Chapter 6. Alkenes: Structure and Stability

Degrees of unsaturation

- saturated hydrocarbon: \( C_nH_{2n+2} \)
- cycloalkane (1 ring): \( C_nH_{2n} \)
- alkene (1 \( \pi \)-bond): \( C_nH_{2n} \)
- alkyne (2 \( \pi \)-bonds): \( C_nH_{2n-2} \)

For each ring or \( \pi \)-bond, -2H from the formula of the saturated alkane.

Degrees of unsaturation: # of rings and/or \( \pi \)-bonds in a molecule. Information can be obtained from the molecular formula.

Correction for other elements:

For Group VII elements (halogens):
- subtract 1H from the H-deficiency for each halogen,
- or add 1H to the molecular formula of each halogen.

For Group VI elements (O and S):
- No correction is needed.

For Group V elements (N and P):
- add 1H to the H-deficiency for each N or P,
- or subtract 1H from the molecular formula for each N or P.
Systematic Nomenclature (IUPAC System)

Prefix-Parent-Suffix

Naming Alkenes
Suffix: -ene

Many of the same rules for alkanes apply to alkenes

1. Name the parent hydrocarbon by locating the longest carbon chain that contains the double bond and name it according to the number of carbons with the suffix -ene.

```
H3C—CH2
H5C—CH2—CH2
Parent = pentene
```

```
H3C—CH2
H6C—CH—CH2
```

2a. Number the carbons of the parent chain so the double bond carbons have the lowest possible numbers.

```
H3C—CH2—CH—CH2—CH3
6 5 4 3 2 1
```

2-hexene

b. If the double bond is equidistant from each end, number so the first substituent has the lowest number.

```
H3C—CH2
H5C—CH==CH==CH==CH3
1 2 3 4 5 6
```

2-methyl-1-hexene

3. Write out the full name, numbering the substituents according to their position in the chain and list them in alphabetical order.
4. Indicate the double bond by the number of the first alkene carbon.

\[
\begin{array}{c}
H_2C-CH\equiv CH-CH=CH_3 \\
\text{2-hexene}
\end{array}
\]

5. If more than one double bond is present, indicate their position by using the number of the first carbon of each double bond and use the suffix -diene (for 2 double bonds), -triene (for 3 double bonds), -tetraene (for 4 double bonds), etc.

\[
\begin{array}{ccc}
H_2C&\equiv &CH\equiv CH=CH_2 \\
&1&2&3&4&5 \\
&1,4\text{-pentadiene}
\end{array}
\quad
\begin{array}{ccc}
H_2C&\equiv &CH-CH=CH=CH_3 \\
&1&2&3&4&5 \\
&1,3\text{-pentadiene}
\end{array}
\]

6a. Cycloalkenes are named in a similar way. Number the cycloalkene so the double bond carbons get numbers 1 and 2, and the first substituent is the lowest possible number.

\[
\begin{array}{c}
\text{3-methylcyclohexene} \\
\text{NOT} \\
6\text{-methylcyclohexene}
\end{array}
\]

b. If there is a substituent on one of the double bond carbons, it gets number 1.

\[
\begin{array}{c}
\text{1,5-dimethylcyclopentene} \\
\text{NOT} \\
2,3\text{-dimethylcyclopentene}
\end{array}
\]
Alkenes as substituents:

- Ethenyl or vinyl (vinylcyclohexane)
- 2-Propenyl or allyl (allylcyclohexane)
- Methylene (methylene cyclohexane)
- Ethylidene (ethylidene cyclohexane)

Non-IUPAC Alkenes (Table 6.1, pg. 194)

- Ethylene (ethene)
- Propylene (propene)
- Isobutylene (2-methyl propene)
- Isoprene (2-methyl-1,3-butadiene)

Isoprene ($C_5$)

- Delta-carotene ($C_{40}$, 8 isoprene units)

Squalene ($C_{30}$, 6 isoprene units)

