

Chapter 10

Radical Reactions

Created by
Professor William Tam & Dr. Phillis Chang

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About The Authors

These Powerpoint Lecture Slides were created and prepared by Professor William Tam and his wife Dr. Phillis Chang.

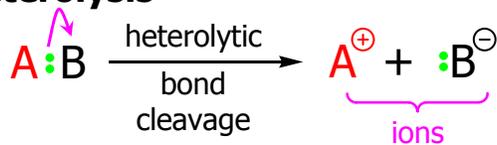
Professor William Tam received his B.Sc. at the University of Hong Kong in 1990 and his Ph.D. at the University of Toronto (Canada) in 1995. He was an NSERC postdoctoral fellow at the Imperial College (UK) and at Harvard University (USA). He joined the Department of Chemistry at the University of Guelph (Ontario, Canada) in 1998 and is currently a Full Professor and Associate Chair in the department. Professor Tam has received several awards in research and teaching, and according to *Essential Science Indicators*, he is currently ranked as the Top 1% most cited Chemists worldwide. He has published four books and over 80 scientific papers in top international journals such as *J. Am. Chem. Soc.*, *Angew. Chem.*, *Org. Lett.*, and *J. Org. Chem.*

Dr. Phillis Chang received her B.Sc. at New York University (USA) in 1994, her M.Sc. and Ph.D. in 1997 and 2001 at the University of Guelph (Canada). She lives in Guelph with her husband, William, and their son, Matthew.

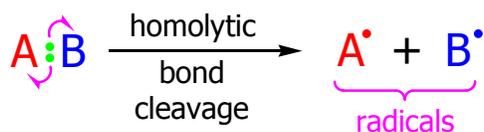
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1. Introduction: How Radicals Form and How They React

❖ Heterolysis



❖ Homolysis

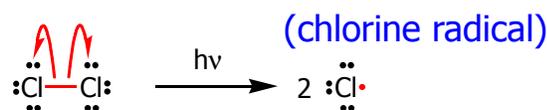
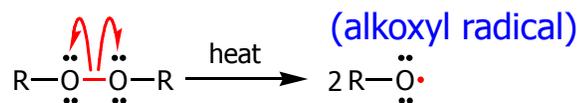


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1A. Production of Radicals

❖ Homolysis of covalent bonds

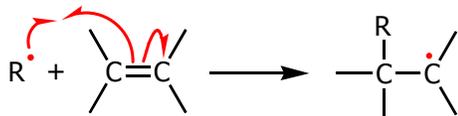
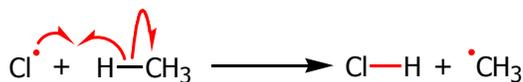
- Need heat or light (hv)



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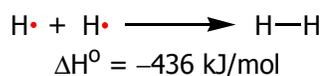
1B. Reactions of Radicals

- ❖ Almost all small radicals are short-lived, highly reactive species



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2. Homolytic Bond Dissociation Energies (ΔH°)



Bond formation is an exothermic process.



Reactions in which only bond breaking occurs are always endothermic.

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❖ The energies required to break covalent bonds homolytically are called **homolytic bond dissociation energies**, and they are usually abbreviated by the symbol ***DH*[°]**

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❖ Single-Bond Homolytic Dissociation Energies (*DH*[°]) at 25°C

Bond Broken	kJ/mol
H-H	436
F-F	159
Cl-Cl	243
Br-Br	193
I-I	151

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❖ Single-Bond Homolytic Dissociation Energies (*DH*[°]) at 25°C

Bond Broken	kJ/mol
H-F	570
H-Cl	432
H-Br	366
H-I	298

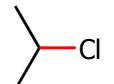
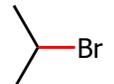
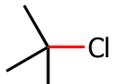
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❖ Single-Bond Homolytic Dissociation Energies (*DH*[°]) at 25°C

