Chemistry 20  
Chapter 3  
Alkenes, Alkynes

**Alkene**: an unsaturated hydrocarbon that contains one or more carbon-carbon double bonds. The molecular formula of this group is \( C_nH_{2n} \) (\( n \) is the number of carbon atoms). Alkenes have less hydrogen atoms than alkanes.

\[
\begin{align*}
C_2H_4 & \quad \text{CH}_2=\text{CH}_2 \\
C_3H_6 & \quad \text{CH}_2=\text{CH}-\text{CH}_3
\end{align*}
\]

**Alkynes**: an unsaturated hydrocarbon that contains one or more carbon-carbon triple bonds. The molecular formula of this group is \( C_nH_{2n-2} \) (\( n \) is the number of carbon atoms). Alkynes have less hydrogen atoms than alkanes and alkenes.

\[
\begin{align*}
C_2H_2 & \quad \text{CH} \equiv \text{CH} \\
C_3H_4 & \quad \text{CH} \equiv \text{C}-\text{CH}_3
\end{align*}
\]

**Naming unbranched alkenes and alkynes**: we use the IUPAC system of naming for alkanes. For alkenes, we replace the suffix “-ane” of alkanes by “-ene”. For alkynes, we replace the suffix “-ane” of alkanes by “-yne”.

**Naming branched alkenes and alkynes**: 1. Name the longest carbon chain that contains the double or triple bond. 2. Number the carbon chain starting from the end nearest the double or triple bond. 3. Give the location and name of each substituent (alphabetical order) as a prefix to the alkene or alkyne name.

\[
\begin{align*}
\text{Ethane} & \quad \text{H}_2\text{C} \equiv \text{CH}_3 \\
\text{Propene (propylene)} & \quad \text{CH}_2=\text{CH} \equiv \text{CH}_2
\end{align*}
\]

**Note**: Some alkenes and alkynes (particularly those of low molecular weight) are known almost exclusively by their common names (we show them here in the parenthesis).

**Conformation**: under normal conditions, no rotation is possible about the carbon-carbon double and triple bonds.

**Cis and trans isomers**: isomers that have the same connectivity of their atoms (and the same molecular formulas) but a different arrangement of their atoms in space. Specifically, **cis and trans stereoisomers** result from the presence of either a ring or a carbon-carbon double bond.
(not a carbon-carbon triple bond). Cis and trans isomers are different compounds and have different physical and chemical properties.

\[
\begin{align*}
\text{trans-2-Butene} & \\
\text{cis-2-Butene}
\end{align*}
\]

**Note:** Both boiling and melting points of the cis isomers are lower than the trans isomers (because the surface areas of cis isomers are smaller and molecules are more compact).

**Naming of cycloalkenes:** number the carbon atoms of the ring double bond 1 and 2 in the direction that gives the substituent encountered first the lower number. It is not necessary to use a location number for the carbons of the double bond. Because, they will always be 1 and 2. Number substituents and list them in alphabetical order.

\[
\begin{align*}
\text{3-Methylcyclopentene} & \\
\text{4-Ethyl-1-methylcyclohexene}
\end{align*}
\]

**Dienes, Trienes, and Polyenes:** alkenes that contain more than one double bond are named alkadienes (two double bond), alkatrienes (three double bonds), and polyenes (several double bonds). To name these compounds, we drop “-ne” from the name of alkenes and we replace by “-diene”, “-triene”, and so on.

\[
\begin{align*}
\text{1,4-Pentadiene} & \\
\text{2-Methyl-1,3-butadiene} & \\
\text{1,3-Cyclopentadiene}
\end{align*}
\]

**Note:** For an alkene with \( n \) carbon-carbon double bonds, each of which can show cis-trans isomerism, \( 2^n \) stereoisomers are possible.

**Physical properties of alkenes and alkynes:** their physical properties are similar to those of alkanes with the same carbon skeletons.

