Chapter 5

Reading: 5.1-5.10, 5.12, and 5.16-5.17

Practice problems: in text problems and 33-35, 37, 40, 43, 45, 46, 48-51, 68-70

The Reactions of Alkenes and Alkynes

Electrophilic Addition

Electrophilic addition to the double bond is a two-step process
First, the π bond reacts with an electrophile.
Second, the resulting carbocation reacts with a nucleophile
Electrophilic Addition

Electrophilic reagents we can use are hydrogen halides: HF, HCl, HBr, HI

They all follow the same reaction scheme.

\[
\text{cyclopentene} + HCl \rightarrow \text{chloro-cyclopentane}
\]

\[
\text{cyclopentene} + HI \rightarrow \text{iodo-cyclopentane}
\]

Electrophilic Addition

Reactions of olefins with identical substituents on both carbons lead to one product.

\[
\text{cyclopentene} + HBr \rightarrow \text{bromo-cyclopentane}
\]
Electrophilic Addition

In case the olefin has different, or different number of substituents, two products are possible.

![Chemical structure diagram]

Electrophilic Addition

Experiment shows that (A) is preferred over (B)

![Chemical structure diagram]

The preference for (A) is explained by the mechanism
Electrophilic Addition

We could obtain two structurally different Carbocations; however, A is formed much faster.

Comparing many reactions with different alkenes leads to a classification of carbocation intermediates.

The more substituents, the more stable the cation
Electrophilic Addition

The difference in the stabilities of the transition states

\[ \Delta G^\dagger \]

The difference in the stabilities of the carboxations

\[ \Delta G^\bullet \]

Progress of the reaction

Copyright © 2006 Pearson Education, Inc.

---

**ADDITION REACTIONS OF ALKENES**

**12.5 CHEMISTRY IN DEPTH**

**Carbocation Stability and the Markovnikov Rule**

We have seen that many organic reactions have more than one possible product. As in the addition of HCl (an asymmetrical reagent) to propene (an asymmetrical alkene), the two products are usually not formed in equal amounts. Each product is the result of a different mechanistic pathway, one of which will be favored over the other. Often the reason has to do with the presence of carbocation intermediates (see Box 12.4).

In the addition of HCl to propene, the two reaction pathways are:

- **PATHWAY 1**
  - \( CH_2\text{CH}CH_3 \)
  - \( CH(CH_3)_2 CH_3 \)
- **PATHWAY 2**
  - \( CH(CH_3)_2 CH_3 \)
  - \( H CH(CH_3)_2 \)

Each pathway begins with the formation of a different carbocation, and there are differences in stability between them. These differences determine the winner of the competition between the two possible pathways for this reaction. The pathway proceeding through the more stable carbocation is the winner.

The stability of carbocations follows the order:

- \( R-CH_2-CH_2-R > R-CH-CH_3 > R-CH_2-CH_3 > R-CH_3 \)

Tertiary, secondary, and primary carbocations are carbocations having three, two, and one non-hydrogen substituent, respectively, attached to the carbon carrying the positive (+) charge. The more stable a carbocation, the more easily and quickly it is formed. Reactions that proceed through more-stable carbocations take place at faster rates.

In the addition of HCl to propene, pathway 1 contains a secondary carbocation, whereas pathway 2 contains a primary carbocation. Because secondary carbocations are more stable and form faster than primary carbocations, more molecules of propene travel down pathway 1 than pathway 2. The overall result is that more 2-chloropropene than 1-chloropropane is formed. This result is predicted by the Markovnikov rule.
Electrophilic Addition

We obtain both products; however, one is the major product.

We have a *regioselective* reaction.
Electrophilic Addition

The molecular formula of both products is identical:

\[ C_7H_{13}I \]

However, the way the atoms are connected is different:

**CONSTITUTIONAL ISOMERS**

Electrophilic Addition

The regioselectivity of this reaction was first observed by Markovnikov.

He found that the hydrogen, which is the **electrophile**, adds to the carbon that contains the larger number of hydrogens.
Electrophilic Addition

When adding water to alkenes, NO reaction takes place.

Electrophilic Addition

When small amounts of acid are present, hydration of the double bond takes place.
**Electrophilic Addition**

1\textsuperscript{st} step is electrophilic attack of \( \text{H}^+ \)

**Electrophilic Addition**

2\textsuperscript{nd} step is nucleophilic attack of \( \text{H}_2\text{O} \)
Electrophilic Addition

3rd step is deprotonation to generate the alcohol.

H+ is regenerated,
so that only catalytic amounts of acid are necessary.

