

Organic Chemistry, *Fourth Edition*

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Chapter 15 Lecture Outline

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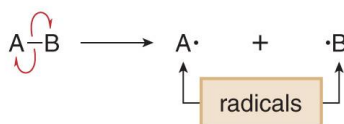
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Radicals

- A small but significant group of reactions involve radical intermediates.
- A **radical** is a reactive intermediate with a single unpaired electron, formed by homolysis of a covalent bond.
- A radical contains an atom that does not have an octet of electrons.
- **Half-headed arrows** are used to show the movement of electrons in radical processes.

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Structure of Radicals

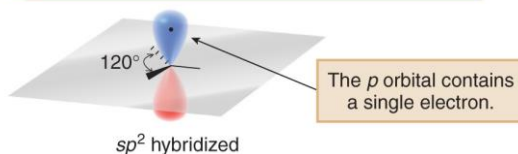
- Carbon radicals are classified as 1°, 2°, or 3°.
- A carbon radical is sp^2 hybridized and trigonal planar, like carbocations.
- The unhybridized p orbital contains the unpaired electron and extends above and below the trigonal planar carbon.

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Classification of carbon radicals



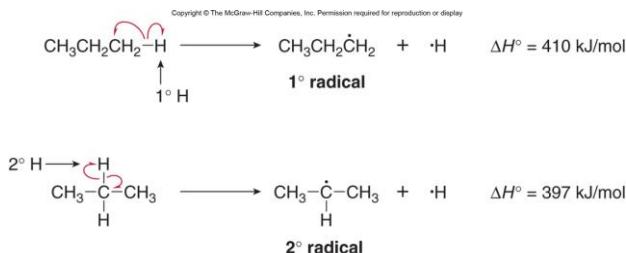
The trigonal planar geometry of a carbon radical



3

Bond Dissociation Energies

- **Bond dissociation energies** for the cleavage of C—H bonds are used to measure stability.
- They are determined by calculating the energy needed to break the bond into two radicals.
- Cleaving a stronger bond requires more energy.
- In the example below, the 2° radical is more stable than the 1° radical because less energy is required to produce it.

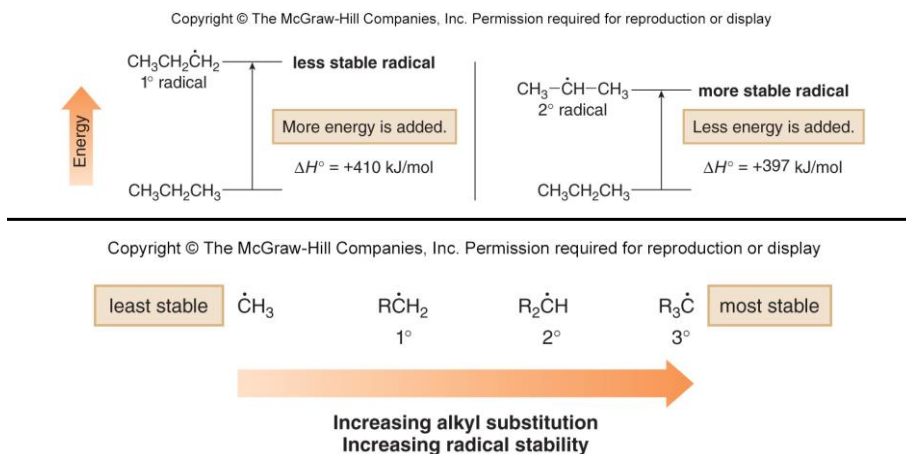


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Stability of Radicals

Figure 15.1

The relative stability of 1° and 2° carbon radicals



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General Features of Radical Reactions

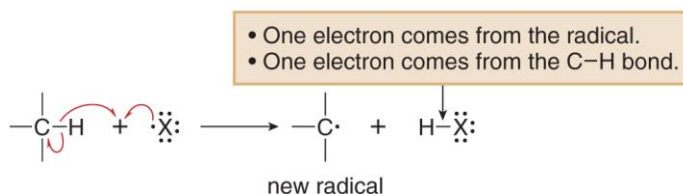
- Radicals are formed from covalent bonds by adding energy in the form of heat (Δ) or light ($h\nu$).
- Some radical reactions are carried out in the presence of a radical initiator.
- Radical initiators, such as peroxides of general structure, $\text{RO}-\text{OR}$, contain an especially weak bond that serves as a source of radicals.
- Heating a peroxide readily causes homolysis of the weak $\text{O}-\text{O}$ bond, forming two $\text{RO}\cdot$ radicals.
- Radicals undergo two main types of reactions—they react with σ bonds, and they add to π bonds.

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Reaction of a Radical X• with a C–H Bond

- A radical X•, once formed, rapidly reacts with whatever is available, usually a stable σ or π bond.
- A radical X• abstracts a hydrogen atom from a C–H σ bond to form H–X and a carbon radical.

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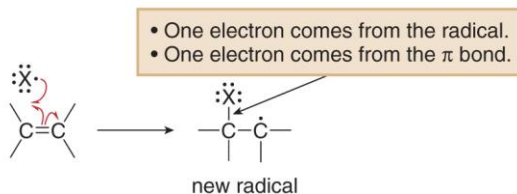


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Reaction of a Radical X• with a C=C Bond

- A radical X• can also add to the π bond of a carbon–carbon double bond.

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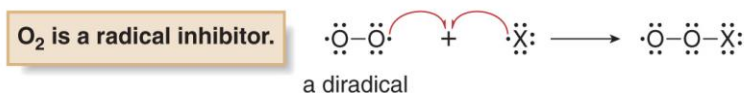
- In either type of radical reaction (with a σ or π bond) a new radical is created.

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Inhibition of Radicals by Molecular Oxygen

- Occasionally, two radicals react to form a sigma bond.
- An example is the reaction of a radical with oxygen (a diradical in its ground state electronic configuration).

