

Reactions of Alkenes: Addition Reactions

SUMMARY

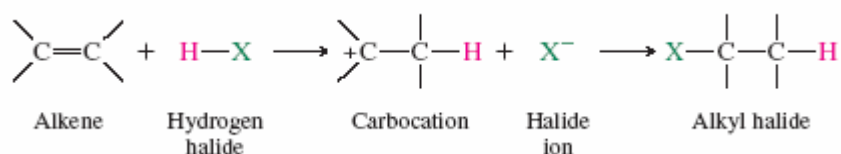
Alkenes are **unsaturated hydrocarbons** and react with substances that add to the double bond.

Section 6.1 See Table 6.6.

Section 6.2 Hydrogenation of alkenes is exothermic. Heats of hydrogenation can be measured and used to assess the stability of various types of double bonds. The information parallels that obtained from heats of combustion.

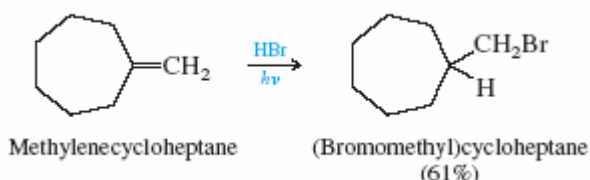
Section 6.3 Hydrogenation of alkenes is a syn addition.

Sections 6.4–6.7 See Table 6.6. Hydrogen halide addition to alkenes proceeds by electrophilic attack of the reagent on the p electrons of the double bond. Carbocations are intermediates. Addition to unsymmetrical alkenes is regioselective.



Protonation of the double bond occurs in the direction that gives the more stable of two possible carbocations.

Section 6.8 Hydrogen bromide is unique among the hydrogen halides in that it can add to alkenes either by electrophilic or free-radical addition. Under photochemical conditions or in the presence of peroxides, free-radical addition is observed, and HBr adds to the double bond with a regioselectivity opposite to that of Markovnikov's rule.



Sections 6.9–6.10 See Table 6.6

Section 6.11 Addition and elimination reactions are often reversible, and proceed spontaneously in the direction in which the free energy G decreases. The reaction is at equilibrium when $\Delta G = 0$. Free energy is related to enthalpy (H) and entropy (S) by the equations

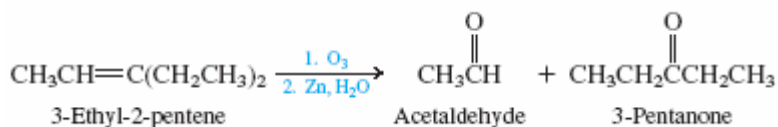
$$G = H - TS \quad \text{and} \quad \Delta G = \Delta H - T\Delta S$$

The standard free energy change ΔG° is related to the equilibrium constant K by the equation

$$\Delta G^\circ = -RT \ln K$$

Sections 6.12–6.20 See Table 6.6

Section 6.20 Alkenes are cleaved to carbonyl compounds by **ozonolysis**. This reaction is useful both for synthesis (preparation of aldehydes, ketones, or carboxylic acids) and analysis. When applied to analysis, the carbonyl compounds are isolated and identified, allowing the substituents attached to the double bond to be deduced.



Section 6.21 The reactions described so far can be carried out sequentially to prepare compounds of prescribed structure from some given starting material. The best way to approach a synthesis is to reason backward from the desired target molecule and to always use reactions that you are sure will work. The 11 exercises that make up Problem 6.36 at the end of this chapter provide some opportunities for practice.

Section 6.22 In their **polymerization**, many individual alkene molecules combine to give a high-molecular-weight product. Among the methods for alkene polymerization, *cationic polymerization*, *coordination polymerization*, and *free-radical polymerization* are the most important. An example of cationic polymerization is on catalytic hydrogenation?

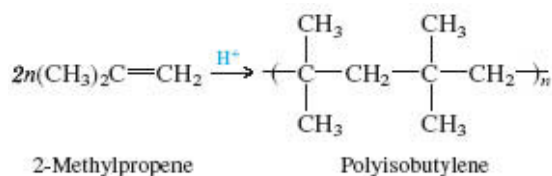
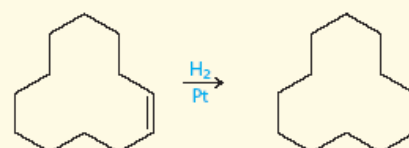
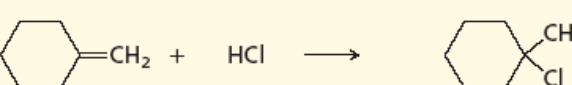
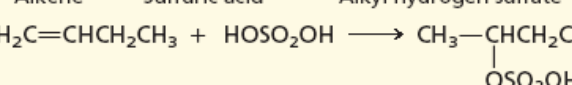
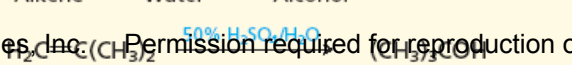


TABLE 6.6 Addition Reactions of Alkenes

Reaction (section) and comments	General equation and specific example
Catalytic hydrogenation (Sections 6.1–6.3) Alkenes react with hydrogen in the presence of a platinum, palladium, rhodium, or nickel catalyst to form the corresponding alkane.	$\text{R}_2\text{C}=\text{CR}_2 + \text{H}_2 \xrightarrow{\text{Pt, Pd, Rh, or Ni}} \text{R}_2\text{CHCHR}_2$ <p style="text-align: center;">Alkene Hydrogen Alkane</p>  <p style="text-align: center;">cis-Cyclododecene Cyclododecane (100%)</p>
Addition of hydrogen halides (Sections 6.4–6.7) A proton and a halogen add to the double bond of an alkene to yield an alkyl halide. Addition proceeds in accordance with Markovnikov's rule; hydrogen adds to the carbon that has the greater number of hydrogens, halide to the carbon that has the fewer hydrogens.	$\text{RCH}=\text{CR}'_2 + \text{HX} \longrightarrow \text{RCH}_2-\underset{\text{X}}{\text{CR}'_2}$ <p style="text-align: center;">Alkene Hydrogen halide Alkyl halide</p>  <p style="text-align: center;">Methylenecyclohexane Hydrogen chloride 1-Chloro-1-methylcyclohexane (75–80%)</p>
Addition of sulfuric acid (Section 6.9) Alkenes react with sulfuric acid to form alkyl hydrogen sulfates. A proton and a hydrogen sulfate ion add to the double bond in accordance with Markovnikov's rule. Alkenes that yield tertiary carbocations on protonation tend to polymerize in concentrated sulfuric acid (Section 6.21).	$\text{RCH}=\text{CR}'_2 + \text{HOSO}_2\text{OH} \longrightarrow \text{RCH}_2-\underset{\text{OSO}_2\text{OH}}{\text{CR}'_2}$ <p style="text-align: center;">Alkene Sulfuric acid Alkyl hydrogen sulfate</p>  <p style="text-align: center;">1-Butene Sulfuric acid sec-Butyl hydrogen sulfate</p>
Acid-catalyzed hydration (Section 6.10) Addition of water to the double bond of an alkene takes place in aqueous acid. Addition occurs according to Markovnikov's rule. A carbocation is an intermediate in the mechanism. The nucleophile of water acting as a nucleophile.	$\text{RCH}=\text{CR}'_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{RCH}_2-\underset{\text{OH}}{\text{CR}'_2}$ <p style="text-align: center;">Alkene Water Alcohol</p>  <p style="text-align: center;">2-Methylpropene tert-Butyl alcohol (55–58%)</p>