Bond Broken	kJ/mol	Bond Broken	kJ/mol
H ₃ C-H	440		
H ₃ C-F	461		
H ₃ C-Cl	352		
H ₃ C-Br	293	H ₃ C-OH	387
H ₃ C-I	240	H ₃ C-OCH ₃	348

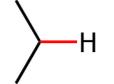
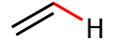
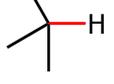
Ch. 10 - 10

❖ Single-Bond Homolytic Dissociation Energies (*DH*[°]) at 25°C

Bond Broken	kJ/mol	Bond Broken	kJ/mol
 -Cl	354	 -Br	294
 -Cl	355	 -Br	298
 -Cl	349	 -Br	292

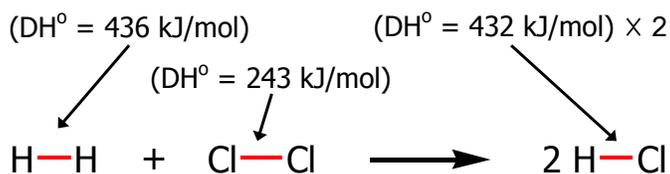
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❖ Single-Bond Homolytic Dissociation Energies (*DH*[°]) at 25°C

Bond Broken	kJ/mol	Bond Broken	kJ/mol
 -H	423	 -H	369
 -H	413	 -H	465
 -H	400	Ph-H	474
Ph-  -H	375	HC≡C-H	547

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2A. Use Homolytic Bond Dissociation Energies to Calculate Heats of Reaction



+679 kJ is required to **cleave** 1 mol of H₂ bonds and 1 mol of Cl₂ bonds

-864 kJ is evolved in **formation** of bonds in 2 mol of HCl

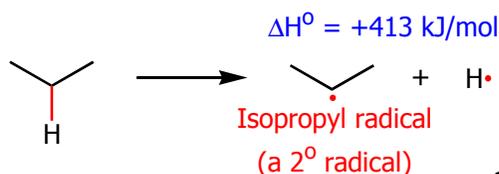
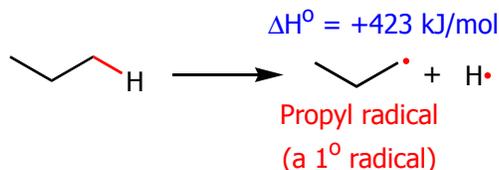
Ch. 10 - 13

$$\begin{aligned}
 \Delta H^\circ &= -2(432 \text{ kJ/mol}) + (436 \text{ kJ/mol} + 243 \text{ kJ/mol}) \\
 &= -864 \text{ kJ/mol} + 679 \text{ kJ/mol} \\
 &= -185 \text{ kJ/mol}
 \end{aligned}$$

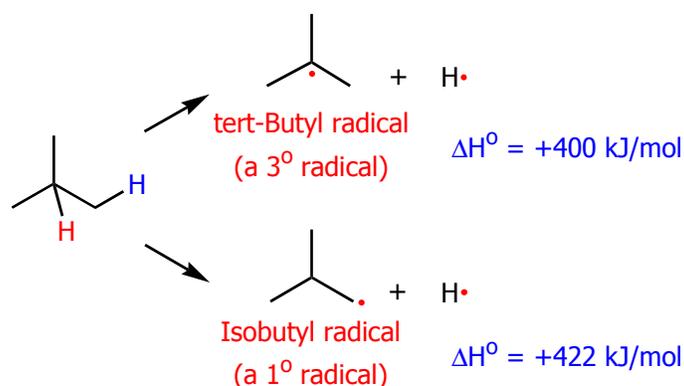
❖ Overall, the reaction of 1 mol of H₂ and 1 mol of Cl₂ to form 2 mol of HCl is exothermic

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2B. Use Homolytic Bond Dissociation Energies to Determine the Relative Stabilities of Radicals