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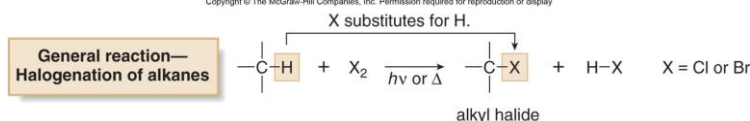
- Reaction with oxygen causes the reaction to slow down or stop, as X-O-O· radicals are not as reactive as halogen radicals.
- Compounds that prevent radical reactions from occurring are called **radical inhibitors** or **radical scavengers**.

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Radical Halogenation of Alkanes

- In the presence of heat or light, alkanes react with halogens to form alkyl halides by a radical substitution reaction.
- Halogenation of alkanes is only useful with Cl₂ or Br₂.
- Reaction with F₂ is too violent, and reaction with I₂ is too slow to be useful.

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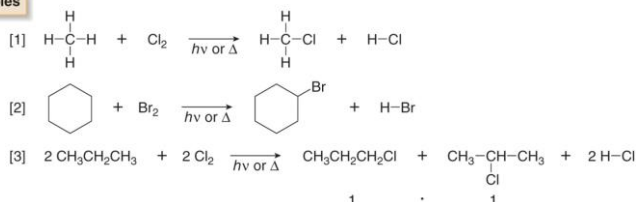
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Radical Halogenation of Alkanes

- With an alkane that has more than one type of hydrogen atom, a mixture of alkyl halides may result.
- When a single hydrogen atom on a carbon has been replaced by a halogen atom, **monohalogenation** has taken place.

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Examples



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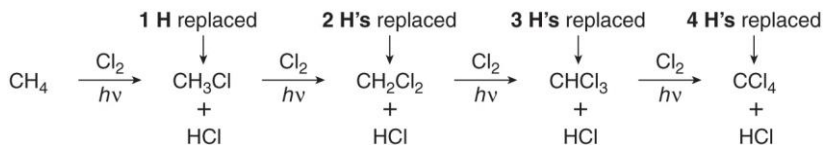
Radical Halogenation of Alkanes

- When excess halogen is used, it is possible to replace more than one hydrogen atom on a single carbon with halogen atoms.
- Monohalogenation can be achieved experimentally by adding halogen X_2 to an excess of alkane.

Figure 15.2

Complete halogenation of CH_4 using excess Cl_2

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Halogenation of Alkanes—Mechanism

- Three facts about halogenation suggest that the mechanism involves radical, not ionic, intermediates:

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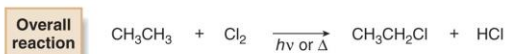
Fact	Explanation
[1] Light, heat, or added peroxide is necessary for the reaction.	Light or heat provides the energy needed for homolytic bond cleavage to form radicals. Breaking the weak O–O bond of peroxides initiates radical reactions as well.
[2] O ₂ inhibits the reaction.	The diradical O₂ removes radicals from a reaction mixture, thus preventing reaction.
[3] No rearrangements are observed.	Radicals do not rearrange.

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Common Steps of Radical Reactions

- Radical halogenation has three distinct steps:

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- Initiation:** Two radicals are formed by homolysis of a σ bond and this begins the reaction.
- Propagation:** A radical reacts with another reactant to form a new σ bond and another radical.
- Termination:** Two radicals combine to form a stable bond. Removing radicals from the reaction mixture without generating any new radicals stops the reaction.

- This type of mechanism that involves two or more repeating steps is called a **chain mechanism**.
- The most important steps of any chain mechanism including radical halogenation are the **propagation steps** which lead to product formation.

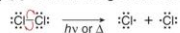
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Mechanism 15.1 Radical Halogenation of Alkanes

Initiation

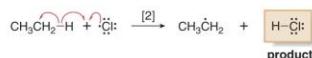
Step [1] Bond cleavage forms two radicals.



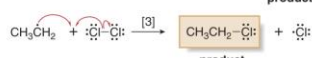
- Homolysis of the weakest bond in the starting materials requires energy from light or heat.
- Thus, the Cl-Cl bond ($\Delta H^\circ = 242 \text{ kJ/mol}$), which is weaker than either the C-C or C-H bond in ethane ($\Delta H^\circ = 368$ and 410 kJ/mol , respectively), is broken to form two chlorine radicals.

Propagation

Steps [2] and [3] One radical reacts and a new radical is formed.



- The Cl· radicals abstract a hydrogen atom from ethane (Step [2]). This forms H-Cl and leaves one unpaired electron on carbon, generating the ethyl radical ($\text{CH}_3\dot{\text{C}}\text{H}_2$).



- $\text{CH}_3\dot{\text{C}}\text{H}_2$ abstracts a chlorine atom from Cl_2 (Step [3]), forming $\text{CH}_3\text{CH}_2\text{Cl}$ and a new chlorine radical ($\text{Cl}^\cdot$).

Repeat Steps [2], [3], [2], [3], [2], [3], again and again.

- The Cl· radical formed in Step [3] is a reactant in Step [2], so Steps [2] and [3] can occur repeatedly without an additional initiation reaction (Step [1]).

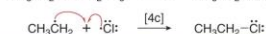
- In each propagation step, one radical is consumed and one radical is formed. The two products— $\text{CH}_3\text{CH}_2\text{Cl}$ and HCl—are formed during propagation.

Termination

Step [4] Two radicals react to form a σ bond.



- To terminate the chain, two radicals react with each other in one of three ways (Steps [4a, b, and c]) to form stable bonds.

