Organic Chemistry

Radical Reactions

by
Dr. Seema Zareen & Dr. Izan Izwan Misnon
Faculty Industrial Science & Technology
seema@ump.edu.my & iezwan@ump.edu.my

Expected Outcomes

In the end of this chapter, student will have the ability to:

- Define and classify radical
- Describe mechanism of radical reactions (alkane halogenation, allylic halogenation, radical addition HBr to alkene, radical polymerization of alkenes)

Contents

- Radical reactions
- Halogenation of alkanes
- Polymers and polymerization

Changes in Bonding During a Chemical Rxn

(Homolysis and Heterolysis)

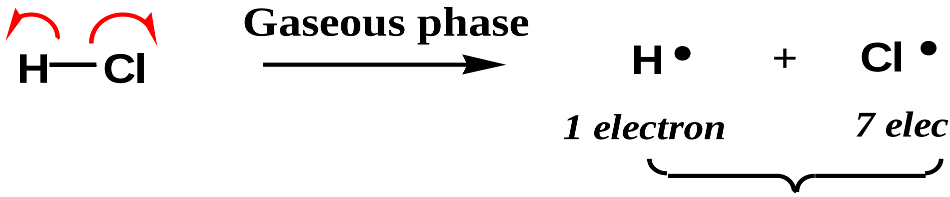
Two possible ways a bond can break:

Homolysis: an equal division of a bonding electron pair

Heterolysis: an unequal division of a bonding electron pair

Homolytic Fission

Less Energy Demand


$H-Cl \xrightarrow{\text{Gaseous phase}} H^{\bullet} + Cl^{\bullet}$

1 electron

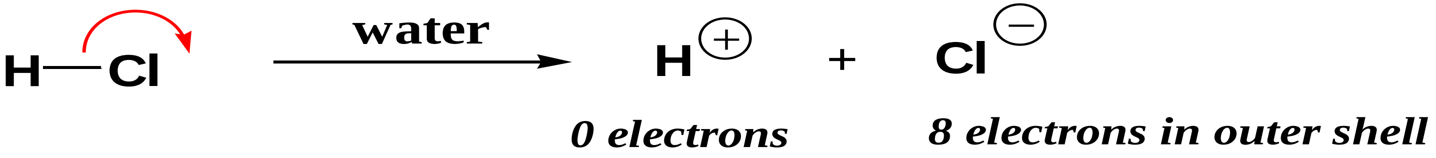
7 electrons in outer shell

Monoatomic - Radicals

When bonds break and the atoms get one electron each

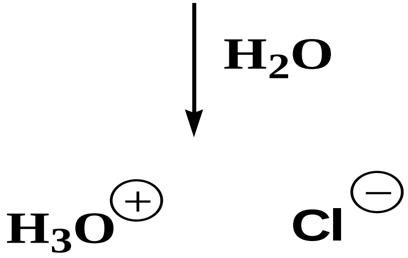
Heterolytic Fission

ONLY POSSIBLE IN SOLUTION


$H-Cl \xrightarrow{\text{water}} H^{\oplus} + Cl^{\ominus}$

0 electrons

8 electrons in outer shell


$\xrightarrow{H_2O}$

$H_3O^{\oplus}$ $Cl^{\ominus}$

When bonds break and one atom gets both bonding electrons- Pairs of Ions – Driven by the Energy of solvation

Homolysis

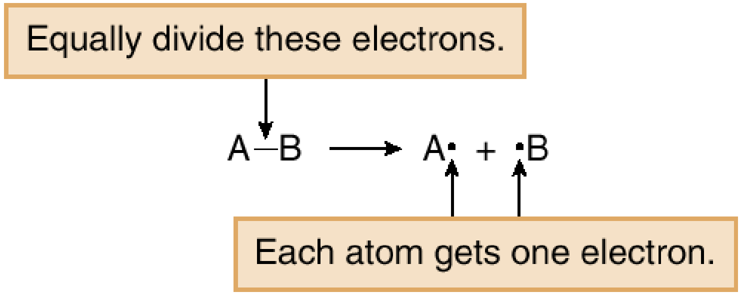
Two **half-headed** curved arrows are needed for two **single** electrons.

Heterolysis

One **full-headed** curved arrow is needed for one electron **pair**.

- Breaking a bond by **equally dividing the electrons** between the two atoms in the bond is called **homolysis** or **homolytic cleavage.**

Homolysis *or* homolytic cleavage

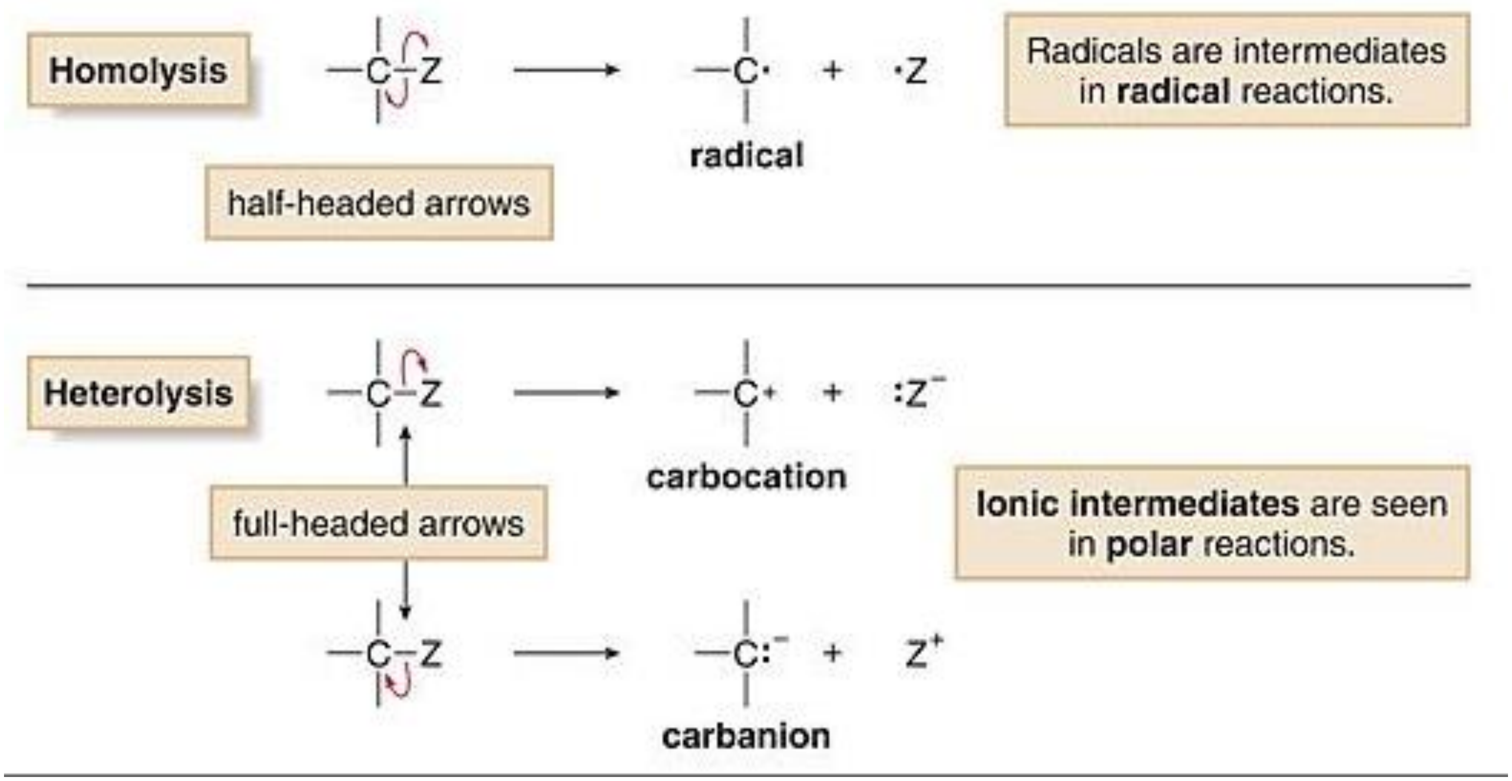


Equally divide these electrons.

Each atom gets one electron.

Bond Breaking forms particles called reaction intermediates.

Three reactive intermediates resulting from Homolysis and heterolysis of a C – Z bond



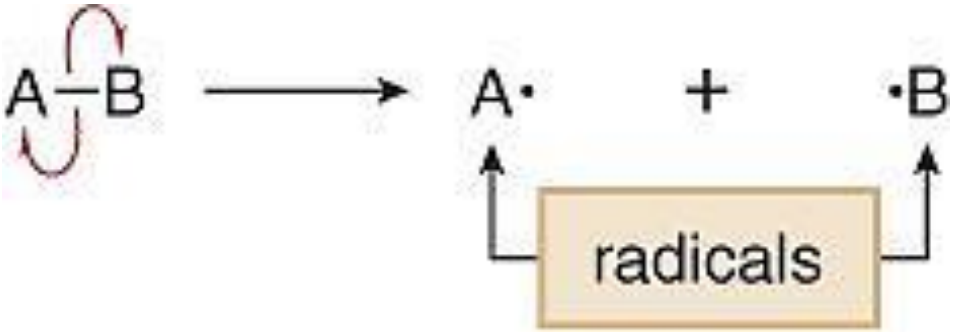
Radicals are intermediates in **radical** reactions.

Ionic intermediates are seen in **polar** reactions.