Cholesterol ($C_{27}H_{46}O$)
3 \( \text{CH}_3\text{CO}_2\text{H} \) \( \rightarrow \) \( \text{“} \text{C} = \text{C} \text{“} + \text{CO}_2 + 2\text{H}_2\text{O} \)

- HMG-CoA Reductase
- Mevalonic acid
- Squalene
- Cholesterol

**C=C double bonds**

- \( \sigma^\circ \) carbon
- \( \sigma^\circ \) carbon
- Carbon-carbon double bond

\( \pi \) bond
\( \sigma \) bond

- \( \pi \) bond (\( \sigma \) orbitals are parallel)
- Broken \( \pi \) bond after rotation (\( \sigma \) orbitals are perpendicular)
Alkenes Stereoisomers

recall cycloalkane stereoisomers: substituents are either on the same side of the ring (cis) or on opposite sides (trans).

Substituents on an alkene can also be either cis (on the same side of the double bond) or trans (on opposite sides of the double bond). Cis/trans isomers of alkenes are stereoisomers- they have the same connectivity but different three-dimensional arrangements of groups.

These two compounds are identical; they are not cis–trans isomers.

These two compounds are not identical; they are cis–trans isomers.
Designating Alkene Stereoisomers
The cis and trans becomes ambiguous when there are three or four substituents on the double bond.

E/Z System: For each carbon of the double bond, the groups are assign a priority (high or low) according to a system of rules. Thus, the high priority groups can be on the same side or on opposite side.

If the high priority groups are on opposite sides then the double bond is designated as E (entgegen- across)
If the high priority groups are on the same side then the double bond is designated as Z (zusammen- together)

Assigning Group Priority: The Cahn, Ingold, Prelog Rules
1. Look at the atoms directly attached to each carbon of the double bond. Rank them according to decreasing atomic number.

priority of common atoms: $I > Br > Cl > S > F > O > N > C > H$

If both high priority atoms are on the same side of the double bond it is designated $Z$. If the high priority atoms are on opposite sides of the double bond, it is designated as $E$. 
2.a. If the two atoms attached to the double bond carbon are identical (designated A and B below), look at all the atoms directly attached to the identical atoms in questions (designated A-1, A-2, A-3 and B-1, B-2, B-3). Assign priorities to all these atoms based on atomic number (1 is the highest priority, 3 the lowest).

![Diagram of A and B groups with atoms labeled A1, A2, A3, B1, B2, B3]

2b. Compare the highest priority atoms, i.e. compare A-1 with B-1. If A-1 is a higher priority atom than B-1, then A is higher priority than B. If A-1 and B-1 are the same atom, then compare the second highest priority atoms directly bonded to A and B (A-2 with B-2); if A-2 is a higher priority atom than B-2, then A is higher priority than B. If A-2 and B-2 are identical atoms, compare A-3 with B-3.

c. If a difference still cannot be found, move out to the next highest priority group (A-1 and B-1 in the diagram) and repeat the process.

Examples:

- \( \text{CH}_3 - \text{CH}_3 \) > \( \text{CH}_3 - \text{CH}_3 \) > \( \text{CH}_2 = \text{CH}_3 \) > \( \text{CH}_3 \) > \( \text{H} \)
- \( \text{CH}_2 \text{-Cl} \) > \( \text{CH}_2 \text{-Cl} \) > \( \text{CH}_3 \) > \( \text{O} - \text{CH}_3 \) > \( \text{O} - \text{H} \)
3. Multiple bonds are considered equivalent to the same number of single bonded atoms.

\[
\begin{align*}
\text{C} & \equiv \text{C} = \text{C} - \text{O} - \text{H} \\
\text{H}_3\text{C} - \text{C} & \equiv \text{CH} = \text{H} & \text{H}_3\text{C} - \text{C} & \equiv \text{O} - \text{H} \\
\text{H}_3\text{C} & - \text{CH}_2 - \text{CH}_3 = \text{H}_3\text{C} & - \text{O} - \text{H} & - \text{C}
\end{align*}
\]