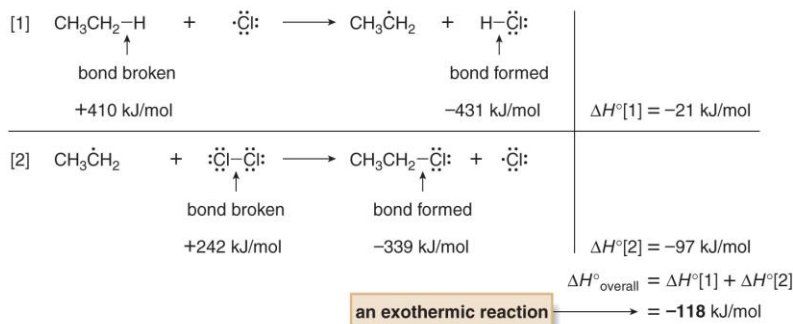


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Energy Changes in Radical Propagation

Figure 15.3

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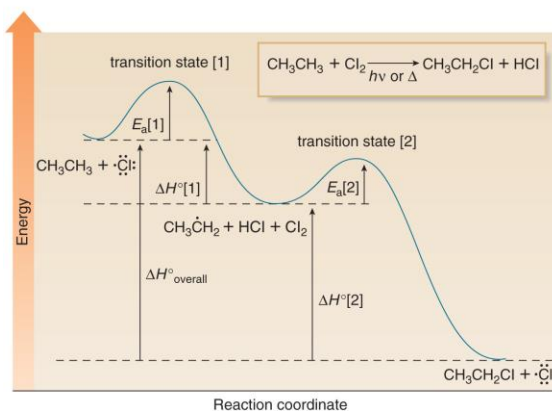
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Energy Diagram for Radical Propagation

Figure 15.4

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- Because radical halogenation consists of two propagation steps, the energy diagram has two energy barriers.
- The first step is rate-determining because its transition state is at higher energy.
- The reaction is exothermic because $\Delta H^\circ_{\text{overall}}$ is negative.

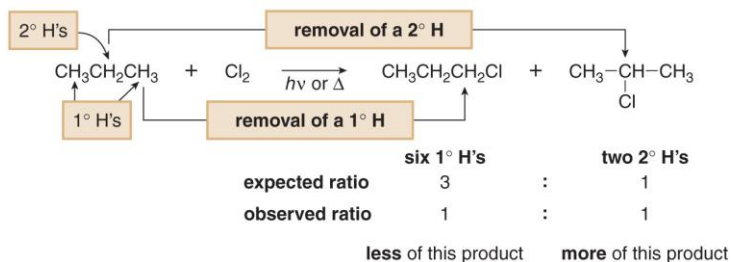


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Product Mixture in Radical Chlorination

- Chlorination of $\text{CH}_3\text{CH}_2\text{CH}_3$ affords a 1:1 mixture of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{CHCl}$.
- $\text{CH}_3\text{CH}_2\text{CH}_3$ has six 1° hydrogens and only two 2° hydrogens, so the expected product ratio of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ to $(\text{CH}_3)_2\text{CHCl}$ (assuming all hydrogens are equally reactive) is 3:1.

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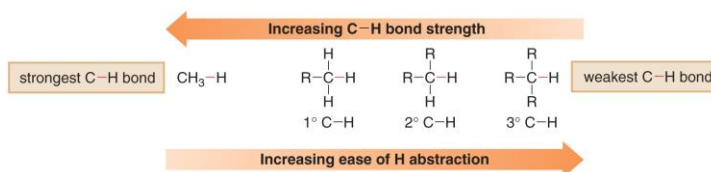
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Radical Halogenation of Alkanes

- Since the observed ratio between $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{CHCl}$ is 1:1, the 2° C-H bonds must be more reactive than the 1° C-H bonds.

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- The weaker the C-H bond, the more readily the hydrogen atom is removed in radical halogenation.



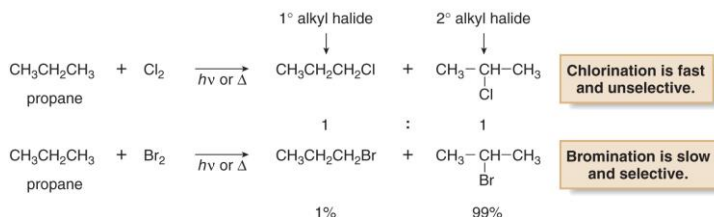
- Thus, when alkanes react with Cl_2 , a mixture of products results, with more product formed by cleavage of the weaker C-H bond than you would expect on statistical grounds.

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Chlorination vs Bromination

- Although alkanes undergo radical substitutions with both Cl_2 and Br_2 , chlorination and bromination exhibit two important differences.
 - Chlorination is faster than bromination.
 - Chlorination is unselective, yielding a mixture of products, but bromination is more selective, often yielding one major product.

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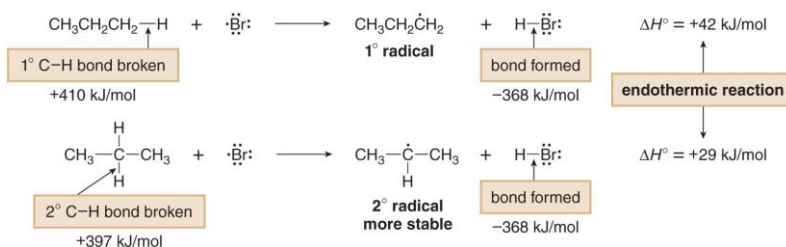


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Energy of Halogenation

- The differences in chlorination and bromination can be explained by considering the relative energetics of their key propagation steps.
- Calculating ΔH° using bond dissociation energies reveals that abstraction of a 1° or 2° hydrogen by $\text{Br}\cdot$ is endothermic.
- However, it takes less energy to form the more stable 2° radical, and this difference is more important in endothermic steps.