Radical Reactions

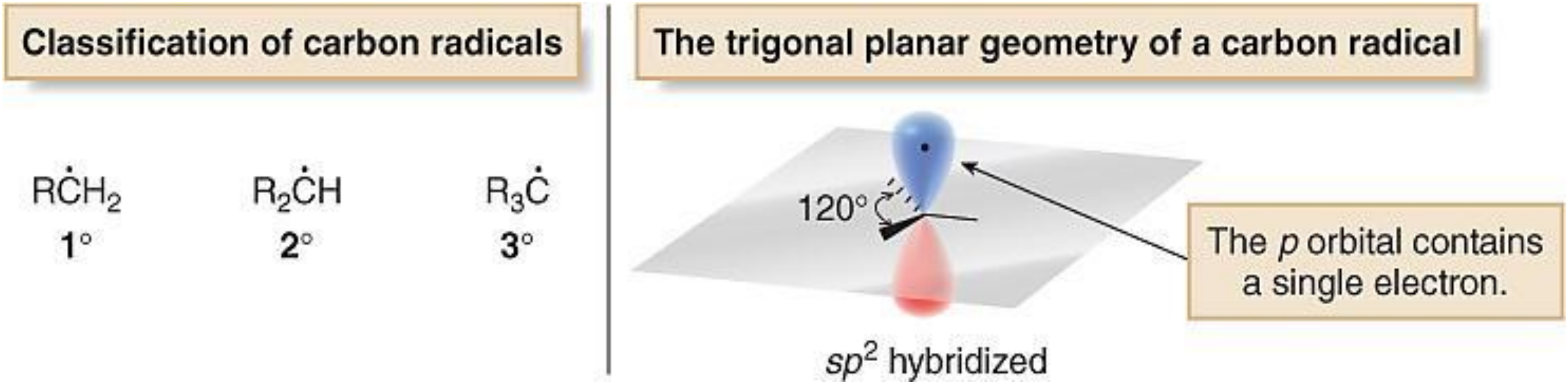
Introduction

- A 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.



Classification and Structure of Radicals

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



Classification of carbon radicals

$R\dot{C}H_2$ 1°

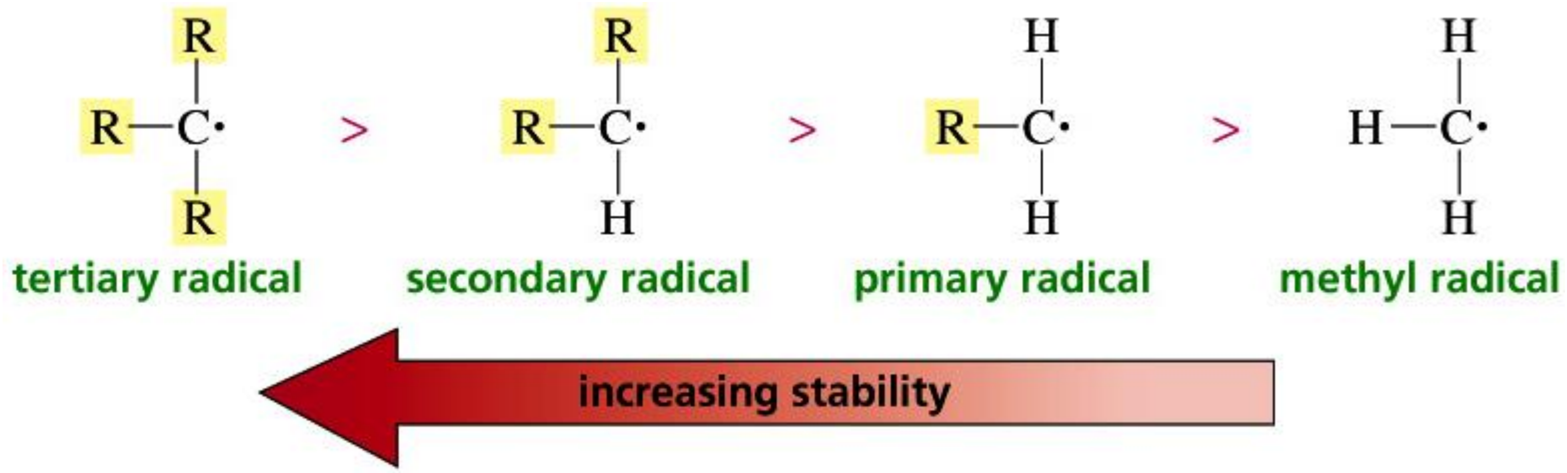
$R_2\dot{C}H$ 2°

$R_3\dot{C}$ 3°

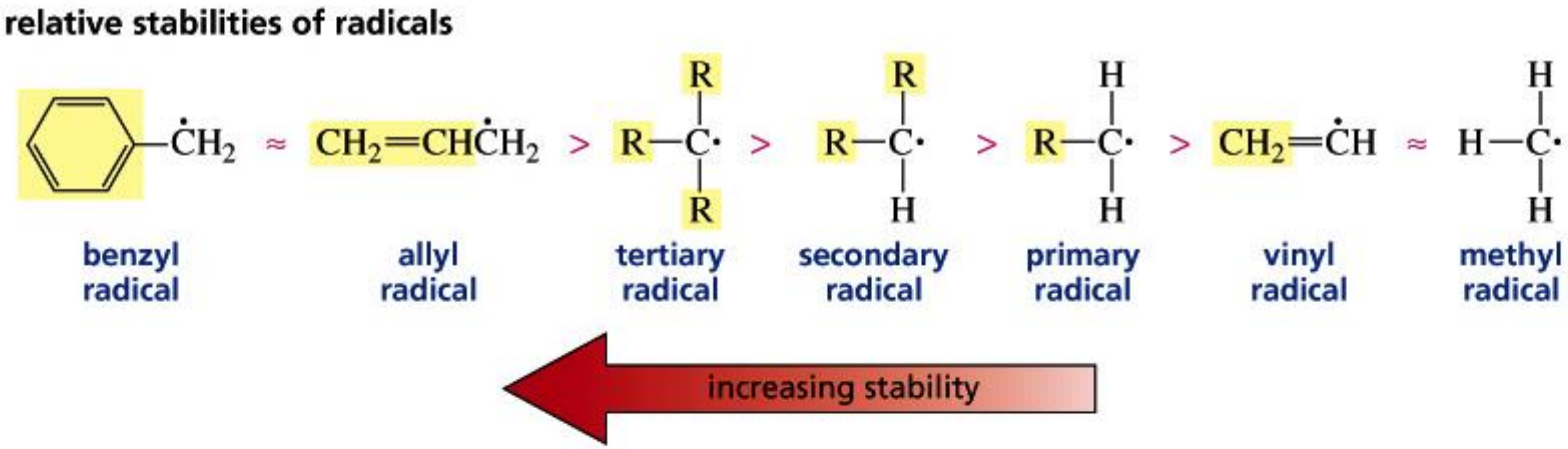
The trigonal planar geometry of a carbon radical

Radicals

Stability of alkyl radicals is similar to stability of carbocations



Crude Radical Stability Index



Formation of Radicals

Carbon radicals are formed by homolytic cleavage of covalent bonds using either:

(1) Light (hυ)

(2) Heat (Δ)

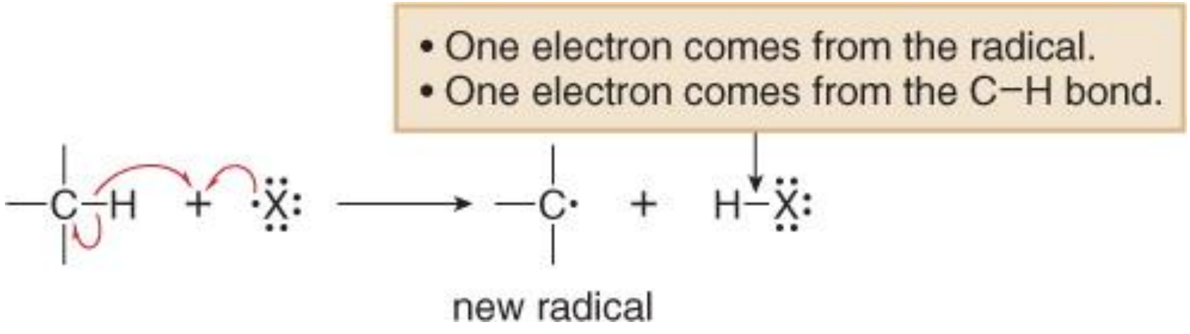
(3) Radical Initiators (*ROOR i.e. peroxides*)

General Features of Radical Reactions

- Radicals are **formed from covalent bonds** by adding **energy** in the form of heat (Δ) or light (**hν**).
- Some radical reactions are carried out in the presence of a **radical initiator**.
- Radical initiators contain an especially **weak bond** that serves as a source of radicals.
- **Peroxides**, compounds having the general structure **RO—OR**, are the most commonly used radical initiators.
- **Heating** a peroxide readily causes homolysis of the weak O—O bond, forming **two RO•** radicals.
- Radicals undergo **two main types of reactions**—they react with σ bonds, and they add to π bonds.

Reaction of a Radical X• with a C-H (σ) Bond:

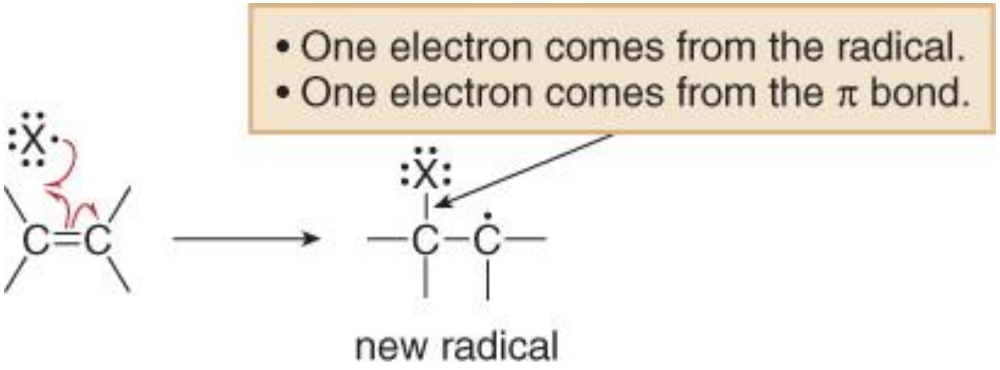
- A radical X• **abstracts a hydrogen atom** from a C—H **σ bond** to from H—X and a carbon radical.



- One electron comes from the radical.
- One electron comes from the C–H bond.

