Chapter 4

Introduction to Alkenes.
Structure and Reactivity

Eric J. Kantorowski
California Polytechnic State University
San Luis Obispo, CA
Chapter 4 Overview

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Alkenes

• Contain one or more C=C double bonds
• Classified as unsaturated hydrocarbons
• Sometime called olefins
• Ethylene is the simplest alkene
Ethylene

Å Geometry is typical of other alkenes
Å Trigonal planar

4.1 Structure and Bonding in Alkenes
4.1 Structure and Bonding in Alkenes
Orbital Picture of Ethylene

Å Trigonal planar geometry → $sp^2$-hybridization
Å 33% $s$ character
Å More $s$ character → electrons are held closer to the nucleus

4.1 Structure and Bonding in Alkenes
σ Bonds and π Bonds

σ bond: head-to-head overlap of orbitals

Cylindrically symmetric

π bond: side-to-side overlap of \( p \) orbitals

4.1 Structure and Bonding in Alkenes
4.1 Structure and Bonding in Alkenes
EPM of Ethylene

Å The filled $\pi$ molecular orbital is the $\pi$ bond

Å Most of the important reactions of alkenes involve the electrons of the $\pi$ bond
Bond Length

Å Bonds with more *s* character are shorter

\[ \text{sp}^3 - \text{sp}^2 \text{ single bond (shorter)} \]
Double-Bond Stereoisomers

Stereoisomers: Same connectivity; different spatial arrangement

 cis-2-butene  
 (Z)-2-butene

 trans-2-butene  
 (E)-2-butene
Restricted Rotation of Alkenes

4.1 Structure and Bonding in Alkenes
Substitutive Nomenclature

Å Find principle chain with greatest number of double bonds
Å The alkene carbons get the lowest number

\[ \text{H}_2\text{C}==\text{CH} \longrightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

Å Use \textit{-adiene}, \textit{-atriene}, etc. for multiple alkenes

\[ \text{H}_2\text{C}==\text{CHCH}_2\text{CH}_2\text{CH}==\text{CH}_2 \]

1,5-hexadiene

4.2 Nomenclature of Alkenes
Substituents Containing Alkenes

Some common groups with alkenes

\[
\begin{align*}
& \text{H}_2\text{C}≡\text{CH} & & \text{H}_2\text{C}≡\text{CH}−\text{CH}_2 & & \text{H}_2\text{C}≡\text{C}−\text{CH}_3 \\
& \text{vinyl} & & \text{allyl} & & \text{isopropenyl}
\end{align*}
\]

Nonsystematic traditional names

\[
\begin{align*}
& \text{Ph}−\text{CH}≡\text{CH}_2 & & \text{H}_2\text{C}≡\text{C}−\text{CH}≡\text{CH}_2 \\
& \text{styrene} & & \text{isoprene}
\end{align*}
\]

4.2 Nomenclature of Alkenes
Nomenclature System

A cis vs trans is not always clear

A Cahn-Ingold-Prelog system: Assign priorities

\[ E \text{ (entgegen): “across”} \]

\[ Z \text{ (zusammen): “together”} \]
Priority Assignments

Å Examine atoms directly attached to each carbon of the C=C
Å Higher atomic # = higher priority
Å Higher isotopic mass = higher priority

Å If the atoms are the same, continue moving outward until the first point of difference

4.2 Nomenclature of Alkenes
Priority Assignments

Å If a group contains a double bond → duplicate

\[
\begin{align*}
\text{CH} & \quad \text{is treated as} \\
\text{CH} & \quad \text{CH}_2 \\
\text{C} & \quad \text{C}
\end{align*}
\]

Å If a group contains a triple bond → triplicate

\[
\begin{align*}
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{C}
\end{align*}
\]

4.2 Nomenclature of Alkenes
Unsaturation Number

- Gives info on number of rings and/or \( \pi \) bonds
- Maximum number of H’s in a hydrocarbon: \( C_n H_{2n+2} \)
- Each ring and/or \( \pi \) bond reduces number of hydrogens by 2
- Aka degree of unsaturation

\[
U = \frac{2C + 2 - II}{2} = \text{number of rings + multiple bonds}
\]
Unsaturation Number

- Oxygen can be ignored
- Halogens are counted as 1 H:

\[ U = \frac{2C + 2 - H}{2} \quad (H = \text{hydrogens plus halogens}) \]