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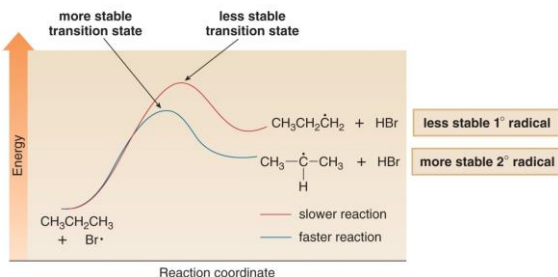


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Energy Diagram for Endothermic Reaction—Bromination

Figure 15.5

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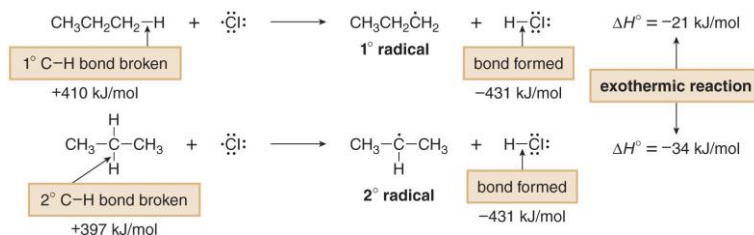
- The transition state to form the less stable 1° radical ($\text{CH}_3\text{CH}_2\dot{\text{C}}\text{H}_2$) is higher in energy than the transition state to form the more stable 2° radical [$(\text{CH}_3)_2\dot{\text{C}}\text{H}$]. Thus, the 2° radical is formed faster.
- Because the rate-determining step is endothermic, the transition state resembles the products.
- The more stable radical is formed faster, and often a single radical halogenation product predominates.

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Energy of Radical Formation

- Calculating ΔH° using bond dissociation energies for chlorination reveals that abstraction of a 1° or 2° hydrogen by $\text{Cl}\cdot$ is exothermic.

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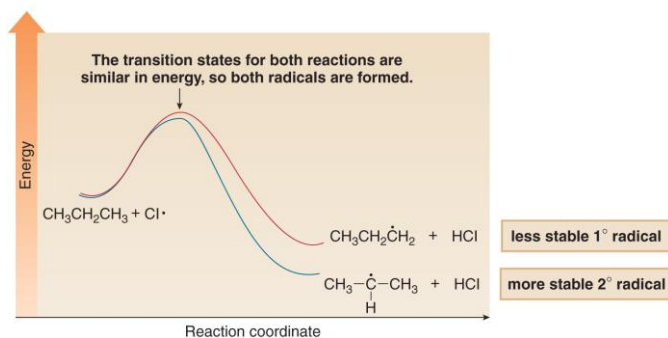
- Since chlorination has an exothermic rate-determining step, the transition state to form both radicals resembles the same starting material, $\text{CH}_3\text{CH}_2\text{CH}_3$.
- Thus, the relative stability of the two radicals is much less important, and both radicals are formed.

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Energy Diagram for Exothermic Reaction—Chlorination

Figure 15.6

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- Because the rate-determining step in chlorination is exothermic, the transition state resembles the starting material, both radicals are formed, and a mixture of products results.

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Predicting Stereochemistry of Reactions

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Table 15.1 Rules for Predicting the Stereochemistry of Reaction Products

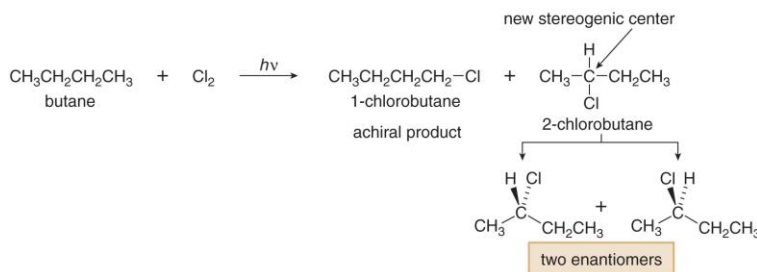
Starting material	Result
Achiral	An achiral starting material always gives either an achiral or a racemic product.
Chiral	- If a reaction does not occur at a stereogenic center, the configuration at a stereogenic center is retained in the product. - If a reaction occurs at a stereogenic center, we must know the mechanism to predict the stereochemistry of the product.

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Stereochemistry from Achiral Starting Material

- Halogenation of an achiral starting material such as $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ forms two constitutional isomers by replacement of either a 1° or 2° hydrogen.

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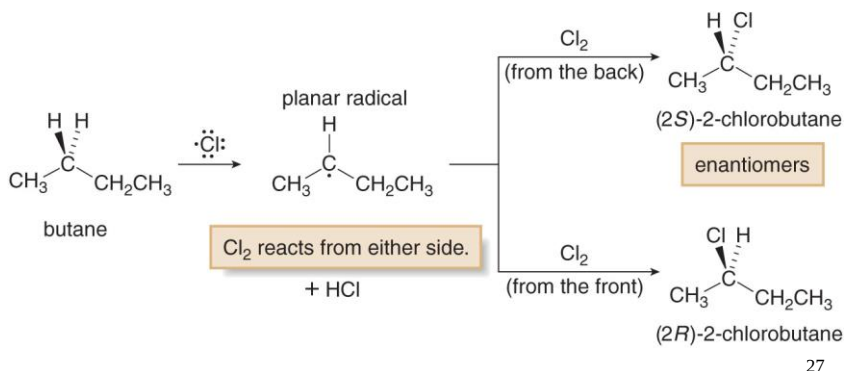
- 1-Chlorobutane has no stereogenic centers and is thus achiral.
- 2-Chlorobutane has a new stereogenic center, and so an equal amount of two enantiomers must form—a racemic mixture.

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Racemates from Achiral Starting Material

- A racemic mixture results because the first propagation step generates a planar sp^2 hybridized radical.
- Cl_2 then reacts with it from either side to form an equal amount of two enantiomers.

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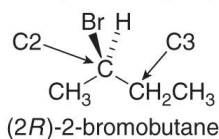


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Stereochemistry from Chiral Starting Material

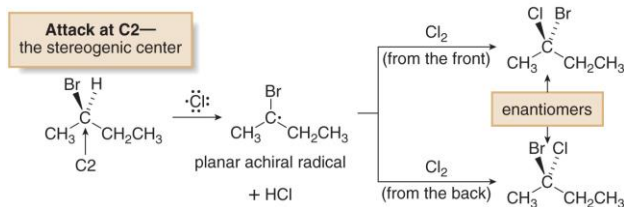
Chlorination at the Chiral Center

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- Chlorination at C2 occurs at the stereogenic center.