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

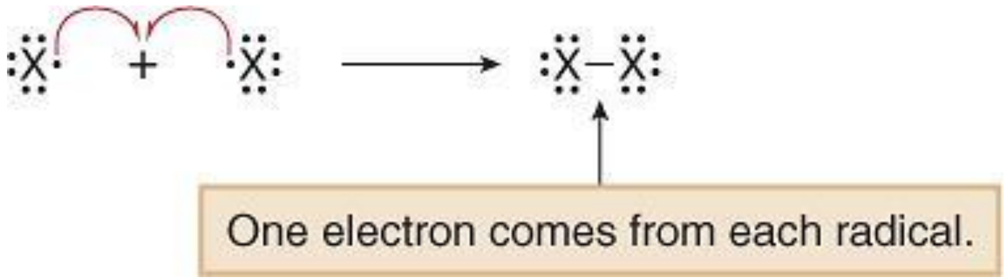
- A radical X• also **adds** to the **π bond** of a carbon—carbon double bond.



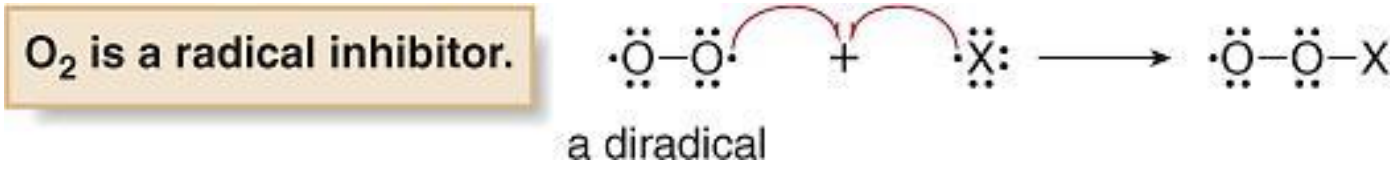
- One electron comes from the radical.
- One electron comes from the π bond.

Two Radicals Reacting with Each Other:

- A radical X•, once formed, rapidly reacts with whatever is available, usually a stable σ or π bond.
- Occasionally, two radicals react to form a sigma bond.


One electron comes from each radical.

- The reaction of a radical with oxygen (a diradical in its ground state electronic configuration) is another example of two radicals reacting with each other.


O_2 is a radical inhibitor.

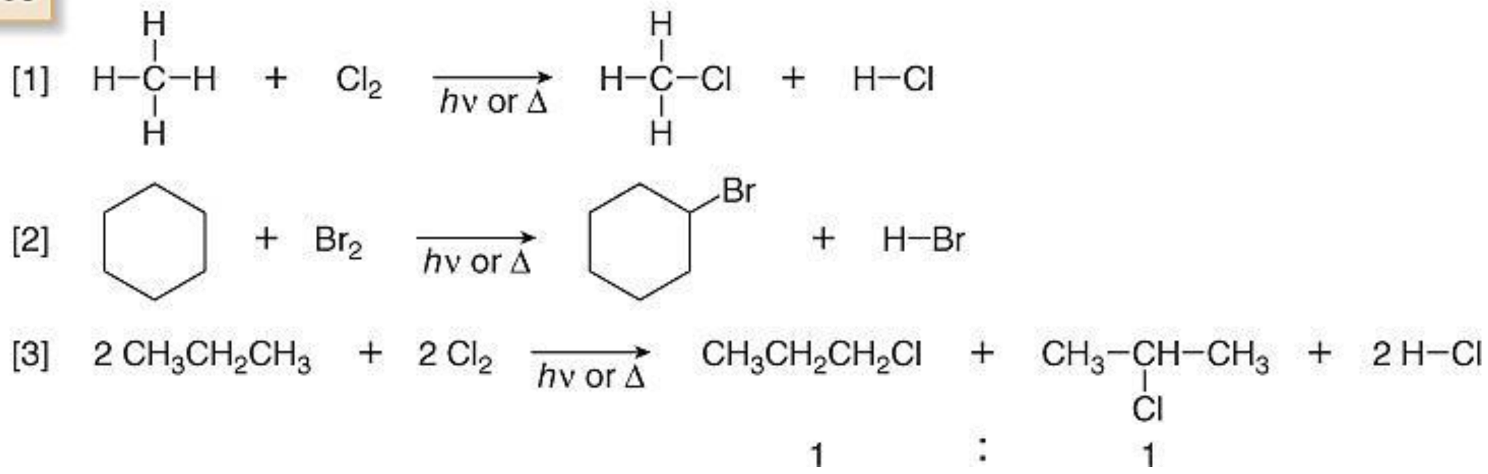
a diradical

- Compounds that prevent radical reactions from occurring are called radical inhibitors or radical scavengers. Besides O_2, vitamin E and other related compounds are radical scavengers.

Halogenation of Alkanes

- In the presence of heat or light, alkanes react with halogens to form alkyl halides.
- Halogenation of alkanes is a radical substitution reaction.
- Halogenation of alkanes is only useful with chlorine (Cl_2) or bromine (Br_2). Reaction with fluorine (F_2) is too violent, and reaction with iodine (I_2) is too slow to be useful.
- With an alkane that has more than one type of hydrogen atom, a mixture of alkyl halides may result.

Examples



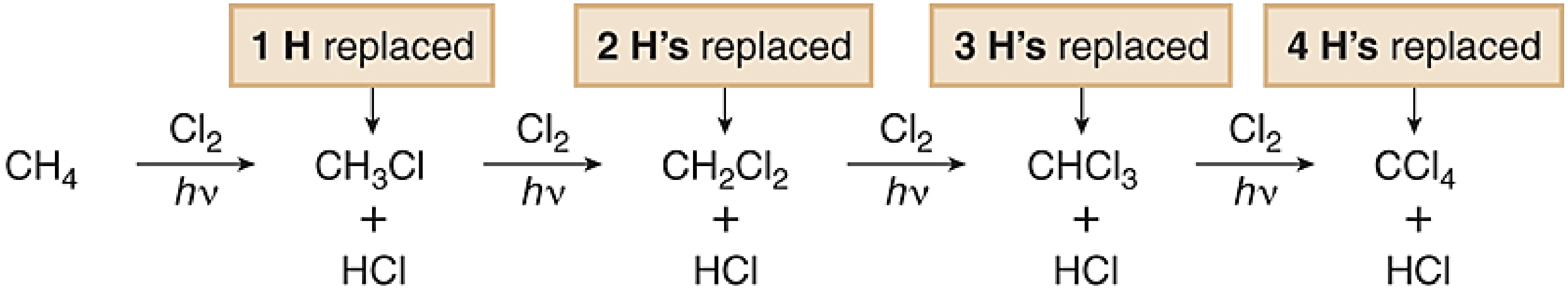
$$2\,CH_3CH_2CH_3 + 2\,Cl_2 \xrightarrow[h\nu \text{ or } \Delta]{} \underset{1}{CH_3CH_2CH_2Cl} + \underset{1}{CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3} + 2\,H-Cl$$

1 : 1

Halogenation of Alkanes

- When a single hydrogen atom on a carbon has been replaced by a halogen atom, monohalogenation has taken place.
- 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.
- When asked to draw the products of halogenation of an alkane, draw the products of monohalogenation only, unless specifically directed to do otherwise.

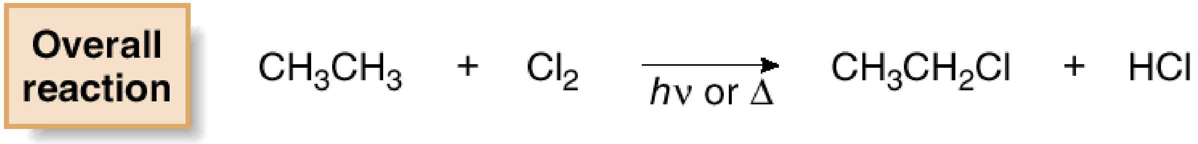
Complete halogenation of CH_4 using excess Cl_2



$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl + HCl \xrightarrow[h\nu]{Cl_2} CH_2Cl_2 + HCl \xrightarrow[h\nu]{Cl_2} CHCl_3 + HCl \xrightarrow[h\nu]{Cl_2} CCl_4 + HCl$$

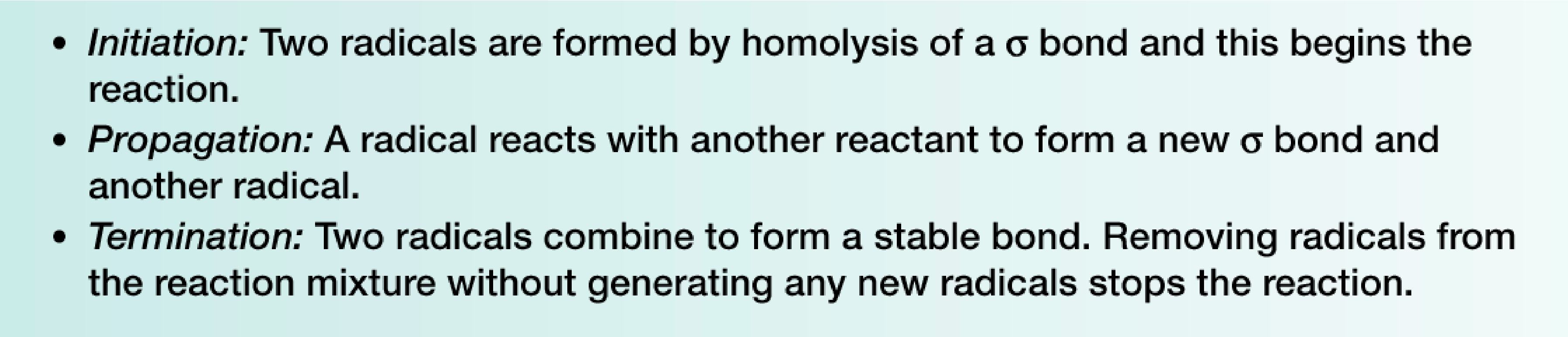
Halogenation of Alkanes—Reaction Mechanism

- Radical halogenation has **three** distinct parts.