Alkene Stability:

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{H} & \text{H}^+ & \text{Catalyst} & \text{H}_3\text{C} & \equiv \text{H} \\
\text{cis-2-butene} & \rightarrow & \text{trans-2-butene}
\end{align*}
\]

at equilibrium, the ratio is 76% trans and 24% cis. \( \Delta G^\circ = -2.8 \text{ KJ/mol} \)

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{H} & \text{H}_3\text{C} & \equiv \text{H} \\
\text{cis-2-butene} & \rightarrow & \text{trans-2-butene}
\end{align*}
\]

\( \Delta H^\circ \) \text{combustion} : -2685.5 KJ/mol \quad -2682.2 KJ/mol

3.3 KJ/mol less energy is given off from trans isomer

\[
\begin{align*}
\text{H}_3\text{C} & \equiv \text{H} & \text{H}_3\text{C} & \equiv \text{H} \\
\text{cis-2-butene} & \rightarrow & \text{trans-2-butene}
\end{align*}
\]

\( \Delta H^\circ \) \text{hydrogenation} : -120 KJ/mol \quad -115 KJ/mol

5 KJ/mol less energy is given off for trans isomer
The greater release of heat, the less stable the reactant.
Table 6.2 (pg 204). Heats of Hydrogenation of Some Alkenes
measure of alkene stability.

<table>
<thead>
<tr>
<th>Alkene</th>
<th>(\Delta H^\circ) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>monosubstituted</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_3\text{C} = \text{CH}_2)</td>
<td>-137</td>
</tr>
<tr>
<td>(\text{H}_3\text{C} = \text{CHCH}_3)</td>
<td>-126</td>
</tr>
<tr>
<td>(\text{H}_3\text{C} = \text{CCH}_3)</td>
<td>-120</td>
</tr>
<tr>
<td>disubstituted</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_3\text{C} = \text{CHCH}_3)</td>
<td>-115</td>
</tr>
<tr>
<td>(\text{H}_3\text{C} = \text{CCH}_3)</td>
<td>-119</td>
</tr>
<tr>
<td>(\text{H}_3\text{C} = \text{CHCH}_2\text{CH}_3)</td>
<td>-113</td>
</tr>
<tr>
<td>trisubstituted</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_3\text{C} = \text{CHCH}_2\text{CH}_3)</td>
<td>-111</td>
</tr>
</tbody>
</table>

Trend: increased substitution decreases \(\Delta H^\circ\) hydrogenation. Increased substitution increases the alkene stability. More substituted alkenes are favored over less substituted alkenes.

Hyperconjugation: stabilizing effect due to “bonding” interactions between a filled C-H orbital and a vacant neighboring orbital.

Increasing the substitution of an alkene, increases the number of possible hyperconjugation interactions.
**Electrophilic Addition of HX to Alkenes**

\[
\text{H}_2\text{C} = \text{CH}_2 + \text{HX} \rightarrow \text{H}_2\text{C} - \text{CH}_2\text{H}_3 + \text{H}_3\text{C} = \text{CH}_2\text{X} \quad \text{(none of this)}
\]

\[
\Delta G^0 < 0 \\
\Delta G^\ddagger \text{ for step one is large (slow)} \\
\Delta G^\ddagger \text{ for step two is small (fast)}
\]

**Markovnikov’s Rule:** For the electrophilic addition of HX across a C=C bond, the H (of HX) will add to the carbon of the double bond with the most H’s (the least substituent carbon) and the X will add to the carbon of the double bond that has the most alkyl groups.

**Markovnikov’s rule can be explained by the comparing the stability of the intermediate carbocations**
Carbocations are $sp^2$ hybridized and have a trigonal planar geometry. Hyperconjugation stabilizes carbocations. Thus, more substituted carbocations are more stable.