- Nitrogen increases H count by 1:

\[ U = \frac{2C + 2C + 2 + N - H}{2} \]
Physical Properties

Very similar to corresponding alkane

\[
\begin{align*}
\text{H}_2\text{C} &\equiv \text{CH(CH}_2\text{)}_3\text{CH}_3 & \text{CH}_3\text{(CH}_2\text{)}_4\text{CH}_3 \\
\text{1-hexene} & 63.4 \, ^\circ\text{C} & \text{hexane} & 68.7 \, ^\circ\text{C} \\
\text{boiling point} & -139.8 \, ^\circ\text{C} & \text{melting point} & -95.3 \, ^\circ\text{C} \\
\text{density} & 0.673 \, \text{g mL}^{-1} & \text{density} & 0.660 \, \text{g mL}^{-1} \\
\text{water solubility} & \text{negligible} & \text{water solubility} & \text{negligible} \\
\text{dipole moment} & 0.46 \, \text{D} & \text{dipole moment} & 0.085 \, \text{D}
\end{align*}
\]

Dipole moments and polarization

4.4 Physical Properties of Alkenes
Calculating Stabilities

Å Standard enthalpy change ($\Delta H^\circ$) for a reaction

\[ \Delta H^\circ (\text{reaction}) = H^\circ (\text{products}) - H^\circ (\text{reactants}) \]

Å Exothermic reactions: $\Delta H^\circ < 0$
Å Endothermic reactions: $\Delta H^\circ > 0$

4.5 Relative Stabilities of Alkene Isomers
Relative Stabilities of Alkene Isomers

From heats of formation ($\Delta H_f^\circ$):

More alkyl substituents $\rightarrow$ more stable alkene

4.5 Relative Stabilities of Alkene Isomers
Stabilities of Alkene Isomers

A trans places larger groups farther apart

\[ \text{trans places larger groups farther apart} \]

\[ \begin{align*}
R & \quad R \\
\text{H} & \quad \text{H} \\
\text{C} = \text{C} & < \text{C} = \text{C} \\
\text{H} & \quad \text{H} \\
& \quad \text{R}
\end{align*} \]

van der Waals repulsions

(a) cis 2-butene

(b) trans 2-butene

4.5 Relative Stabilities of Alkene Isomers
Addition Reactions

A characteristic reaction of alkenes

The π bond is *electron rich* = nucleophilic

\[ \text{C} = \text{C} \quad + \quad \text{X} - \text{Y} \quad \rightarrow \quad \text{C} - \text{C} \]

HF, HCl, HBr, HI add to alkenes → alkyl halides

\[ \text{CH}_3\text{CH} = \text{CHCH}_3 \quad + \quad \text{H} - \text{Br} \quad \rightarrow \quad \text{CH}_3\text{CH} - \text{CHCH}_3 \]

2-butene
(Z or E)

\[ \text{H} \quad \quad \text{Br} \]

2 bromobutane
(an alkyl halide)

4.6 Addition Reactions of Alkenes
Regioselectivity of Addition

Unsymmetrical alkenes can give regioisomers

\[ \text{H}_2\text{C} = \text{CH}(\text{CH}_2)_3\text{CH}_3 + \text{HI} \rightarrow \text{H}_3\text{C} - \text{CH}(\text{CH}_2)_3\text{CH}_3 \text{ or } \text{CH}_2 - \text{CH}_2(\text{CH}_2)_3\text{CH}_3 \]

1-hexene

2-iodohexane (observed)

1-iodohexane (not observed)

Generally, the halogen goes to the most substituted carbon

\[ \text{H}_2\text{C} = \text{CH}(\text{CH}_2)_3\text{CH}_3 \]

H goes here

I goes here

4.7 Addition of Hydrogen Halides to Alkenes
Carbocation Intermediates

Addition occurs in two successive steps:

\[
\text{electron-deficient carbon (an electrophile)}
\]

\[
\text{a carbocation}
\]

Carbocations are reactive intermediates

4.7 Addition of Hydrogen Halides to Alkenes
and Stability of Carbocations

Å Trigonal planar → $sp^2$-hybridized
Å Electron deficient = Lewis acidic
Å Stabilized by alkyl groups