Overall reaction

$$CH_3CH_3 + Cl_2 \xrightarrow[h\nu \text{ or } \Delta]{} CH_3CH_2Cl + HCl$$

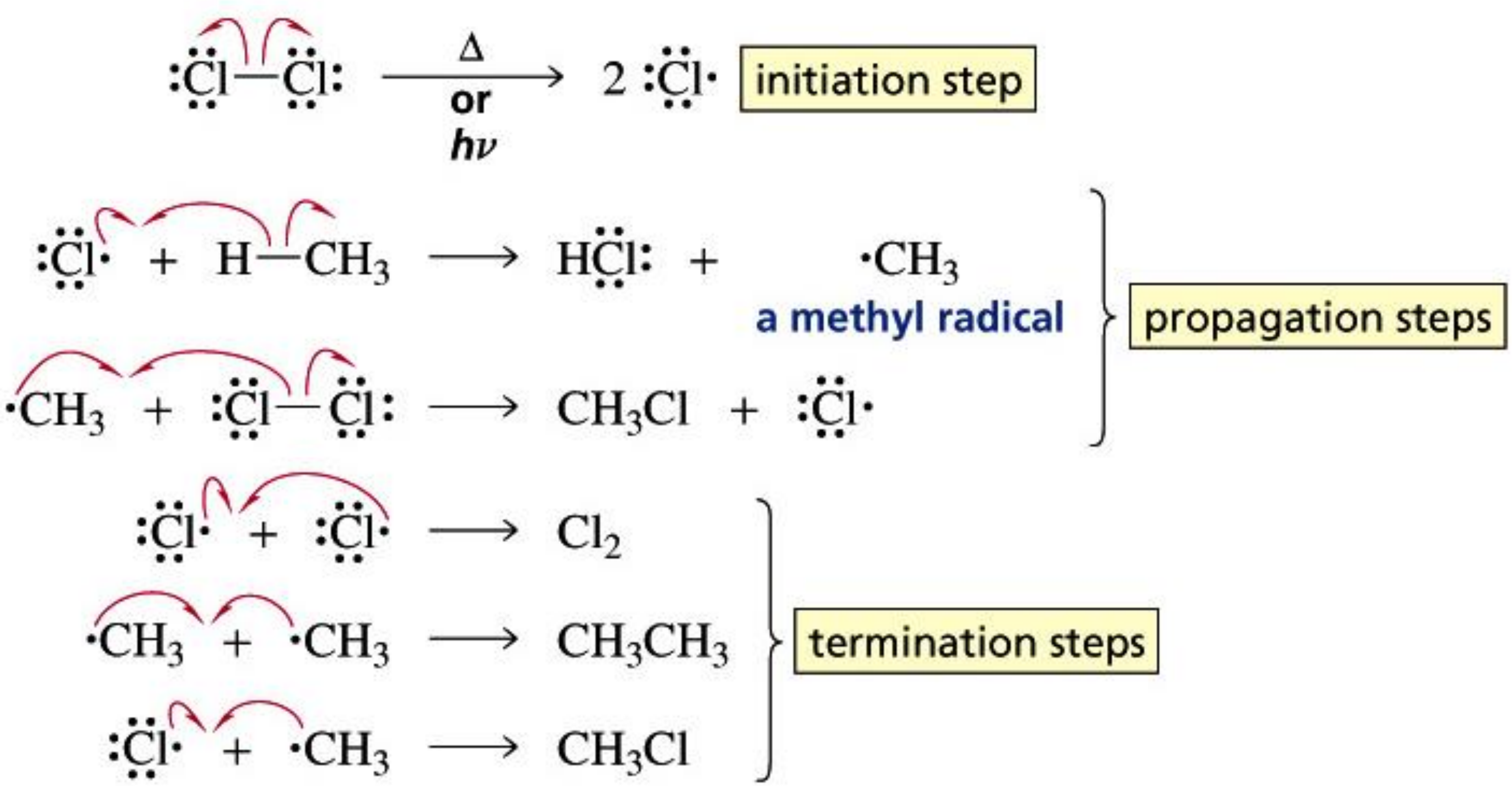


- *Initiation:* Two radicals are formed by homolysis of a σ bond and this begins the reaction.
- *Propagation:* A radical reacts with another reactant to form a new σ bond and another radical.
- *Termination:* Two radicals combine to form a stable bond. Removing radicals from the reaction mixture without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

- A mechanism (such as that observed in radical halogenation) that involves two or more repeating steps is called a **chain mechanism**.
- The most important steps of radical halogenation are those that lead to product formation—the **propagation steps**.

Chlorination and Bromination of Alkanes

mechanism for the monochlorination of methane



$$Cl{-}Cl \xrightarrow[\text{or } h\nu]{\Delta} 2\,Cl\cdot$$ initiation step

$$Cl\cdot + H{-}CH_3 \longrightarrow HCl + \cdot CH_3$$ a methyl radical

$$\cdot CH_3 + Cl{-}Cl \longrightarrow CH_3Cl + Cl\cdot$$

propagation steps

$$Cl\cdot + Cl\cdot \longrightarrow Cl_2$$

$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3$$

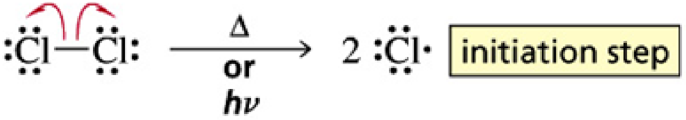
$$Cl\cdot + \cdot CH_3 \longrightarrow CH_3Cl$$

termination steps

Step [1]:

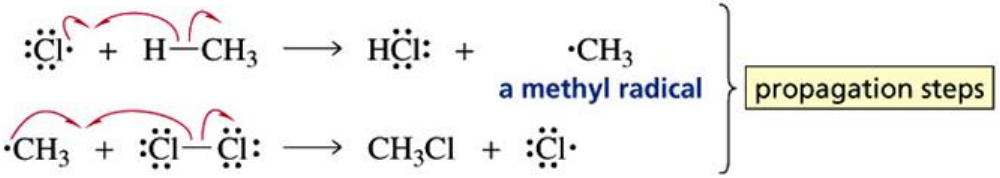
Radical Initiation:

When two radicals are formed by homolysis of an sigma bond, starting the reaction.



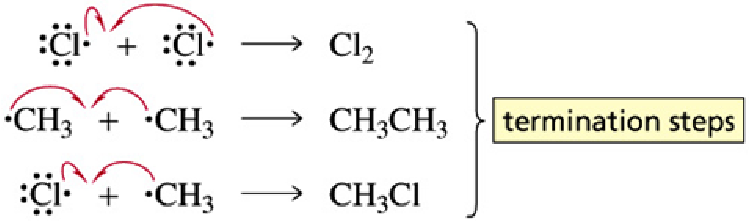
Step [2]:

Radical Propagation: A radical reacts with a reactant, forming a new sigma bond and a radical. (A radical makes a radical in propagation sub-steps).



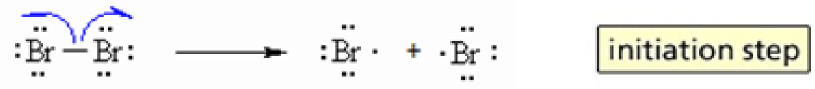
Step [3]:

Radical Termination: Two radicals combine to form a stable bond.



Step 1 (Initiation)

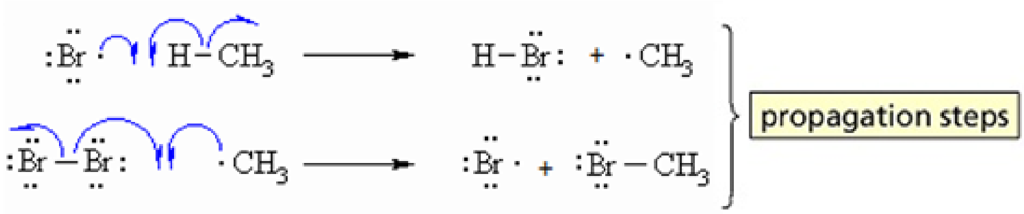
Heat or UV light cause the weak halogen bond to undergo homolytic cleavage to generate two bromine radicals and starting the chain process.



Step 2 (Propagation)

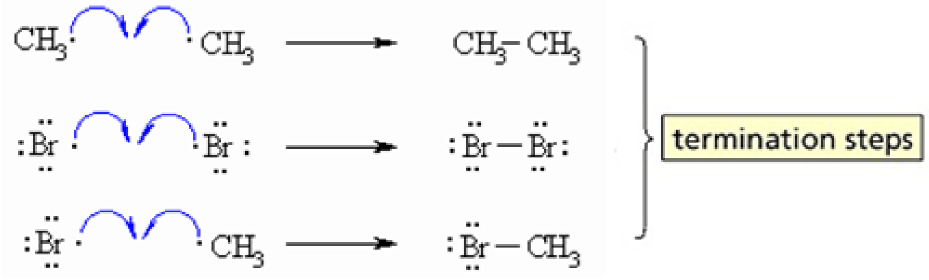
(a) A bromine radical abstracts a hydrogen to form HBr and a methyl radical, then

(b) The methyl radical abstracts a bromine atom from another molecule of Br_2 to form the methyl bromide product and ***another*** bromine radical, which can then itself undergo reaction 2(a) creating a cycle that can repeat.