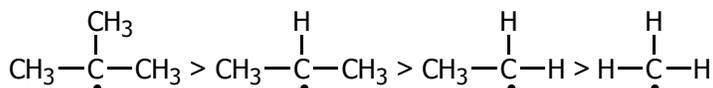
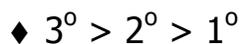
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❖ Relative Stability

- Carbon radicals are considered to be electron deficient (similar to carbocations), thus electron donating groups stabilize radicals



(positive inductive effect of alkyl groups stabilize radical)

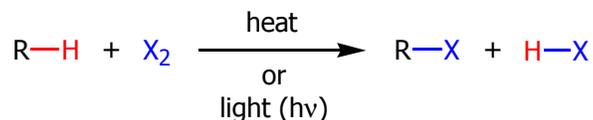
Ch. 10 - 17

3. The Reactions of Alkanes with Halogens

- ❖ Alkanes have no functional group and are inert to many reagents and do not undergo many reactions
- ❖ Halogenation of alkanes is one of the most typical free radical reactions

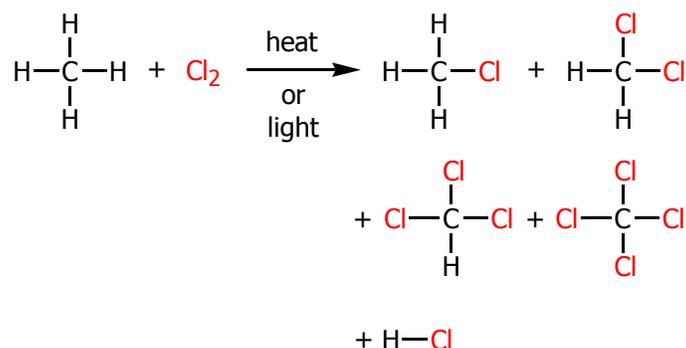
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- ❖ Alkanes react with molecular halogens to produce alkyl halides by a substitution reaction called **radical halogenation**



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3A. Multiple Halogen Substitution



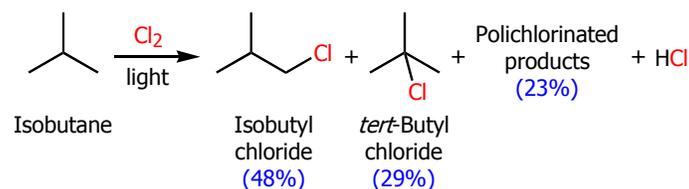
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3B. Lack of Chlorine Selectivity

- ❖ **Chlorination** of most higher alkanes gives a mixture of isomeric monochloro products as well as more highly halogenated compounds

- Chlorine is relatively **unselective**; it does not discriminate greatly among the different types of hydrogen atoms (primary, secondary, and tertiary) in an alkane

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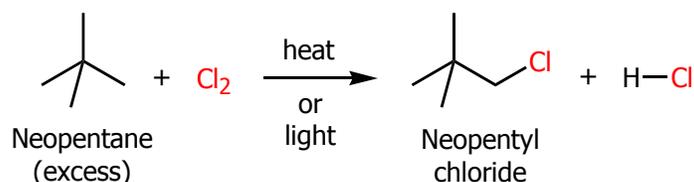


- Because alkane chlorinations usually yield a complex mixture of products, they are not useful as synthetic methods when the goal is preparation of a specific alkyl chloride

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- An exception is the halogenation of an alkane (or cycloalkane) whose hydrogen atoms *are all equivalent*. [Equivalent hydrogen atoms are defined as those which on replacement by some other group (e.g., chlorine) yield the same compound.]