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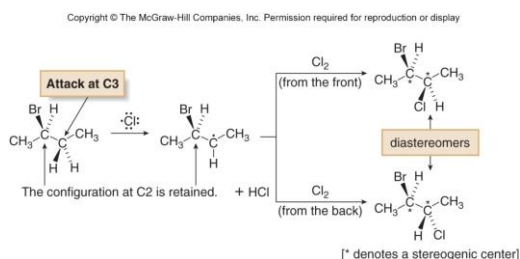
- Radical halogenation reactions at a stereogenic center occur with racemization.

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Stereochemistry from Chiral Starting Material

Chlorination Away from the Chiral Center

- Chlorination at C3 does not occur at the stereogenic center, but forms a new stereogenic center.
- Since no bond is broken to the stereogenic center at C2, its configuration is retained during the reaction.
- The trigonal planar sp^2 hybridized radical is attacked from either side by Cl_2 , forming a new stereogenic center.
- A pair of diastereomers is formed.



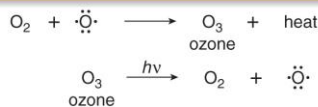
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The Ozone Layer and CFCs

- Ozone is vital to life, and acts as a shield, protecting the earth's surface from harmful UV radiation.

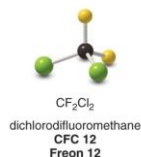
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The synthesis and decomposition of O_3 in the upper atmosphere



- Current research suggests that **chlorofluorocarbons (CFCs)**, used extensively as refrigerants and propellants, are responsible for destroying ozone in the upper atmosphere.

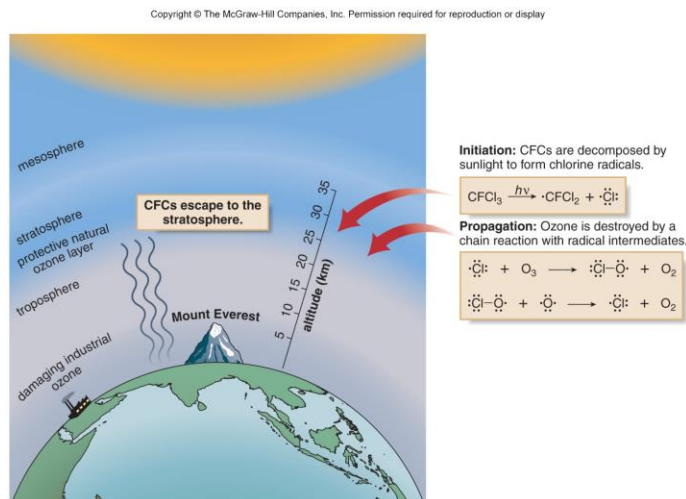
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CFCs and the Destruction of the Ozone Layer

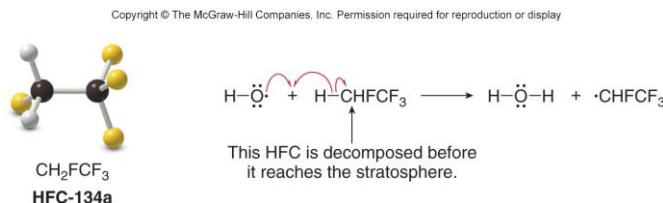
Figure 15.7



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Alternatives to CFCs

- The overall result is that O_3 is consumed as a reactant and O_2 is formed.
- In this way, a small amount of CFC can destroy a large amount of O_3 .
- New alternatives to CFCs are **hydrochlorofluorocarbons (HCFCs)** and **hydrofluorocarbons (HFCs)** such as CH_2FCF_3 .
- These compounds are decomposed by $\text{HO}\cdot$ before they reach the stratosphere and therefore, they do not take part in the radical reactions resulting in O_3 destruction.

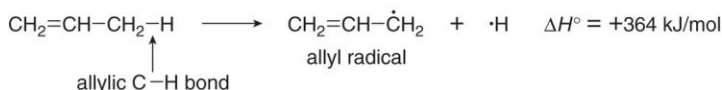


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Radical Halogenation at an Allylic Carbon

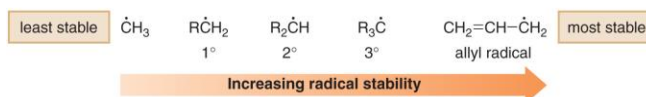
- An **allylic carbon** is a carbon adjacent to a double bond.
- Homolysis of the allylic C–H bond in propene generates an **allylic radical** which has an unpaired electron on the carbon adjacent to the double bond.

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- The bond dissociation energy for this process is even less than that for a 3° C–H bond (91 kcal/mol).
- This means that an allyl radical is more stable than a 3° radical.

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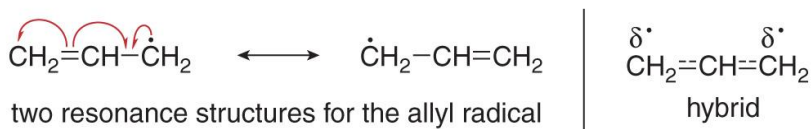


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Stability of Allyl Radicals

- The allyl radical is more stable than other radicals because the π bond and the unpaired electron are delocalized.
- The “true” structure of the allyl radical is a hybrid of the two resonance structures.
- Declocalizing electron density lowers the energy of the hybrid, thus stabilizing the allyl radical.

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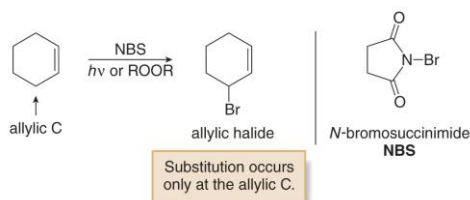


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NBS—a Radical Bromination Reagent

- Because allylic C–H bonds are weaker than other sp^3 hybridized C–H bonds, the allylic carbon can be selectively halogenated using NBS in the presence of light or peroxides.