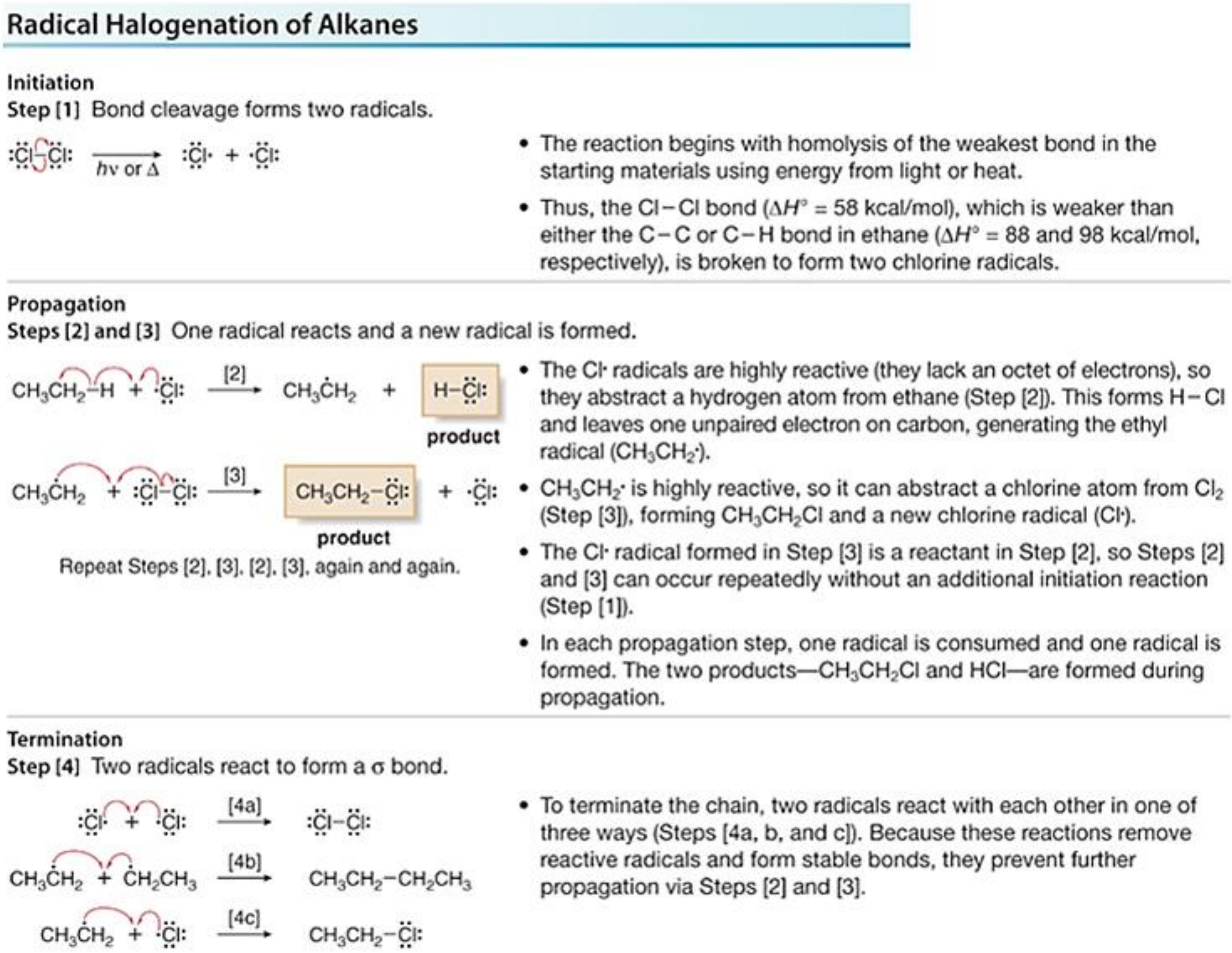


Step 3 (Termination)

Various reactions between the possible pairs of radicals allow for the formation of ethane, Br_2 or the product, methyl bromide. These reactions remove radicals and do not perpetuate the cycle.



Radical Reactions—Mechanism



Radical Halogenation of Alkanes

Initiation

Step [1] Bond cleavage forms two radicals.

$$:\ddot{Cl}-\ddot{Cl}: \xrightarrow[h\nu \text{ or } \Delta]{} :\ddot{Cl}\cdot + \cdot\ddot{Cl}:$$

- The reaction begins with homolysis of the weakest bond in the starting materials using energy from light or heat.
- Thus, the Cl–Cl bond ($\Delta H^\circ = 58$ kcal/mol), which is weaker than either the C–C or C–H bond in ethane ($\Delta H^\circ = 88$ and 98 kcal/mol, respectively), is broken to form two chlorine radicals.

Propagation

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

$$CH_3CH_2-H + \cdot\ddot{Cl}: \xrightarrow{[2]} CH_3\dot{C}H_2 + \boxed{H-\ddot{Cl}:}$$

product

$$CH_3\dot{C}H_2 + :\ddot{Cl}-\ddot{Cl}: \xrightarrow{[3]} \boxed{CH_3CH_2-\ddot{Cl}:} + \cdot\ddot{Cl}:$$

product

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

- The Cl· radicals are highly reactive (they lack an octet of electrons), so they abstract a hydrogen atom from ethane (Step [2]). This forms H–Cl and leaves one unpaired electron on carbon, generating the ethyl radical ($CH_3CH_2\cdot$).
- $CH_3CH_2\cdot$ is highly reactive, so it can abstract a chlorine atom from Cl_2 (Step [3]), forming CH_3CH_2Cl and a new chlorine radical (Cl·).
- 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—CH_3CH_2Cl and HCl—are formed during propagation.

Termination

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

$$:\ddot{Cl}\cdot + \cdot\ddot{Cl}: \xrightarrow{[4a]} :\ddot{Cl}-\ddot{Cl}:$$

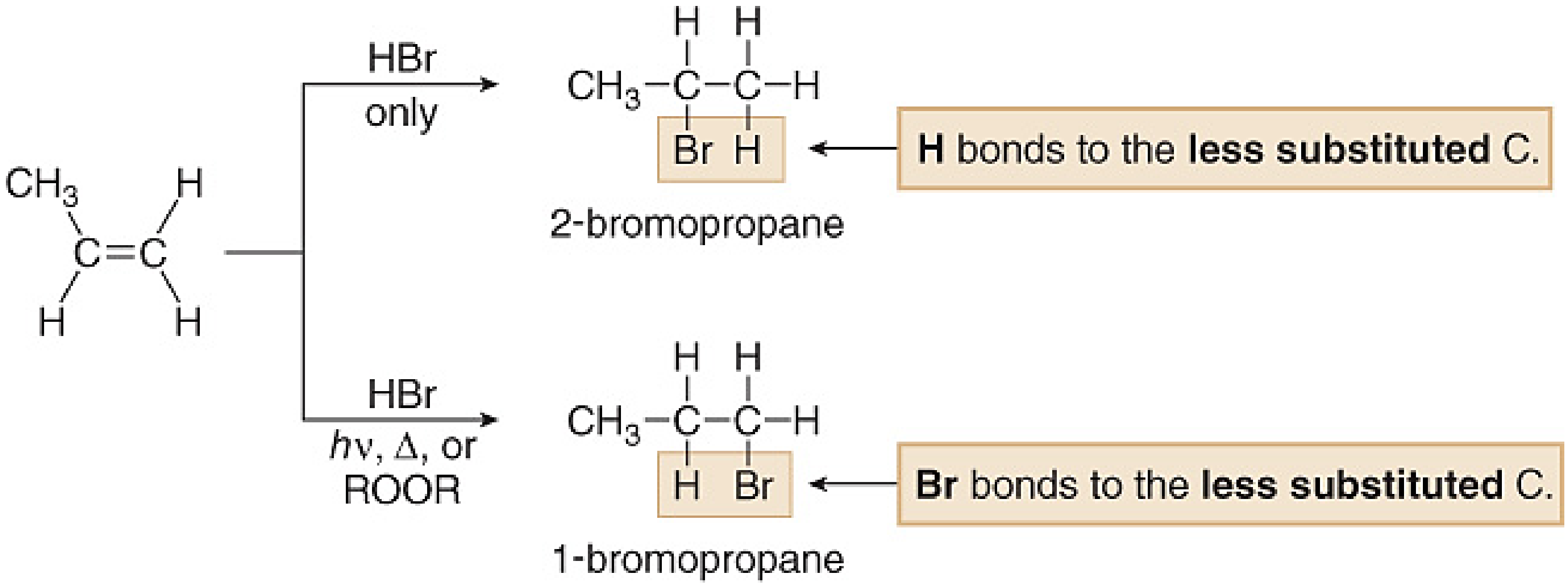
$$CH_3\dot{C}H_2 + \dot{C}H_2CH_3 \xrightarrow{[4b]} CH_3CH_2-CH_2CH_3$$

$$CH_3\dot{C}H_2 + \cdot\ddot{Cl}: \xrightarrow{[4c]} CH_3CH_2-\ddot{Cl}:$$

- To terminate the chain, two radicals react with each other in one of three ways (Steps [4a, b, and c]). Because these reactions remove reactive radicals and form stable bonds, they prevent further propagation via Steps [2] and [3].

Radical Additions to Double Bonds

- **HBr adds to alkenes to form alkyl bromides (**1-bromopropane**) in the presence of heat, light, or peroxides.**
- **The addition of HBr to form** 2-bromopropane **in the absence of heat, light or peroxides.**



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

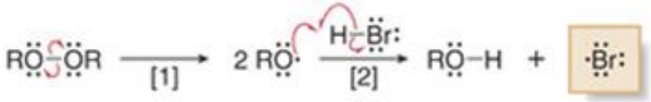
Radical Additions to Double Bonds

MECHANISM

Radical Addition of HBr to an Alkene

Initiation

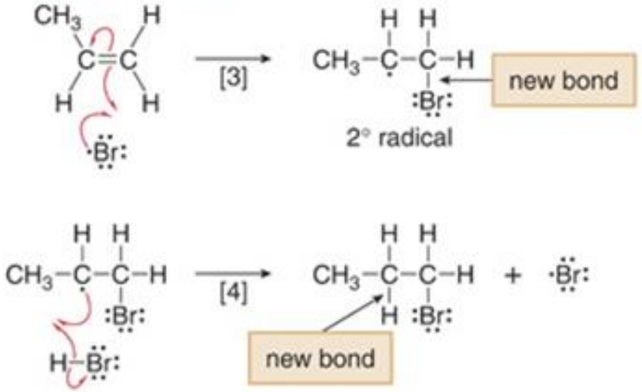
Steps [1] and [2] Abstraction of H from HBr occurs by a two-step process.



