5.1 ALKENES

Vitamin A

[Chemical structure of Vitamin A]
Figure 5.1 Structure of Ethene
(a) The $\pi$ bond is formed by sideways overlap of the parallel 2p orbitals of adjacent carbon atoms. Carbon forms sigma bonds with $sp^2$ hybrid orbitals.
(b) Schematic diagram of bonding in ethene. (c) The highest occupied molecular orbital of ethene is the $\pi$ bond.

Structure and Bonding of Alkenes
Bond Lengths and Bond Energies

(c) The $\pi$ bond of ethene
Table 5.1
Bonds Lengths and Bond Strengths in Alkanes vs Alkenes

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length (pm)</th>
<th>$DH^o$ kJ mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3-\text{CH}_3$ (sp$^3$ — sp$^3$)</td>
<td>154</td>
<td>347</td>
</tr>
<tr>
<td>$\text{CH}_2=\text{CH}_2$ (sp$^2$ — sp$^2$)</td>
<td>133</td>
<td>610</td>
</tr>
<tr>
<td>$\text{CH}_2=\text{CH}-\text{CH}_3$</td>
<td>151</td>
<td>121</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2-\text{H}$</td>
<td>109</td>
<td>422</td>
</tr>
<tr>
<td>$\text{CH}_2=\text{CH}-\text{H}$</td>
<td>107</td>
<td>452</td>
</tr>
</tbody>
</table>
5.2 STRUCTURE AND BONDING OF ALKENES
Classification of Alkenes

monosubstituted: \( \text{RCH=CH}_2 \)
disubstituted: \( \text{RCH=CHR or R}_2\text{C=CH} \)
trisubstituted: \( \text{R}_2\text{C=CHR} \)
tetrasubstituted: \( \text{R}_2\text{C=CR}_2 \)
5.3 UNSATURATION NUMBER

unsaturation number = \[\frac{[2(\text{number of carbon atoms}) + 2] - \text{number of H atoms}}{2}\]

3-bromo-1-propene

replacing Br with H gives propene

unsaturation number = \[\frac{[2(3) + 2] - 6}{2}\] = 1
5.4 GEOMETRIC ISOMERISM

Figure 5.2 Rotation About the $\pi$ Bond
For rotation to occur about a carbon—carbon double bond, the $\pi$ bond must break. Loss of overlap between parallel 2p orbitals requires about 240 kJ mole$^{-1}$.
Figure 5.3 Geometric Isomers of Alkenes

All six atoms lie in the same plane. In the *cis* isomer two “X” and “Y” groups lie on the same side of the double bond. In the *trans* isomer “X” and “Y” groups lie on opposite sides of the double bond. They do not interconvert because rotation around the $\pi$ bond does not occur.

C
\[
\begin{align*}
&\text{all atoms coplanar} \\
&\text{no rotation around double bond} \\
&\text{*trans* geometric isomer} \\
&\text{*cis* geometric isomer}
\end{align*}
\]
5.5 E,Z NOMENCLATURE OF GEOMETRICAL ISOMERS

- **cis-2-butene**
- **trans-2-butene**
- **Z isomer**
- **E isomer**
Sequence Rules-1

1. If two atoms with different atomic numbers are directly bonded to a double bond, the atom with the higher atomic number receives a higher priority.

The priority order of some common elements is $\text{Br} > \text{Cl} > \text{F} > \text{O} > \text{N} > \text{C} > \text{H} > \text{H}$.

Sequence Rule-2

2. If the atoms directly attached to the carbon atom of the double bond have the same atomic number, consider the second, third, and farther atoms until a difference is found. Then apply rule 1.
Sequence Rule-3

3. A multiple bond is considered equivalent to the same number of single bonds to like atoms. Thus, a double bond is counted as two single bonds for both of the atoms in the double bond. The same principle is used for a triple bond.

\[
\begin{align*}
\text{\( \text{C} \equiv \text{C} \)} & \quad \text{is treated as} \quad \begin{array}{c}
\text{C} \\
\text{C}
\end{array} \\
\text{\( \text{C} \equiv \text{C} \)} & \quad \text{is treated as} \quad \begin{array}{c}
\text{C} \\
\text{C}
\end{array}
\end{align*}
\]

\[
\begin{align*}
\text{\( \text{C} = \text{O} \)} & \quad \text{is treated as} \quad \begin{array}{c}
\text{C} \\
\text{O}
\end{array} \\
\text{\( \text{C} \equiv \text{N} \)} & \quad \text{is treated as} \quad \begin{array}{c}
\text{N} \\
\text{C}
\end{array}
\end{align*}
\]
Common Names of Alkenyl Groups

- Vinyl \( \text{CH}_2=\text{CH} \)
- Allyl \( \text{CH}_2=\text{CH}-\text{CH}_2 \)
- Isopropenyl \( \text{CH}_2=\text{CH}-\text{CH}_3 \)
Rule 1

1. The longest continuous chain of carbon atoms that contains the double bond is the parent alkene.

There are eight carbons in this chain, so it is an octene.