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- Bromine is generally less reactive toward alkanes than chlorine, and bromine is **more selective** in the site of attack when it does react

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4. Chlorination of Methane: Mechanism of Reaction

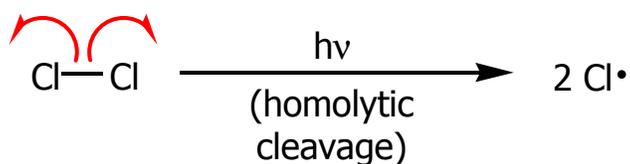
❖ Most radical reactions include 3 stages (steps)

- (1) chain initiation
- (2) chain propagation
- (3) chain termination

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❖ Mechanism of Free Radical Chlorination of CH₄

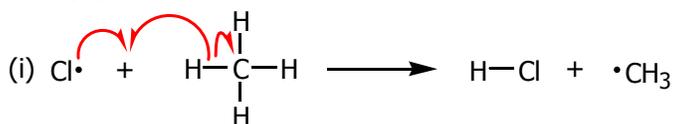
(1) Chain initiation



- Radicals are created in this step

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(2) Chain propagation

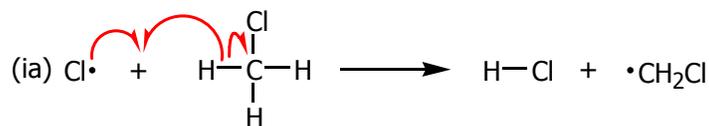


- Repeating (i) and (ii) in a chain reaction provides the product CH₃Cl
- In chain propagation, one radical generates another and the process goes on

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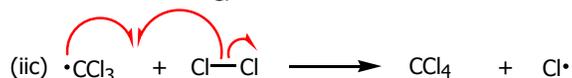
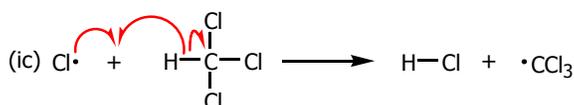
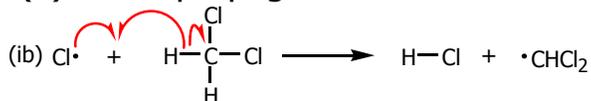
(2) Chain propagation

- Other than CH₃Cl, other chlorination products can be formed in the chain propagation step



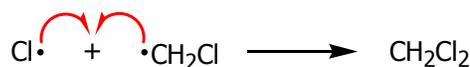
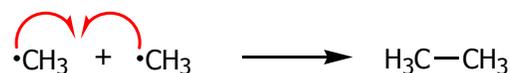
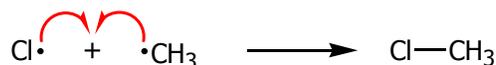
Ch. 10 - 28

(2) Chain propagation



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(3) Chain termination



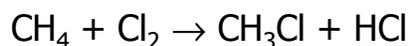
Ch. 10 - 30

5A. The Overall Free-Energy Change

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

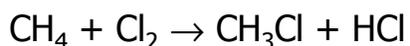
- ❖ For many reactions the entropy change is so small that the term $T\Delta S^\circ$ in the above expression is almost zero, and ΔG° is approximately equal to ΔH°

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- ❖ 2 mol of the products are formed from the same number of moles of the reactants
 - Thus the number of translational degrees of freedom available to products and reactants is the same
- ❖ CH_3Cl is a tetrahedral molecule like CH_4 , and HCl is a diatomic molecule like Cl_2
 - This means that vibrational and rotational degrees of freedom available to products and reactants should also be approximately the same

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- ❖ $\Delta S^\circ = +2.8 \text{ J K}^{-1} \text{ mol}^{-1}$
- ❖ At room temperature (298 K) the $T\Delta S^\circ$ term is 0.8 kJ mol^{-1}
- ❖ $\Delta H^\circ = -101 \text{ kJ mol}^{-1}$
- ❖ $\Delta G^\circ = -102 \text{ kJ mol}^{-1}$

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5B. Activation Energies

- ❖ A low energy of activation means a reaction will take place rapidly; a high energy of activation means that a reaction will take place slowly