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- NBS contains a weak N–Br bond that is homolytically cleaved with light to generate a bromine radical, initiating an allylic halogenation reaction.
- Propagation then consists of the usual two steps of radical halogenation.

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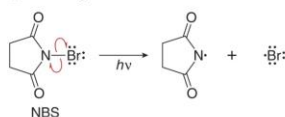
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Mechanism 15.2 Allylic Bromination with NBS

Initiation

Step [1] Cleavage of the N–Br bond forms two radicals.



- The reaction begins with homolysis of the weak N–Br bond in NBS using light energy. This generates a $\text{Br}\cdot$ radical that begins the radical halogenation process.

Propagation

Steps [2] and [3] One radical reacts and a new radical is formed in each step.



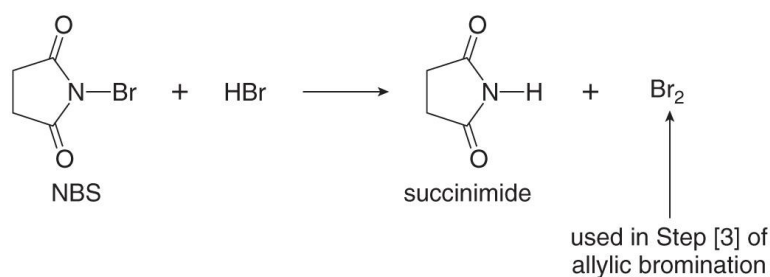
- The $\text{Br}\cdot$ radical abstracts an allylic hydrogen atom to afford an allylic radical in Step [2]. (Only one Lewis structure of the allylic radical is drawn.)
- The allylic radical reacts with Br_2 in the second propagation step to form the product of allylic halogenation. Because the $\text{Br}\cdot$ radical formed in Step [3] is also a reactant in Step [2], Steps [2] and [3] repeatedly occur without the need for Step [1].

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Formation of Bromine from NBS

- The HBr formed in Step [2] reacts with NBS to form a low concentration of Br_2 .
- This is then used for halogenation in Step [3] of the mechanism.

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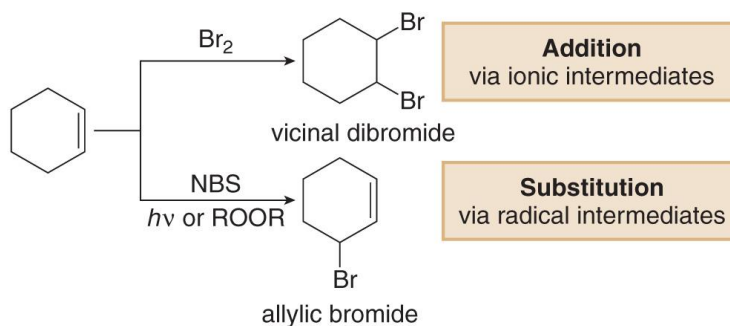


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Radical vs Ionic Bromination

- An alkene with allylic C-H bonds undergoes two different reactions depending on the reaction conditions.
 - Addition and Substitution

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Why NBS Favors Substitution Over Addition

A low concentration of Br_2 (from NBS) favors allylic substitution over ionic addition to form the dibromide.

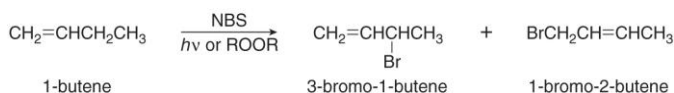
- The Br_2 produced from NBS, present in very low concentrations, must first react with the double bond to form the bridged bromonium ion.
- The bridged bromonium ion must then react with more bromine (in the form of Br^-) in a second step to form the dibromide.
- If concentrations of both intermediates—the bromonium ion and Br^- are low (as is the case here), the overall rate of addition is very slow, and the products of the very fast and facile radical chain reaction predominate.

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Regiochemistry of Allylic Halogenation

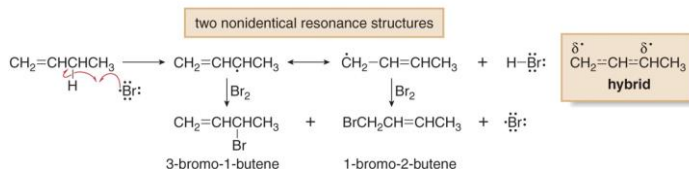
- Halogenation at an allylic carbon often results in a mixture of products.

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- A mixture results because the reaction proceeds by way of a resonance-stabilized radical.

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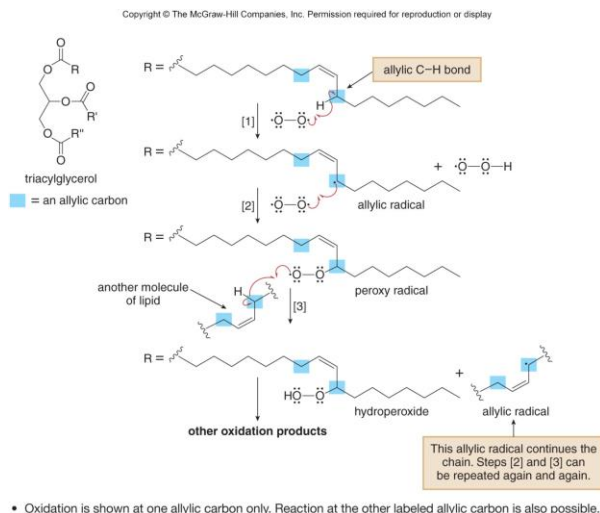


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Oxidation of Unsaturated Lipids

- Oils are susceptible to allylic free radical oxidation.