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

Propagation

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

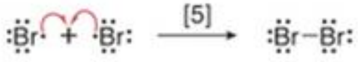


Repeat Steps [3], [4], [3], [4], and so forth.

- Chain propagation occurs in two steps, and in each step one radical is consumed and another is formed.
- The first step of propagation forms the C–Br bond when the Br· 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 Br· radical is also formed in this step, Steps [3] and [4] occur repeatedly.

Termination

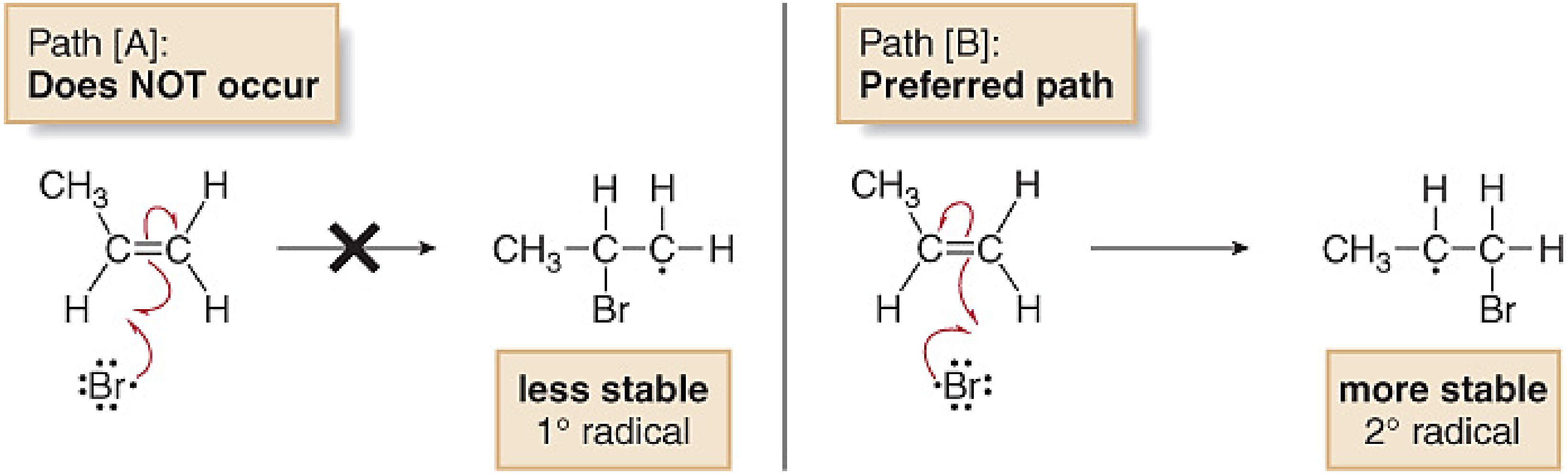
Step [5] Two radicals react to form a bond.



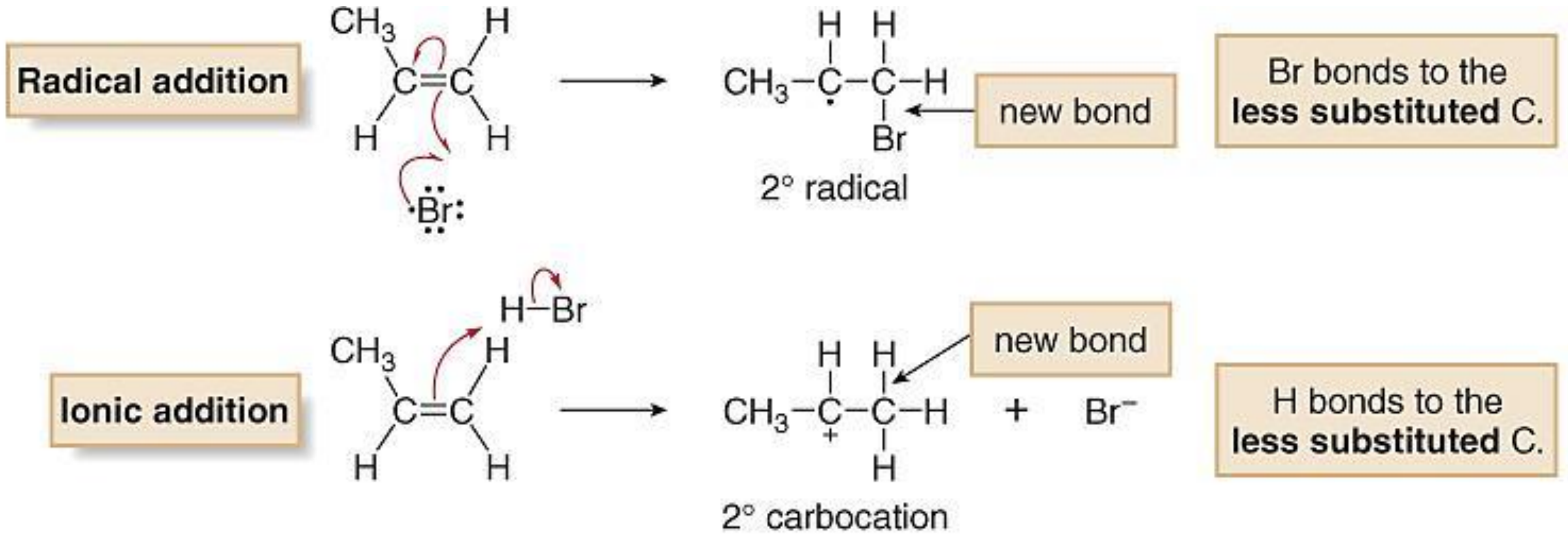
- To terminate the chain, two radicals (for example two Br· radicals) react with each other to form a stable bond, preventing further propagation via Steps [3] and [4].

Radical Additions to Double Bonds

- Note that in the first propagation step, the addition of Br• to the double bond, there are two possible paths:
  1. Path [A] forms the less stable 1^0 radical
  2. Path [B] forms the more stable 2^0 radical
- The more stable 2^0 radical forms faster, so Path [B] is preferred.



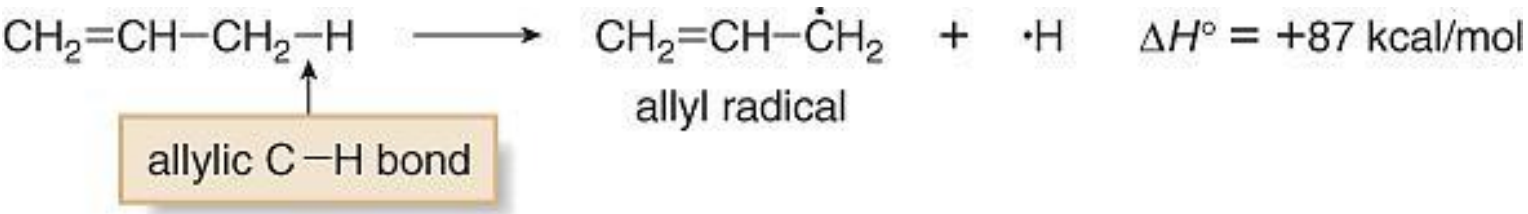
Radical Additions to Double Bonds



- In radical addition (HBr with added light, heat, or ROOR), *Br· adds first* to generate the more stable radical.
- In ionic addition (HBr alone), *H^+ adds first* to generate the more stable carbocation.

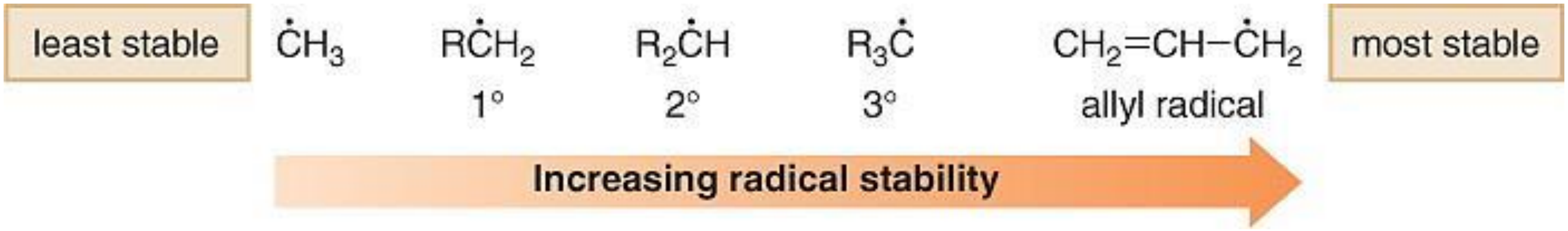
Radical Halogenation at an Allylic Carbon

- 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.



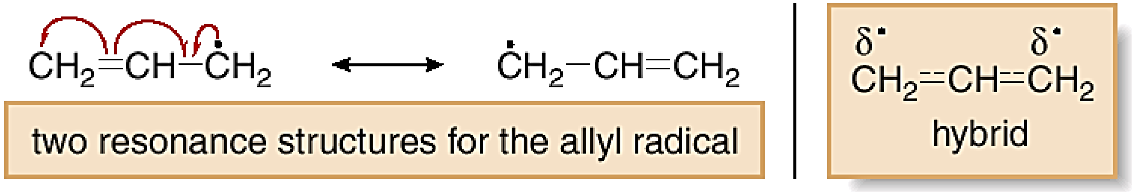
$$CH_2{=}CH{-}CH_2{-}H \longrightarrow CH_2{=}CH{-}\dot{C}H_2 + \cdot H \quad \Delta H^\circ = +87\ \text{kcal/mol}$$

- The bond dissociation energy for this process is even less than that for a 3^0 C—H bond (91 kcal/mol).
- This means that an allyl radical is more stable than a 3^0 radical.