Rule 2

2. If the atoms directly attached to the carbon atom of the double bond have the same atomic number, the second, third, and farther atoms are considered until a difference is found. Then apply rule 1.
Rule 3
3. Number the carbon atoms in the longest continuous chain starting from the end of the chain nearer the first branch.

![Diagram of a substituted 3-heptene]

This is a substituted 3-heptene, not a substituted 4-heptene.

Rule 4
4. Alkyl groups and other substituents are named, and their positions on the chain are identified, according to the numbering established by rule 3. Names and numbers are prefixed to the parent name.

![Diagram of a 2,3-dimethyl-2-pentene]

This is 2,3-dimethyl-2-pentene, not 3,4-dimethyl-3-pentene.
Rule 5
5. If the compound can exist as an E or Z isomer, the appropriate prefix followed by a hyphen is placed within parentheses in front of the name.

This is (E)-3-methyl-3-hexene.

Rule 6
6. If the compound contains more than one double bond, specify the location of each double bond by a number. A prefix to -ene indicates the number of double bonds.

1,3,5-heptatriene
Rule 7
7. Name cycloalkenes by numbering the ring to give the double-bonded carbon atoms the numbers 1 and 2. Choose the direction of numbering so that the first substituent on the ring receives the lower number. The position of the double bond is not given because it is known to be between the C-1 and C-2 atoms.

\[
\begin{align*}
\text{3-methylcyclopentene} & : & \text{1-methylcyclohexene} \\
\end{align*}
\]

Rule 8
8. Compounds with a carbon–carbon double bond positioned between a ring carbon atom and a substituent on the ring are named using -ylidene to name the group as a substituent. However, the (==CH\textsubscript{2}) group is named methene rather than methylidene.

\[
\begin{align*}
\text{ethyldinecyclopropane} & : & \text{methylene cyclohexane} \\
\end{align*}
\]
### 5.7 PHYSICAL PROPERTIES OF ALKENES

#### Density of Alkenes

**Table 5.2 Densities of Alkenes**

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Density $d^{20}$ (g cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-pentene</td>
<td>$2.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>cis-2-pentene</td>
<td>$8.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>trans-2-pentene</td>
<td>$2.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>2-methyl-2-butene</td>
<td>$7.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>3-methyl-1-butene</td>
<td>0.648</td>
</tr>
<tr>
<td>1-hexene</td>
<td>0.675</td>
</tr>
<tr>
<td>2,3-dimethyl-2-butene</td>
<td>0.705</td>
</tr>
<tr>
<td>1-heptene</td>
<td>0.698</td>
</tr>
<tr>
<td>1-octene</td>
<td>0.716</td>
</tr>
<tr>
<td>1-nonene</td>
<td>0.731</td>
</tr>
<tr>
<td>1-decene</td>
<td>0.743</td>
</tr>
</tbody>
</table>
5.7 PHYSICAL PROPERTIES OF ALKENES

Polarity of Alkenes

- Chloroethene (1.4 D)
- Propene (0.3 D)
- Trans-1-chloropropene (1.7 D)
### Table 5.3
Boiling Points of Alkenes

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethene</td>
<td>-103.7</td>
</tr>
<tr>
<td>propene</td>
<td>-47.4</td>
</tr>
<tr>
<td>1-butene</td>
<td>-6.3</td>
</tr>
<tr>
<td>2-methylpropene</td>
<td>-6.9</td>
</tr>
<tr>
<td>cis-2-butene</td>
<td>+3.7</td>
</tr>
<tr>
<td>trans-2-butene</td>
<td>0.9</td>
</tr>
<tr>
<td>1-pentene</td>
<td>30.0</td>
</tr>
<tr>
<td>cis-2-pentene</td>
<td>36.9</td>
</tr>
<tr>
<td>trans-2-pentene</td>
<td>36.4</td>
</tr>
<tr>
<td>1-hexene</td>
<td>63.5</td>
</tr>
<tr>
<td>1-heptene</td>
<td>93</td>
</tr>
<tr>
<td>1-octene</td>
<td>122.5</td>
</tr>
<tr>
<td>1-nonene</td>
<td>146</td>
</tr>
<tr>
<td>1-decene</td>
<td>171</td>
</tr>
</tbody>
</table>

- **1-pentene** (bp 30 °C)
- **3-methyl-1-butene** (bp 25 °C)
- **cis-1,2-chloroethene** (bp 60 °C)
- **trans-1,2-chlorodichloroethene** (bp 47 °C)
5.8 STABILITY OF ALKENES

1-butene < cis-2-butene < trans-2-butene < 2-methylpropene

increasing stability (decreasing $\Delta H^\circ$)

Figure 5.4 Heats of Combustion of Isomeric Butenes
The heats of combustion of the isomeric butenes are plotted on the vertical axis in kJ mole$^{-1}$. All compounds are at higher energy than the common products, carbon dioxide and water.
5.8 STABILITY OF ALKENES

Figure 5.5 Steric Effects and Stability of Alkenes
Some of the hydrogen atoms of the two methyl groups in cis-2-butene are within their van der Waals radii. These atoms are in a 1,6 relationship, and they sterically interfere with each other. There is no steric effect in the trans isomer.