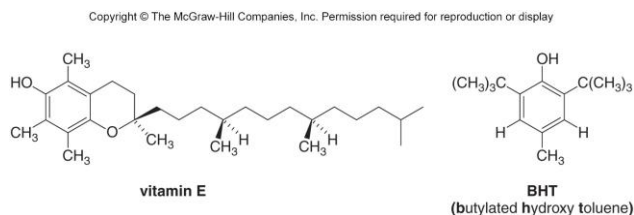
Figure 15.8



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Antioxidants

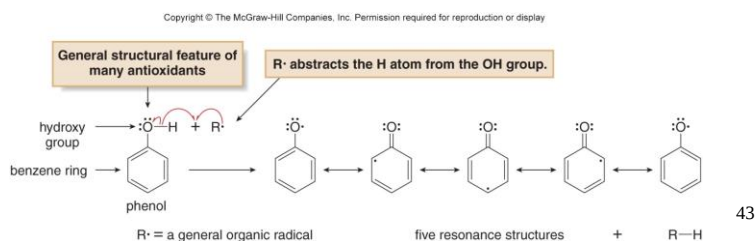
- An **antioxidant** is a compound that stops an oxidation reaction from occurring.
- Naturally occurring antioxidants such as vitamin E prevent radical reactions that can cause cell damage.
- Synthetic antioxidants such as **BHT—butylated hydroxy toluene**—are added to packaged and prepared foods to prevent oxidation and spoilage.
- Vitamin E and BHT are radical inhibitors, which terminate radical chain mechanisms by reacting with the radical.



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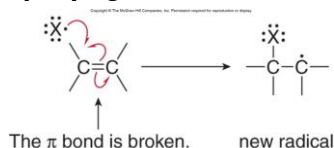
Mechanism of Antioxidant Behavior

- To trap free radicals, both vitamin E and BHT use a hydroxy group bonded to a benzene ring—a general structure called a **phenol**.
- Radicals ($R^\bullet$) abstract a hydrogen atom from the OH group of an antioxidant, forming a new resonance-stabilized radical.
- This new radical does not participate in chain propagation, but rather terminates the chain and halts the oxidation process.
- Because oxidative damage to lipids in cells is thought to play a role in the aging process, many antiaging formulations contain antioxidants.

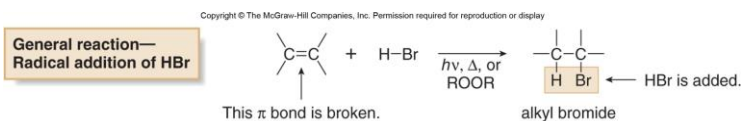


General Radical Additions to Alkenes

- Electron rich alkenes react with electron deficient radicals.
- Radicals react with alkenes via radical chain mechanisms consisting of:
 - Initiation, propagation and termination steps



- HBr adds to alkenes to form alkyl bromides in the presence of heat, light, or peroxides.

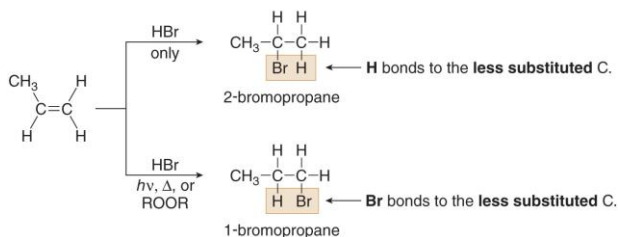


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Radical Additions to Alkenes

- The regioselectivity of the addition to unsymmetrical alkenes is different from that for addition of HBr in the absence of heat, light, or peroxides.

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- The addition of HBr to alkenes in the presence of heat, light, or peroxides proceeds via a radical mechanism.

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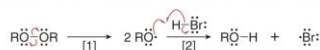
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Mechanism 15.3 Radical Addition of HBr to an Alkene

Initiation

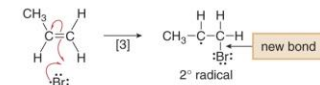
Steps [1] and [2] Abstraction of H from HBr occurs by a two-step process.



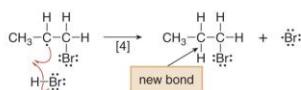
- With ROOR to initiate the reaction, two steps are needed to form $\text{Br}\cdot$. Homolysis of the weak O–O bond of the peroxide forms $\text{RO}\cdot$, which abstracts a hydrogen atom from HBr to form $\text{Br}\cdot$.

Propagation

Steps [3] and [4] The π bond is broken and the C–H and C–Br σ bonds are formed.



- The first step of propagation forms the C–Br bond when the $\text{Br}\cdot$ radical adds to the terminal carbon, leading to a 2° carbon radical.



- The 2° radical abstracts a H atom from HBr, forming the new C–H bond and completing the addition reaction. Because a new $\text{Br}\cdot$ radical is also formed in this step, Steps [3] and [4] occur repeatedly.

Repeat Steps [3], [4], [3], [4], and so forth.

Termination

Step [5] Two radicals react to form a bond.



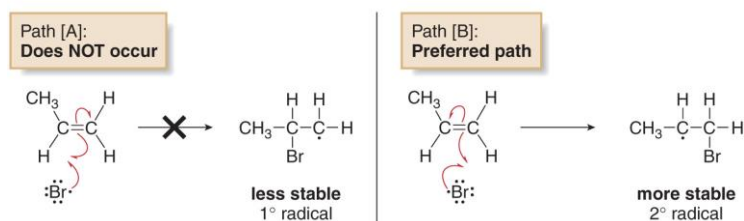
- To terminate the chain, two radicals (for example two $\text{Br}\cdot$ radicals) react with each other to form a stable bond, preventing further propagation via Steps [3] and [4].

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Regiochemistry of Radical Addition to Alkenes

- In the first propagation step, the addition of $\text{Br}\cdot$ to the double bond, there are two possible paths:
 - Path [A] forms the less stable 1° radical.
 - Path [B] forms the more stable 2° radical.
- The more stable 2° radical forms faster, so Path [B] is preferred.