Radical Halogenation at an Allylic Carbon

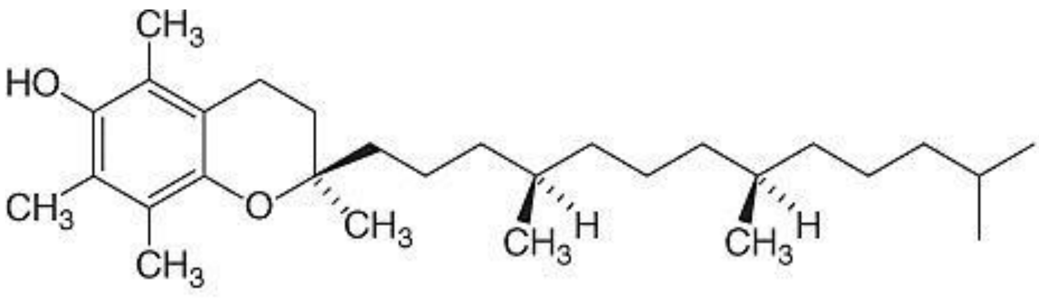
- The allyl radical is more stable than other radicals because two resonance forms can be drawn for it.



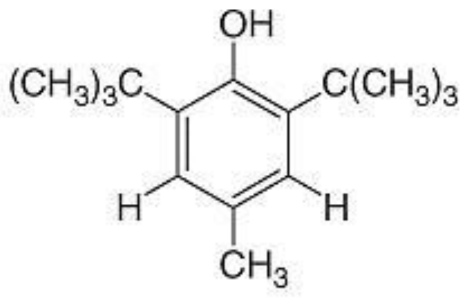
- The “true” structure of the allyl radical is a hybrid of the two resonance structures. In the hybrid, the π bond and the unpaired electron are delocalized.
- Delocalizing electron density lowers the energy of the hybrid, thus stabilizing the allyl radical.

Antioxidants

- An antioxidant is a compound that stops an oxidation 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, so they terminate radical chain mechanisms by reacting with the radical.



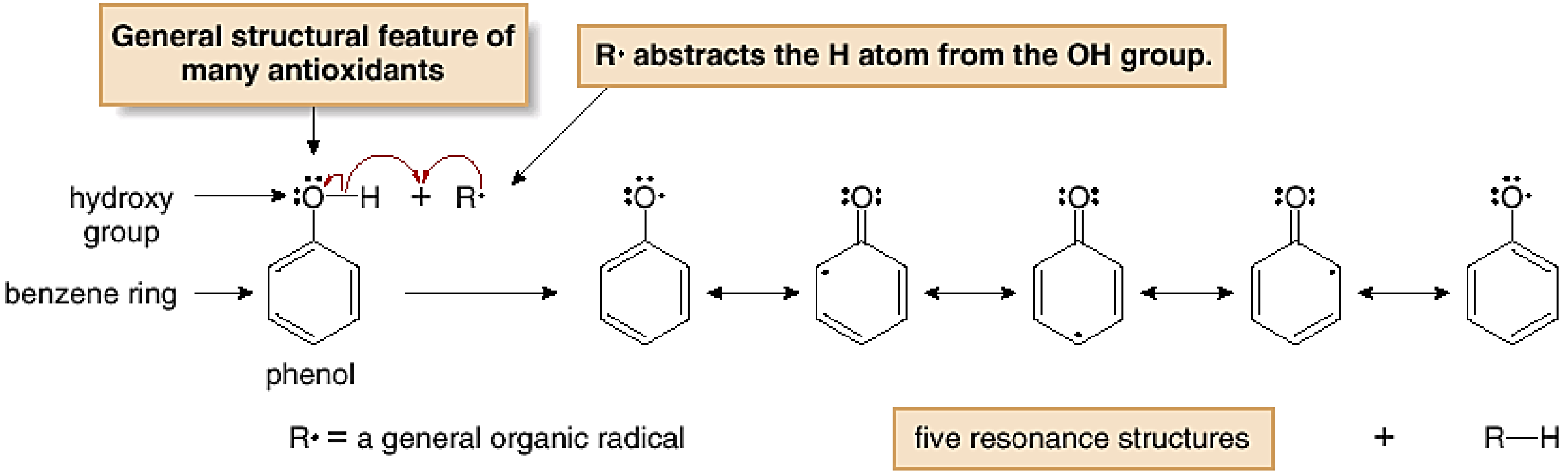
vitamin E



BHT
(butylated hydroxy toluene)

Antioxidants

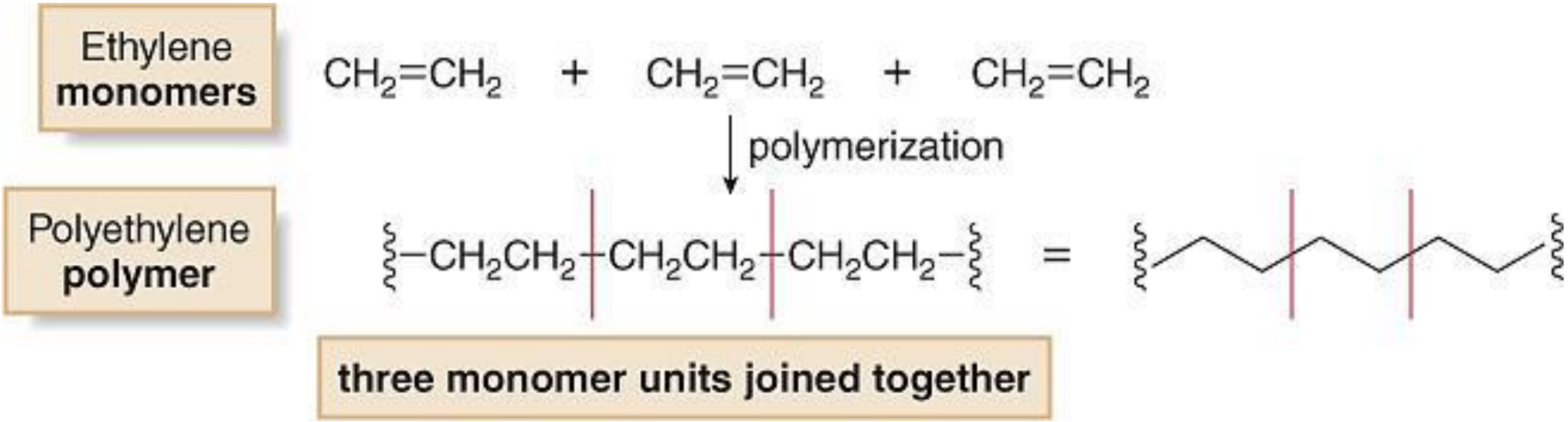
- To trap free radicals, both **vitamin** E and BHT use a hydroxy group bonded to a benzene ring—a general structure called a phenol.
- Radicals (R•) abstract a hydrogen atom from the OH group of an antioxidant, forming a new resonance-stabilized radical. This new radical does not participate in chain 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 (ageing) process, many anti-aging formulations contain antioxidants.



Polymers and Polymerization

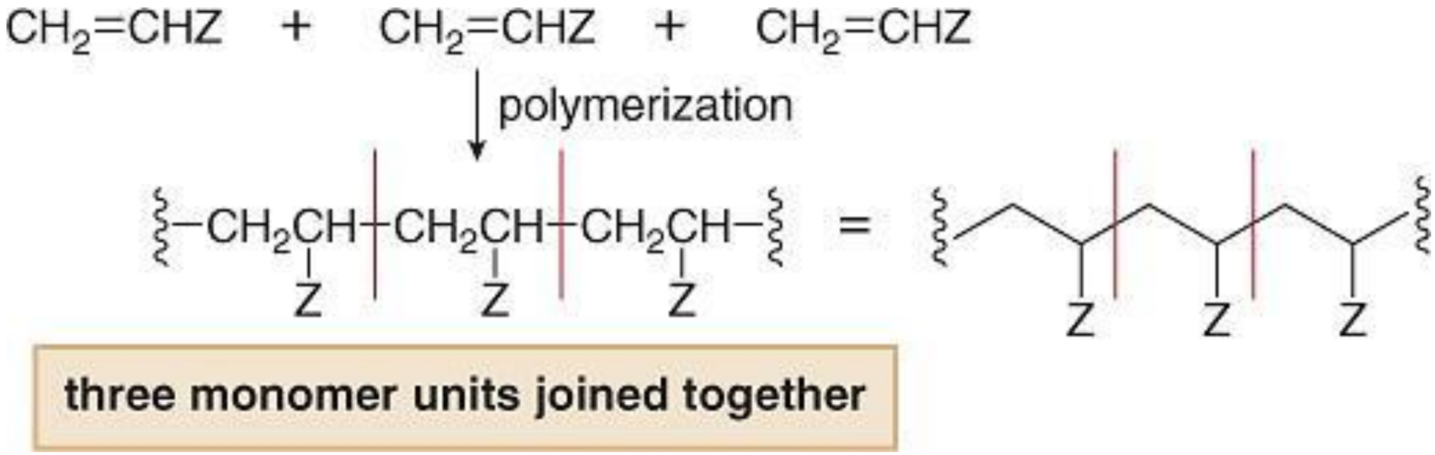
- **Polymers** are large molecules made up of repeating units of smaller molecules called **monomers.** They include biologically important compounds such as proteins and carbohydrates, as well as synthetic plastics such as polyethylene, polyvinyl chloride (PVC) and polystyrene.

- **Polymerization** is the 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.