Electrophilic Addition

Alcohols react the same way as water

Note: the reaction works only in the presence of acid.
Electrophilic Addition

Initiating the reaction: generating a carbocation

\[ \text{2-methylpropene} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}^+} \text{carbocation}\]

The resulting carbocation is attacked by the nucleophilic alcohol

\[ \text{ethanol} + \text{carbocation} \xrightarrow{\text{fast}} \text{product}\]
Electrophilic Addition

Completion of the reaction:
deprotonation of the “alkoxonium species”

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

alkoxonium species

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

t-butyl-ethyl ether

ADDITION REACTIONS OF ALKENES

Example 12.7 Writing equations for addition reactions of alkenes: II

Complete each of the following reactions by writing the structure of the organic product. If no reaction takes place, write “no reaction.” If there is more than one product, indicate which is the major and which is the minor product.

(b) \( \text{CH}_2 = \text{CH} \text{CH} = \text{CH}_2 + \text{H}_2\text{C} = \text{CH}_2 \rightarrow \text{CH}_3\text{C} = \text{CHCH}_2\text{CH}_3 \)

(c) \( \text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{C} = \text{CHCH}_2\text{CH}_2\text{OH} \)
Alkenes, as well as some other families of organic compounds, can add to one another to form a covalently linked chain of molecules called a **polymer**.

The individually linked molecules in the polymer are called **monomers**.

Examples of synthetic polymers include plastics, fibers, and rubbers.

Naturally occurring polymers include carbohydrates, proteins, and nucleic acids.

---

**Addition Polymerization**

Addition polymerization of ethylene produces a long polymeric molecule called polyethylene:

\[
\text{CH}_2=\text{CH}_2 + \text{CH}_2=\text{CH}_2 + \text{CH}_2=\text{CH}_2 + \text{etc.} \rightarrow \text{Polymer}
\]

In this polymerization process π bonds within each monomer are broken and remade as σ bonds between the monomers.

The process can be abbreviated as:

\[
\text{Ethylene} \xrightarrow{\text{polymerization catalyst}} \text{Polyethylene}
\]

where \( n \) is usually in the 1000's.

This type of polymerization requires the presence of a catalyst, and does not occur in the presence of additional reagents which might react preferentially with the double bonds.
Polymers

Alkenes can be used as a monomeric unit to form chain-growth polymers

![Chemical structures of styrene and polystyrene](image)

**ADDITION POLYMERIZATION**

<table>
<thead>
<tr>
<th>Monomer name and structure</th>
<th>Name and structure</th>
<th>Polymer name</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>polyethylene</td>
<td></td>
<td>food and detergent bottles; toys and houseware; electrical wire and cable insulation; plastic sheeting for agricultural use</td>
</tr>
<tr>
<td>propylene</td>
<td>polypropylene</td>
<td></td>
<td>outdoor carpeting for home, sports stadiums; food packaging; housings for appliances</td>
</tr>
<tr>
<td>styrene</td>
<td>polystyrene</td>
<td></td>
<td>fast-food containers, hot-beverage cups; food-packaging trays; hairbrush handles; toys</td>
</tr>
<tr>
<td>tetrafluoroethylene</td>
<td>polytetrafluoroethylene</td>
<td></td>
<td>nonstick cookware; high-performance mechanical parts and electrical insulation; chemical-resistant gaskets</td>
</tr>
<tr>
<td>vinyl chloride</td>
<td>poly(vinyl chloride)</td>
<td></td>
<td>home vinyl siding; rain gutters; flooring (sheet, tile); garden hose; surgical gloves; wire and cable insulation</td>
</tr>
<tr>
<td>acrylonitrile</td>
<td>polyacrylonitrile</td>
<td></td>
<td>acrylic textile fibers</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>polymethyl methacrylate</td>
<td></td>
<td>factory and aircraft windows; bathtubs; contact lenses; dentures and dental fillings</td>
</tr>
</tbody>
</table>
Polymers

For the polymerization reaction we can use electrophilic addition reactions.

In the initiation step an electrophile (BF₃) adds to the alkene to form a carbocation intermediate.

Polymers

Subsequent propagation steps grow the polymer until all monomers are consumed.
Polymers

Termination can also be accomplished by adding a nucleophile.

Polymer

An alternative way to initiate polymerization is starting with a radical initiator.

\[
RO - OR \overset{\Delta}{\underset{(h\nu)}{\rightarrow}} 2 \text{RO}^*\text{radicals}
\]

The radical adds onto the alkene to form a new radical. Propagation is accomplished via subsequent radical additions.
Polymers

Termination takes place when the polymeric chain comes across another radical and they combine.