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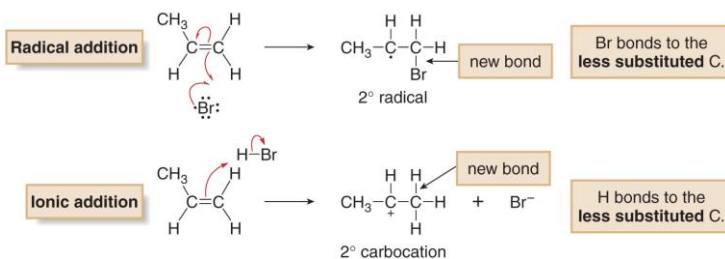


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Radical vs Ionic Addition of HBr

- Depending on the reaction conditions, a different species initially reacts with the π bond accounting for the difference in regioselectivity.
 - Radical addition involves initial attack by a bromine radical.
 - Ionic addition involves initial attack by a proton.

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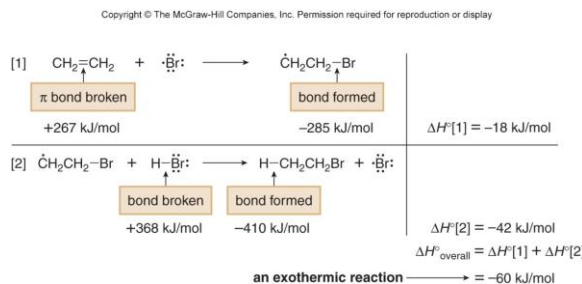


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Energy Changes of Radical HBr Addition

- HBr adds to alkenes under radical conditions, but HCl and HI do not, due to differences in bond dissociation energies.
- Both propagation steps for HBr addition are exothermic, so propagation is exothermic (energetically favorable) overall.
- For addition of HCl or HI, one of the chain propagating steps is quite endothermic, and thus too difficult to be part of a repeating chain mechanism.

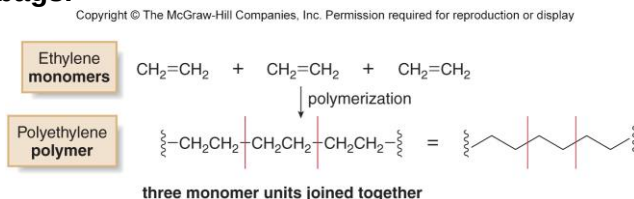
Figure 15.9



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Polymers and Polymerization

- **Polymers** are large molecules made up of repeating units of smaller molecules called **monomers**.
- They include biologically important compounds such as proteins and carbohydrates, as well as synthetic plastics such as polyethylene, polyvinyl chloride (PVC) and polystyrene.
- **Polymerization** is the process of joining together of monomers to make polymers.
- For example, joining ethylene monomers together forms the polymer polyethylene, a plastic used in milk containers and plastic bags.

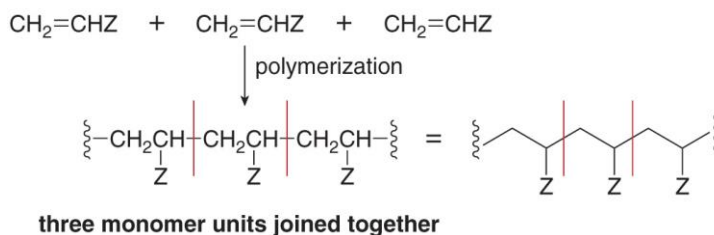


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Polymers from Ethylene Derivatives

- Many ethylene derivatives having the general structure $\text{CH}_2=\text{CHZ}$ are also used as monomers for polymerization.
- The identity of Z affects the physical properties of the resulting polymer.
- Polymerization of $\text{CH}_2=\text{CHZ}$ usually affords polymers with Z groups on every other carbon atom in the chain.

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Table 15.2 Common Monomers and Polymers Used in Medicine and Dentistry

Monomer	Polymer	Consumer product
$\text{CH}_2=\text{CHCl}$ vinyl chloride	$\sim\text{CH}_2\text{CH}(\text{Cl})\text{CH}_2\text{CH}(\text{Cl})\text{CH}_2\text{CH}(\text{Cl})\sim$ poly(vinyl chloride) PVC	 PVC blood bags and tubing
$\text{CH}_2=\text{CHCH}_3$ propene	$\sim\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\sim$ polypropylene	 polypropylene syringes
$\text{CF}_2=\text{CF}_2$ tetrafluoroethylene	$\sim\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\sim$ polytetrafluoroethylene Teflon	 dental floss

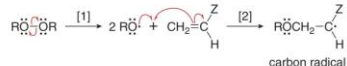
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Mechanism 15.4 Radical Polymerization of $\text{CH}_2=\text{CHZ}$

Initiation

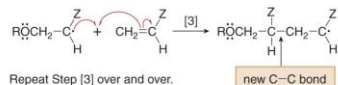
Steps [1] and [2] A carbon radical is formed by a two-step process.



- Chain initiation begins with homolysis of the weak O–O bond of the peroxide to form $\text{RO}\cdot$, which then adds to a molecule of monomer to form a carbon radical.

Propagation

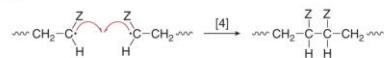
Step [3] The polymer chain grows.



- Chain propagation consists of a single step that joins monomer units together.
- In Step [3], the carbon radical formed during initiation adds to another alkene molecule to form a new C–C bond and another carbon radical. Addition always forms the more substituted carbon radical—that is, the **unpaired electron is always located on the carbon atom having the Z substituent**.
- This carbon radical reacts with more monomer, so that Step [3] occurs repeatedly, and the polymer chain grows.

Termination

Step [4] Two radicals combine to form a bond.



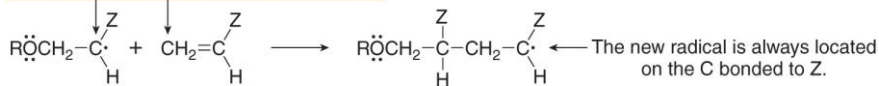
- To terminate the chain, two radicals combine to form a stable bond, thus ending the polymerization process.

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Radical Polymerization

- In radical polymerization, the more substituted radical always adds to the less substituted end of the monomer, a process called **head-to-tail polymerization**.

The **more substituted radical** adds to the **less substituted end** of the double bond.



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