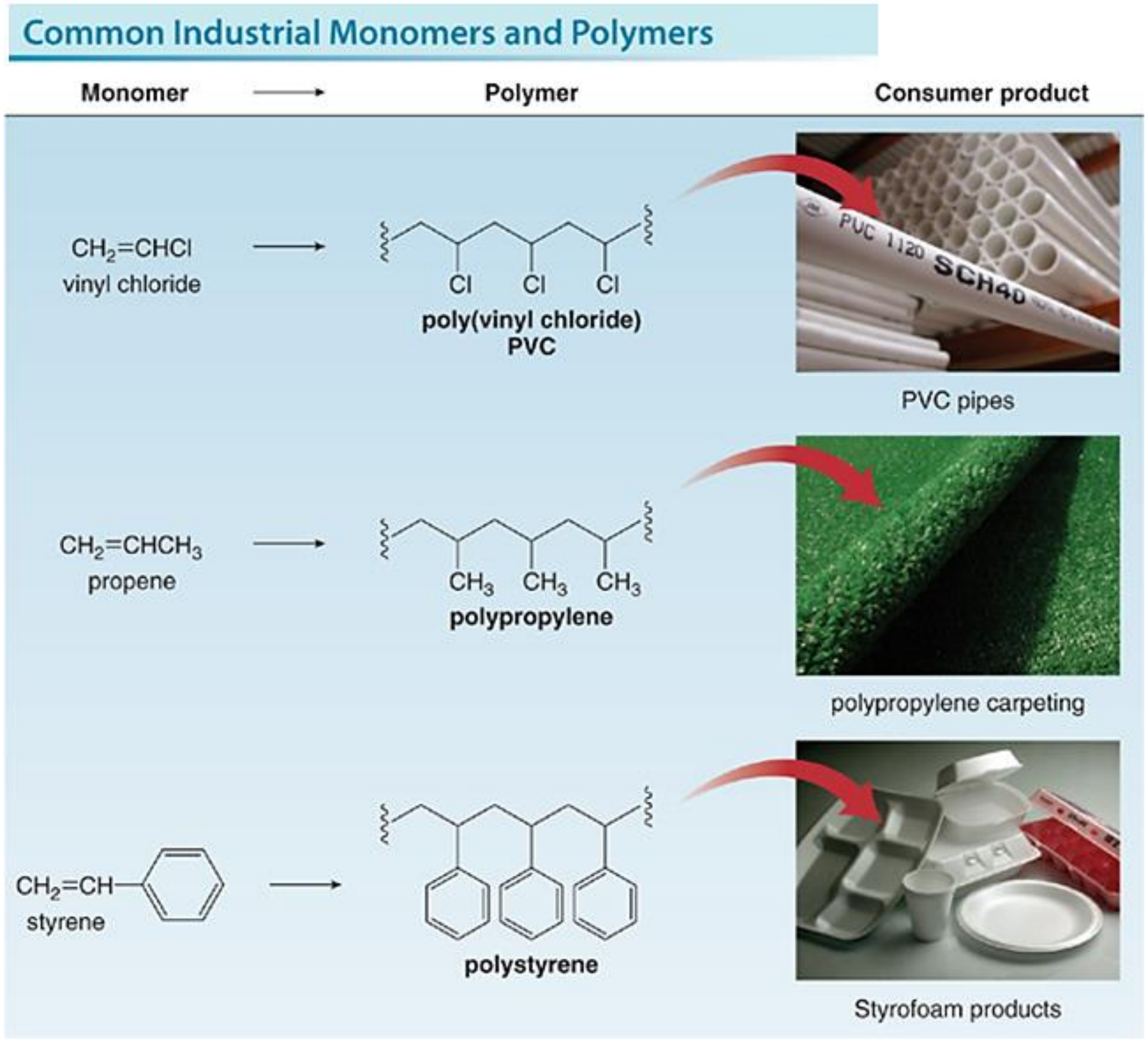


Polymers and Polymerization

- Many ethylene derivatives having the general structure $CH_2=CHZ$ are also used as monomers for polymerization.
- The identity of **Z** affects the physical properties of the resulting polymer (in radical polymerization **Z** contains a benzene ring, as in styrene, which stabilizes the radical by resonance).
- Polymerization of $CH_2=CHZ$ usually affords polymers with Z groups on every other carbon atom in the chain.



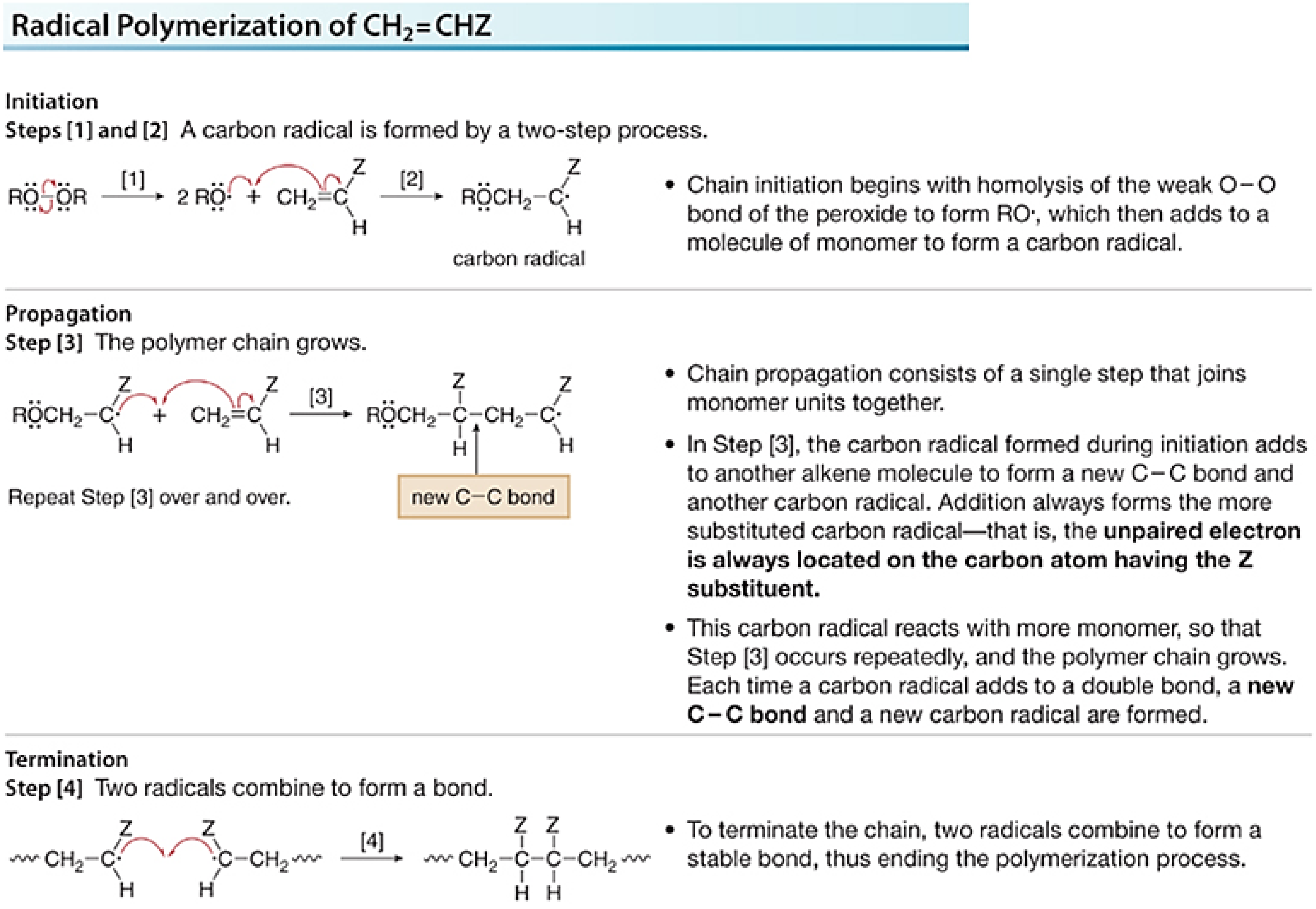
Polymers and Polymerization



Common Industrial Monomers and Polymers

Monomer	Polymer	Consumer product
$CH_2{=}CHCl$ vinyl chloride	**poly(vinyl chloride)** **PVC**	PVC pipes
$CH_2{=}CHCH_3$ propene	**polypropylene**	polypropylene carpeting
$CH_2{=}CH{-}C_6H_5$ styrene	**polystyrene**	Styrofoam products

Mechanism of Radical Polymerization



Radical Polymerization of $CH_2=CHZ$

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 RO·, which then adds to a molecule of monomer to form a carbon radical.

Propagation

Step [3] The polymer chain grows.

Repeat Step [3] over and over.

- 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. Each time a carbon radical adds to a double bond, a **new C–C bond** and a new carbon radical are formed.

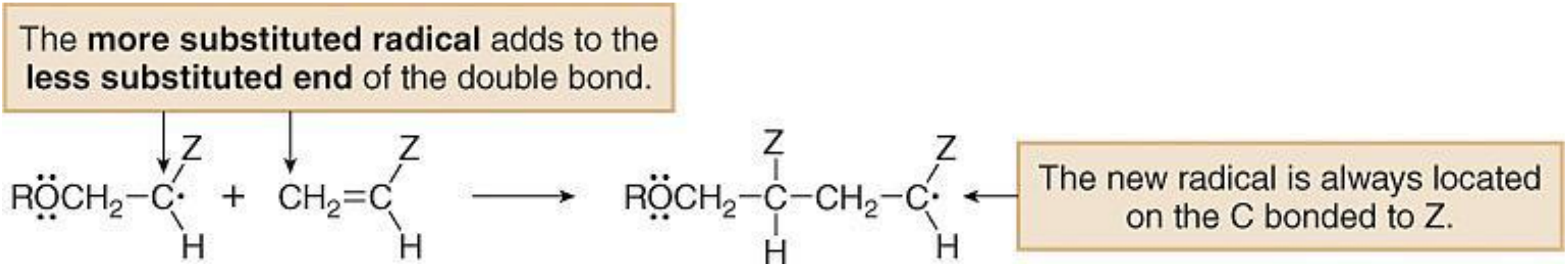
Termination

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.

Polymers and 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**.



$$R\ddot{\underset{\cdot\cdot}{O}}CH_2-\overset{Z}{\underset{H}{C}}\cdot + CH_2=\overset{Z}{\underset{H}{C}} \longrightarrow R\ddot{\underset{\cdot\cdot}{O}}CH_2-\overset{Z}{\underset{H}{C}}-CH_2-\overset{Z}{\underset{H}{C}}\cdot$$

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

The new radical is always located on the C bonded to Z.