

Organic Chemistry, *Fourth Edition*

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Chapter 15 Lecture Outline

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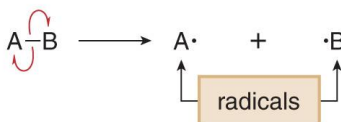
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Radicals

- 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

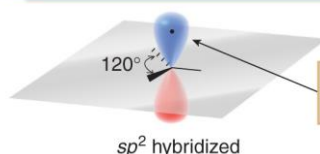
- Carbon radicals are classified as 1°, 2°, or 3°.
- A carbon radical is sp^2 hybridized and trigonal planar, like carbocations.
- The unhybridized p orbital contains the unpaired electron and extends above and below the trigonal planar carbon.

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Classification of carbon radicals



The trigonal planar geometry of a carbon radical



The p orbital contains a single electron.

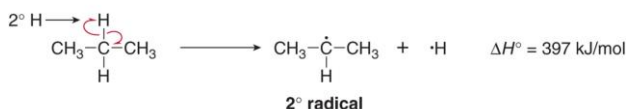
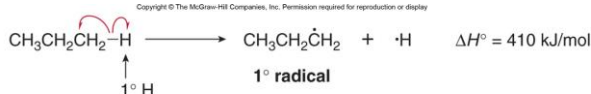
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Bond Dissociation Energies

- 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.

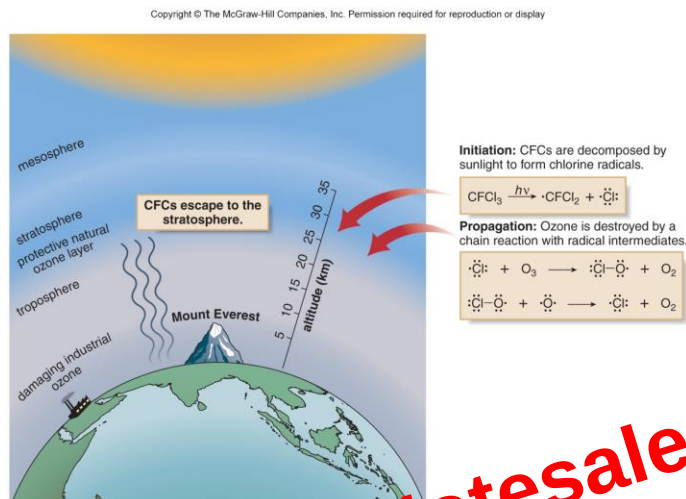
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CFCs and the Destruction of the Ozone Layer

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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This HFC is decomposed before it reaches the stratosphere.

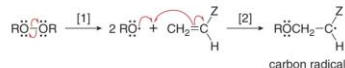
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Mechanism 15.4 Radical Polymerization of $\text{CH}_2=\text{CHZ}$

Initiation

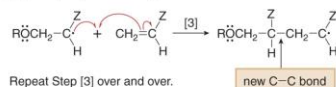
Steps [1] and [2] A carbon radical is formed by a two-step process.



- 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

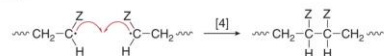
Step [3] The polymer chain grows.



- 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.

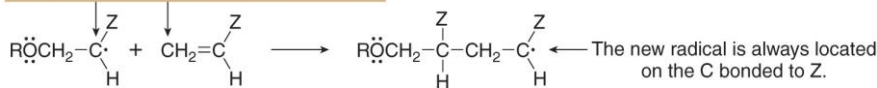
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Radical Polymerization

- 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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