**Chemical properties of alkenes and alkynes:** these organic compounds are more reactive than alkanes. The most characteristic reaction of alkenes (alkynes) is addition to the carbon-carbon double bond (triple bond).
Addition reactions: in these kind of reactions, the double bond is broken and in its place single bonds form to two new atoms or groups of atoms. Almost all the addition reactions of alkenes are exothermic, which means that the products are more stable (have lower energy) than the reactants.

\[
\text{-C}=\text{-} \quad \rightarrow \quad \text{-C-}
\]


1. Addition of hydrogen (Hydrogenation or Reduction): atoms of hydrogen add to the carbons in a double or triple bond to form alkanes. A catalyst as platinum (Pt), nickel (Ni), or palladium (Pd) is added to speed up the reaction. The transition metal catalysts used in this hydrogenation are able to absorb large quantities of hydrogen onto their surfaces, probably by forming metal-hydrogen bonds.

2. Addition of hydrogen halides (Hydrohalogenation): the hydrogen halides HCl, HBr, and HI add to alkenes to give haloalkanes (alkyl halides). Addition of HCl to propene is regioselective (hydrogen adds to the doubly bonded carbon that has the greater number of hydrogens already bonded to it; halogen adds to the other carbon. This rule is called Markovnikov’s rule).

3. Addition of water (Hydration): in the presence of an acid catalyst, most commonly concentrated sulfuric acid, water adds to the carbon-carbon double bond of an alkene to give an alcohol. Addition of water is called hydration. Hydration follows Markovnikov’s rule: H of H\textsubscript{2}O adds to the carbon of the double bond with the greater number of hydrogens and OH of H\textsubscript{2}O adds to the carbon with the smaller number of hydrogens.

4. Addition of bromine and chlorine (Halogenation): chlorine and bromine react with alkenes (alkynes) at room temperature by addition of halogen atoms to the carbon atoms of
the double bond (triple bond). We do not need any catalysts for this reaction (in general, we use an inert solvent, such as dichloromethane, CH\textsubscript{2}CH\textsubscript{2}).

\[ \text{CH}_3\text{CH}=\text{CHCH}_3 + \text{Br}_2 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{CH}_3\text{CH}-\text{CHCH}_3 \]

2-Butene → 2,3-Dibromobutane

**Note:** Addition of bromine is a useful qualitative test for the presence of an alkene (or an alkyne). If we dissolve bromine in carbon tetrachloride, the solution is red. In contrast, alkenes (alkynes) and dibromoalkanes are colorless. The disappearance of the red color as bromine adds to the double bond (triple bond) tells us that alkene (alkyne) is, indeed present.

**Note:** Addition of halogen to an alkene (an alkyne) is an **addition reaction** and two atoms of halogens are added to the carbon atoms of the double bond (triple bond). However, addition of halogen to an alkane is a **substitution reaction** and only one atom of halogen is replaced by one hydrogen atom.

**Polymerization:** in presence of certain compounds called **initiators**, many alkenes form polymers made by the stepwise addition of **monomers** to a growing polymer chain. \( n \) is a large number, typically several thousand of monomers. We place parentheses around the repeating monomer unit.

**Polymer:** a long-chain molecule produced by bonding together many single parts called monomers.

\[ n\text{CH}_2=\text{CH}_2 \xrightarrow{\text{initiator}} (\text{polymerization}) \left\{\text{CH}_2\text{CH}_2\right\}_n \]

**Polyethylene**

**Naming of polymers:** attach the prefix “poly-” to the name of the monomer from which the polymer is synthesized:

\[ \text{Ethylene} \rightarrow \text{Polyethylene} \]

**Note:** When the name of the monomer consists of two words, its name is enclosed in parentheses:

\[ \text{Vinyl chloride} \rightarrow \text{Poly(vinyl chloride)} \text{ or } \text{PVC} \]

**Low-Density Polyethylene (LDPE):** the first commercial process for ethylene polymerisation used peroxide initiators at 500°C and 1000 atm and yielded a tough, transparent polymer known as low-density polyethylene (LDPE). LDPE chains are highly branched, with the result that they do not pack well together and London dispersion forces between them are weak. LDPE softens and melts at about 115°C, which means that it cannot be used in products that are exposed to boiling water. We use it for the manufacture of films, trash bags, and packaging baked goods and vegetables.

**High-Density polyethylene (HDPE):** has little chain branching and its chains pack together more closely than those of LDPE, with the result that London dispersion forces between
chains of HDPE are stronger than those in LDPE. HDPE has a higher melting point than LDPE and is three to ten times stronger. We use it for consumer items such as milk and water jugs, grocery bags, and squeezable bottles.