8.8 Oxidation of Alkenes: Cleavage to Carbonyl Compounds

Ozone ($O_3$) is a useful double-bond cleavage reagent:
- Ozone is generated by passing a stream of oxygen through a high-voltage electrical discharge.
- Ozone adds rapidly to $C=\text{C}$ bond at low temperature to give molozonide which spontaneously rearranges to ozonide.
- Ozonide is treated with reducing agent to convert it to carbonyl compounds.

![Diagram of ozone and ozonide formation](image)

Oxidation of Alkenes: Cleavage to Carbonyl Compounds

- If tetrasubstituted double bond is ozonized, two ketone fragments result.
- If a carbon of the alkene is bonded to hydrogen, ozonolysis will cleave the double bond to yield an aldehyde.

![Diagram of ketone formation](image)

Potassium permanganate ($KMnO_4$) in neutral or acidic solution cleaves alkenes to give carbonyl-containing products:
- If a carbon of the alkene is bonded to hydrogen, a carboxylic acid is produced.
- If a carbon of the alkene is bonded to two hydrogens, $CO_2$ is formed.

![Diagram of carboxylic acid formation](image)
Oxidation of Alkenes: Cleavage to Carbonyl Compounds

Alkenes are also cleaved by hydroxylation to a 1,2-diol followed by treatment with periodic acid, HIO₄.

- If the two –OH groups of the diol are in an open chain, two carbonyl compounds result
- If the two –OH groups of the diol are on a ring, a single, open-chain dicarbonyl compound is formed

Worked Example 8.3

Predicting the Reactant in an Ozonolysis Reaction

What alkene would yield a mixture of cyclopentanone and propanal on treatment with ozone followed by reduction with zinc?

8.9 Addition of Carbenes to Alkenes: Cyclopropane Synthesis

A carbenic, R₂C═, is a neutral molecule containing a divalent carbon with only six electrons in its valence shell
- One simple method for generating dichlorocarbene is by treatment of CHCl₃ with KOH
- Carbenes behave as electrophiles, adding to alkenes to yield cyclopropanes

\[
\text{C} = \text{C} + \text{CHCl}_3 \overset{\text{KOH}}\rightarrow \text{Cl} \quad \text{Cl}
\]
Mechanism of the formation of dichlorocarbene

1. Base abstracts the hydrogen from chloroethene, leaving behind the electron pair from the C-H bond and forming the trichlorocarbenium ion.

2. Spontaneous loss of chloride ion then yields the neutral dichlorocarbene.

Addition of Carbenes to Alkenes: Cyclopropane Synthesis

- Dichlorocarbene carbon atom is sp2-hybridized with a vacant p orbital extending above and below the plane of the three atoms with an unshared pair of electrons occupying the third sp2 lobe.

- Reaction of dichlorocarbene with an alkene results in a dichlorocyclopropane.
- Addition is stereospecific, meaning that only a single stereoisomer is formed as product.
Radicals add to alkene double bonds
- Radicals remove one electron from double bond
- One electron left behind yielding a new radical

**Polymer**
- A large molecule built up by repetitive bonding together of many smaller molecules called monomers
- Cellulose (glucose polymer)

![Cellulose structure](image)

**Radical Addition to Alkenes: Alkene Polymers**
- Proteins (amino acid polymers)
  - *Protein*—an amino acid polymer
  ![Amino acid and protein structure](image)
- Nucleic acid (nucleotide polymer)
  - *Nucleic acid*—a nucleotide polymer
  ![Nucleic acid structure](image)

**Simplest polymerization**
- Result when an alkene is treated with a small amount of a radical as an initiator

![Polyethylene structure](image)
Radical Addition to Alkenes: Alkene Polymers

Initiation
1. Small amount of benzoyl peroxide catalyst is heated breaking weak O-O bonds and yielding radicals
2. Benzoyloxy radical adds to C=C bond of ethylene forming a carbon radical
3. a) One electron from C=C bond pairs up with electron of benzoyloxy radical to form C-O bond
   b) Other electron remains on carbon (a carbon-centered radical)

\[
\begin{align*}
\text{Benzoyl peroxide} & \quad \text{Benzoyloxy radical} \\
\text{init.} & \quad 2 \\
\text{BzO} & \quad \text{BzO}^- \\
\text{H}_2\text{C} &= \text{CH}_2 \\
\rightarrow & \\
\text{BzO}^- & \quad \text{BzO}^- \\
\end{align*}
\]

\[
\begin{align*}
\text{BzCH}_2\text{CH}_2 & \quad \text{BzCH}_2\text{CH}_2 \text{CH}_2 \text{CH}_2 \\
\rightarrow & \\
\text{BzO}^- \text{CH}_2\text{CH}_2 \text{CH}_2 \text{CH}_2 & \quad \text{R}^- \text{CH}_2\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{R} \\
\end{align*}
\]

Propagation
- Polymerization occurs when the carbon radical adds to another ethylene molecule to yield another radical

\[
\begin{align*}
\text{Bz0CH}_2\text{CH}_2 & \quad \text{Bz0CH}_2\text{CH}_2 \text{CH}_2 \text{CH}_2 \\
\rightarrow & \\
\text{R}^{-} \text{CH}_2\text{CH}_2 \text{CH}_2 \text{CH}_2 & \quad \text{R}^{-} \text{CH}_2\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{R} \\
\end{align*}
\]

Termination
- Chain process ends by a reaction that consumes a radical
  - Combination of two growing chains

\[
2 \text{R}^{-} \text{CH}_2\text{CH}_2 \rightarrow \text{R}^{-} \text{CH}_2\text{CH}_2 \text{CH}_2 \text{CH}_2 \text{R}
\]

Vinyl monomers
- Substituted ethylene
- Undergo polymerization to yield polymer with substituted groups regularly spaced in alternating carbon atom long chain
  - Polypropylene

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

- Styrene

\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH} \\
\text{Styrene} & \quad \text{Polystyrene} \\
\end{align*}
\]
Polymerization of unsymmetrically substituted vinyl monomers
Propylene or Styrene
- Radical addition steps can take place at either end of the double bond to yield:
  - A primary radical intermediate (RCH$_2$.)
  - A secondary radical (R$_2$CH.)
- Similar to electrophilic addition reaction
- More highly substituted, secondary radical is formed

Worked Example 8.4
Predicting the Structure of a Polymer
Show the structure of poly(vinyl chloride), a polymer made from H$_2$C=CHCl, by drawing several repeating units

8.11 Biological Additions of Radicals to Alkenes
Radical vs. Electrophilic Addition Reactions
Electrophilic addition
- Reaction occurs once
- Intermediate is then quenched and reaction stops.