The C-H $\pi$-bond on the neighboring carbon lines up with the vacant p-orbital and can donate electron density to the carbon cation. This is a "bonding" interaction and is stabilizing. The more hyperconjugation that are possible, the more stable the carbocation.
**Inductive Effects** (section 2.1): shifting of electrons in a \( \sigma \)-bond in response to the electronegativity of a nearby atom (or group).

Carbon is a good electron donor. Substitution can also stabilize carbocations by donating electron density through the \( \sigma \)-bond.

![Chemical structures](image)

3°: three alkyl groups donating electrons  
2°: two alkyl groups donating electrons  
1°: one alkyl group donating electrons  
Methyl: no alkyl groups donating electrons

For the electrophilic addition of HX to an unsymmetrically substituted alkene:

- The more highly substituted carbocation intermediate is formed.

- More highly substituted carbocations are more stable than less substituted carbocations. (hyperconjugation)

- The more highly substituted carbocation is formed faster than less substituted carbocation. Once formed, the more highly substituted carbocation goes on to the final product more rapidly as well.
The rate of a reaction is dependent upon $\Delta G^\ddagger$
There is no formal relationship between $\Delta G^\ddagger$ and $\Delta G^\circ$
What is the structure of a transition state?
How can the structures of the reactants and products affect $\Delta G^\ddagger$

**Hammond Postulate:** provides an intuitive relationship between rate ($\Delta G^\ddagger$) and product stability ($\Delta G^\circ$).

**The Hammond Postulate:** The structure of the transition state more closely resembles the nearest stable species (i.e., the reactant, intermediate or product)
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For an endergonic reaction ($\Delta G^0 > 0$), the TS is nearer to the products. The structure of the TS resembles that of the products. Therefore, things that stabilize the product will also stabilize the TS leading to those products.

For an exergonic reaction ($\Delta G^0 < 0$), the TS is nearer to the reactants. The structure of the TS resembles that of the reactants.

For the electrophilic addition of HX to alkenes:
**Carbocation Rearrangements**: In reactions involving carbocation intermediates, the carbocation may sometimes rearrange if a more stable carbocation can be formed by the rearrangement. These involve hydride and methyl shifts.

\[
\text{H-Cl} \quad \rightarrow \quad \begin{array}{c}
\text{H}_3\text{C} \quad \text{H} \\
\text{H}_3\text{C} \quad \text{H}
\end{array}
\quad + \quad \begin{array}{c}
\text{H}_3\text{C} \quad \text{H} \\
\text{H}_3\text{C} \quad \text{H}
\end{array}
\]

\[
\sim 50\% \quad \text{expected product} \quad \sim 50\% 
\]

*Note that the shifting atom or group moves with its electron pair. A MORE STABLE CARBOCATION IS FORMED.*

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**Steroid Biosynthesis: Polyene Cyclizations**

[Diagram of the steroid biosynthesis process involving polyene cyclizations.]

- Farnesyl pyrophosphate \( (C_{15}H_{26}) \)
- Squalene \( (C_{30}H_{50}) \)
- Preketosterol \( (C_{27}H_{44}O_2) \)
Oxidative Stress - a free radical chain process

Cellular respiration

\[
\begin{align*}
O_2 & \rightarrow 4 e^- + 4H^+ \\
& \rightarrow 2H_2O
\end{align*}
\]

Superoxide: one-electron reduction of \( O_2 \)

Reacting Oxygen Species (ROS)

\[
\begin{align*}
O_2^- + Fe(III) & \rightarrow Fe(II) + O_2 \\
Fe(II) + H_2O_2 & \rightarrow HO^- + HO^- + Fe(II) \\
O_2^- + \cdot NO & \rightarrow ONOO^- \\
& \rightarrow ONOOH \quad \text{peroxynitrate} \\
& \rightarrow NO_2^- + HO^-
\end{align*}
\]
Linoleic Acid (unsaturated fatty acid)

H-atom abstraction ala the free radical chlorination of methane

Termination
anti-oxidants
(vitamin e)

Degradation
(lipid peroxidation)

Linked to DNA damage, protein damage,
neurodegenerative disease, diabetes, cardiovascular disease