Å Stability: primary < secondary < tertiary

4.7 Addition of Hydrogen Halides to Alkenes
Hyperconjugation

Alkyl groups can share electrons with the empty neighboring p orbital

4.7 Addition of Hydrogen Halides to Alkenes
Carbocation Rearrangements

Identified by a rearranged carbon skeleton

\[
\begin{align*}
  &\text{CH}_3 \quad \text{H}_3\text{C} - \text{C} - \text{CH} = \text{CH}_2 + \text{HCl} \rightarrow \text{CH}_3 \quad \text{H}_3\text{C} - \text{C} - \text{CH} - \text{CH}_3 + \text{H}_3\text{C} - \text{C} - \text{CH} - \text{CH}_3 \\
  &\text{CH}_3 \quad \text{CH}_3 \quad \text{Cl} \quad \text{Cl} \\
  &\text{CH}_3 \quad \text{CH}_3 \\
  &\text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

(17% of product)  (83% of product)

Rearrangement is favored if a more stable carbocation can form

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

4.7 Addition of Hydrogen Halides to Alkenes

Carbocation Rearrangements

- Migrations not limited to alkyl groups
- Hydride shifts are also possible
- Hydride = H with its 2 bonding electrons

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\text{H}_3\text{C} - \text{C} - \text{CH} = \text{CH}_2 + \text{HBr} & \rightarrow & \text{H}_3\text{C} - \text{CH} - \text{CH} - \text{CH}_3 + \text{H}_3\text{C} - \text{C} - \text{CH}_2\text{CH}_3 \\
\text{H} & & \text{Br} & & \text{Br}
\end{align*}
\]

(about 45% of product) (about 55% of product)

4.7 Addition of Hydrogen Halides to Alkenes
Reaction Rates

Commonly, two or more reactions are in competition.

4.8 Reaction Rates
The Transition State

Å Forward and reverse reaction have same transition state ($^\ddagger$)

\[
\text{(CH}_3\text{)}_2\text{C} = \text{CH}_2 + \text{I} + \text{Br}^- \leftrightarrow \text{(CH}_3\text{)}_2\text{C}^{+} = \text{CH}_2 + \text{Br}^- \text{H}
\]

\[
\left[\text{(CH}_3\text{)}_2\text{C} \right. \\
\left. \text{H} \right]^{\ddagger}
\]
The Energy Barrier

Å Molecules must possess enough energy to get over the transition state
Å Maxwell-Boltzmann distribution

4.8 Reaction Rates
Multistep Reactions

- Intermediates are formed in many reactions
- Rate-determining step: Controls reaction rate

![Reaction Coordinate Diagram]

4.8 Reaction Rates
Hammond’s Postulate

The structure and energy of the transition state can be approximated by the structure and energy of the intermediate.
Catalysis

Å Catalyst: A substance that increases the reaction rate without being consumed
Å Heterogeneous
Å Homogeneous

4.9 Catalysis
Catalytic Hydrogenation of Alkenes

- Metal catalysts allow for addition of $H_2$
- Heterogeneous

\[
\text{cyclohexene} + H_2 \xrightarrow{\text{Pt/C}} \text{cyclohexane}
\]

- Aromatic $\pi$ bonds are less reactive

\[
\text{styrene} + H_2 \xrightarrow{\text{Pt/C}} \text{ethylbenzene}
\]
Hydration of Alkenes

**Acid-catalyzed** addition of H₂O across an alkene

**Homogeneous**

\[ \text{H}_3\text{C} = \text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH} \]

\[ \text{(CH}_3\text{)}_3\text{C} = \text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{(CH}_3\text{)}_3\text{CHOH} \]

\[ \text{(CH}_3\text{)}_3\text{C} = \text{CH}_2 + \text{H}_2\text{O} \]

\[ \text{(CH}_3\text{)}_3\text{C}^- + \text{OH}^- \]

4.9 Catalysis
Principle of Microscopic Reversibility

Generally, the reverse reaction follows the exact reverse of forward mechanism.

Dehydration is the reverse of hydration.
Enzymes Catalysis

Nature produces catalysts called enzymes.
Most biological mechanisms would be too slow to be useful without enzymes.

\[
\text{fumarate} + H_2O \xrightleftharpoons{\text{fumarase (an enzyme)}} \text{malate}
\]