Heat of Hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH=CHCH₃ + H₂ → CH₃CHCH₂CH₃</td>
<td>$\Delta H^\circ$ (-26.9 kcal/mol)</td>
<td>25.9 kcal/mol</td>
</tr>
<tr>
<td>CH₂=CCH₂CH₃ + H₂ → CH₃CHCH₂CH₃</td>
<td>$\Delta H^\circ$ (-28.5 kcal/mol)</td>
<td>28.5 kcal/mol</td>
</tr>
<tr>
<td>CH₃CHCH=CH₂ + H₂ → CH₃CHCH₂CH₃</td>
<td>$\Delta H^\circ$ (-30.3 kcal/mol)</td>
<td>30.3 kcal/mol</td>
</tr>
</tbody>
</table>

the product of each of the three reactions is 2-methylbutane
Using \( \Delta H^\circ \) Values to Determine the Relative Stabilities of Alkenes

The Relative Stabilities of Alkenes

the more alkyl groups bonded to the \( sp^2 \) carbons, the more stable the alkene
A Trans Alkene is More Stable Than a Cis Alkene

The Relative Stabilities of Alkenes

the relative stabilities of alkenes that have two alkyl groups bonded to the \( sp^2 \) carbons
Reaction Coordinate Diagrams for Fast and Slow Exergonic and Endergonic Reactions

Free Energy of Activation ($\Delta G^\ddagger$)

The free energy of activation is the energy barrier of the reaction.

\[ \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \]

\[ \Delta H^\ddagger = \text{(enthalpy of the transition state)} - \text{(enthalpy of the reactants)} \]

\[ \Delta S^\ddagger = \text{(entropy of the transition state)} - \text{(entropy of the reactants)} \]
Kinetic and Thermodynamic Stability

**Kinetic Stability** is indicated by $\Delta G^\ddagger$

- If $\Delta G^\ddagger$ is large, the reactant is **kinetically stable** because it reacts slowly.
- If $\Delta G^\ddagger$ is small, the reactant is **kinetically unstable** because it reacts rapidly.

**Thermodynamic Stability** is indicated by $\Delta G^\circ$

- If $\Delta G^\circ$ is negative, the product is **thermodynamically stable** compared to the reactant.
- If $\Delta G^\circ$ is positive, the product is **thermodynamically unstable** compared to the reactant.

Rate of a Reaction

\[
\text{rate of a reaction} = \left( \frac{\text{number of collisions per unit of time}}{} \right) \times \left( \frac{\text{fraction with sufficient energy}}{} \right) \times \left( \frac{\text{fraction with proper orientation}}{} \right)
\]

Increasing the **concentration** increases the rate.
Increasing the **temperature** increases the rate.

The rate can be increased by a **catalyst**.
The Rate of a Reaction versus the Rate Constant for a Reaction

\[ A \rightarrow B \]

rate \( \propto [A] \)

rate constant for the reaction

rate = \( k[A] \)

rate of the reaction

The Arrhenius Equation

\[ k = A e^{-E_a/RT} \]

The value of \( A \) pertains to the frequency and orientation of collisions.

\[ e^{-E_a/RT} \]

\( e^{-E_a/RT} \) is the fraction of the collisions with the minimum energy needed for a reaction.
How are Rate Constants Related to the Equilibrium Constant?

\[
\begin{align*}
A & \xrightarrow{k_1} B \\
\text{forward rate} &= \text{reverse rate} \\
\frac{k_1 [A]}{k_{-1}} &= \frac{[B]}{[A]} \\
K_{eq} &= \frac{k_1}{k_{-1}} = \frac{[B]}{[A]}
\end{align*}
\]

The Structure of the Transition State

Transition states have partially formed bonds.
Reaction Coordinate Diagram for Each Step of the Addition of HBr to 2-Butene

The rate-limiting step has its transition state at the highest point on the reaction coordinate diagram.
A Catalyst

A catalyst provides a pathway for a reaction with a lower energy barrier.

A catalyst does not change the energy of the starting point (the reactants) or the energy of the end point (the products).

Enzymes

Most biological reactions require a catalyst.

Most biological catalysts are proteins called enzymes.

The reactant of a biological reaction is called a substrate.
The Active Site of an Enzyme

Enzyme side chains bind the substrate using hydrogen bonds, London dispersion forces, and dipole-dipole interactions.
Some enzyme side chains are **acids**, **bases**, and **nucleophiles** that **catalyze** the reaction.