Steric repulsion between methyl groups.

![cis-2-butene](image1)
![trans-2-butene](image2)
5.9 REDUCTION OF ALKENES

\[ \text{H}_2 + \text{C} = \text{C} \rightarrow \text{H} = \text{H} \text{Pd/C} \rightarrow \text{H} - \text{C} - \text{C} - \text{H} \]
\[ \Delta H^\circ = -136 \text{ kJ mole}^{-1} \]

The double bond is converted to a single bond.

\[ \text{CH}_2 = \text{CH(CH}_2\text{)}_5\text{CH}_3 \xrightarrow{\text{H}_2 / \text{Pd/C}} \text{CH}_3 - \text{CH}_2(\text{CH}_2)_5\text{CH}_3 \]

3-methylcyclopentene

\[ \text{H}_2 / \text{PtO}_2 \]\n
Adams Catalyst

methylcyclopentene
5.10 MECHANISM OF CATALYTIC HYDROGENATION

Stereochemistry of Hydrogenation

\[
\text{1,2-dimethylcyclopentene} \overset{\text{H}_2 / \text{Pd/C}}{\longrightarrow} \text{cis-1,2-dimethylcyclopentane}
\]

Stereoselectivity of Hydrogenation

\[
\alpha\text{-pinene} \overset{\text{H}_2 / \text{Pd/C}}{\longrightarrow} \text{cis-pinene (major)} + \text{trans-pinene (trace)}
\]
5.10 HEATS OF HYDROGENATION OF ALKENES

Structural Effects on Heats of Hydrogenation

1-butene < *cis*-2-butene < *trans*-2-butene

$$\Delta H^\circ_{\text{hydrogenation}} : \text{monosubstituted} > \text{disubstituted} > \text{trisubstituted} > \text{tetrasubstituted}$$

Figure 5.6 Heats of Hydrogenation of Isomeric Butenes
The positions of three isomeric butenes show their relative heats of formation.

CH≡CHCH₂CH₃

1-butene

$$\Delta H^\circ = -126 \text{ kJ mole}^{-1}$$

*cis*-2-butene

$$\Delta H^\circ = -119 \text{ kJ mole}^{-1}$$

*trans*-2-butene

$$\Delta H^\circ = -115 \text{ kJ mole}^{-1}$$

Butane

$$\Delta H^\circ = -119 \text{ kJ mole}^{-1}$$
<table>
<thead>
<tr>
<th>Alkene</th>
<th>$\Delta H^\circ_{\text{hydrogenation}}$ kJ mole$^{-1}$</th>
<th>Alkene</th>
<th>$\Delta H^\circ_{\text{hydrogenation}}$ kJ mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unsubstituted</strong></td>
<td></td>
<td><strong>Internal Disubstituted</strong></td>
<td></td>
</tr>
<tr>
<td>ethene</td>
<td>136</td>
<td>cis-2-butene</td>
<td>119</td>
</tr>
<tr>
<td>Monosubstituted</td>
<td></td>
<td>trans-2-butene</td>
<td>115</td>
</tr>
<tr>
<td>propene</td>
<td>125</td>
<td>cis-2-pentene</td>
<td>117</td>
</tr>
<tr>
<td>1-butene</td>
<td>126</td>
<td>trans-2-pentene</td>
<td>114</td>
</tr>
<tr>
<td>1-hexene</td>
<td>126</td>
<td>cis-4,5-dimethyl-2-hexene</td>
<td>118</td>
</tr>
<tr>
<td>3-methyl-1-butene</td>
<td>127</td>
<td>trans-4,5-dimethyl-2-hexene</td>
<td>113</td>
</tr>
<tr>
<td><strong>Terminal disubstituted</strong></td>
<td></td>
<td><strong>Trisubstituted</strong></td>
<td></td>
</tr>
<tr>
<td>2-methylpropene</td>
<td>117</td>
<td>2-methyl-2-pentene</td>
<td>112</td>
</tr>
<tr>
<td>2-methyl-1-butene</td>
<td>118</td>
<td>2,3-dimethyl-3-hexene</td>
<td>114</td>
</tr>
<tr>
<td>2,3-dimethyl-1-butene</td>
<td>116</td>
<td>2,3-dimethyl-2-hexene</td>
<td>110</td>
</tr>
<tr>
<td>2,3-dimethyl-1-hexene</td>
<td>117</td>
<td>2,3-dimethyl-2-hexene</td>
<td>106</td>
</tr>
</tbody>
</table>