Chain initiation



$$E_{\text{act}} = +243 \text{ kJ/mol}$$

Chain propagation



$$E_{\text{act}} = +16 \text{ kJ/mol}$$



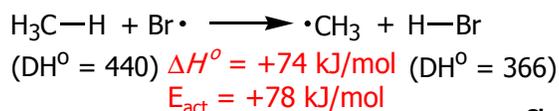
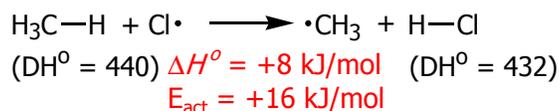
$$E_{\text{act}} = \sim 8 \text{ kJ/mol}$$

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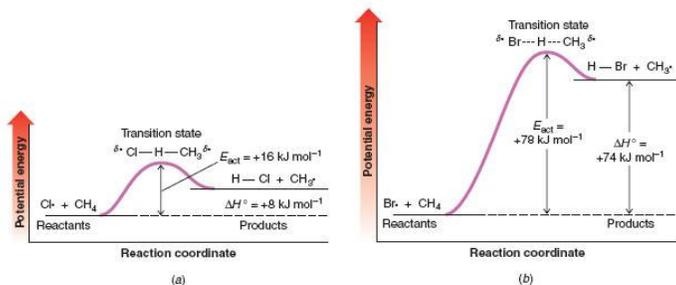
- ❖ Estimates of energies of activation
 - (1) Any reaction in which bonds are broken will have an energy of activation greater than zero. This will be true even if a stronger bond is formed and the reaction is exothermic. The reason: Bond formation and bond breaking do not occur simultaneously in the transition state. Bond formation lags behind, and its energy is not all available for bond breaking

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- ❖ Estimates of energies of activation
 - (2) Activation energies of endothermic reactions that involve both bond formation and bond rupture will be greater than the heat of reaction, ΔH°

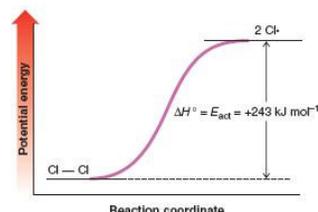
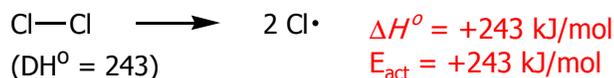


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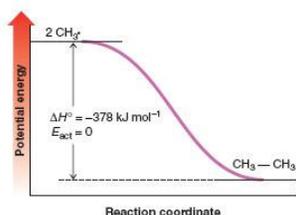
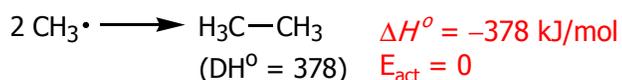
Ch. 10 - 43

- Estimates of energies of activation
 - The energy of activation of a gas-phase reaction where bonds are broken homolytically but no bonds are formed is equal to ΔH^0



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- Estimates of energies of activation
 - The energy of activation for a gas-phase reaction in which small radicals combine to form molecules is usually zero



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5C. Reaction of Methane with Other Halogens

FLUORINATION

	ΔH^0 (kJ/mol)	E_{act} (kJ/mol)
Chain initiation		
$\text{F}_2 \rightarrow 2 \text{F}\cdot$	+159	+159
Chain propagation		
$\text{F}\cdot + \text{CH}_4 \rightarrow \text{HF} + \cdot\text{CH}_3$	-130	+5.0
$\cdot\text{CH}_3 + \text{F}_2 \rightarrow \text{CH}_3\text{F} + \text{F}\cdot$	-302	small
Overall $\Delta H^0 =$	-432	

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CHLORINATION

	ΔH^0 (kJ/mol)	E_{act} (kJ/mol)
Chain initiation		
$\text{Cl}_2 \rightarrow 2 \text{Cl}\cdot$	+243	+243
Chain propagation		
$\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{HCl} + \cdot\text{CH}_3$	+8	+16
$\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$	-109	small
Overall $\Delta H^0 =$	-101	

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BROMINATION

	ΔH^0 (kJ/mol)	E_{act} (kJ/mol)
Chain initiation		
$\text{Br}_2 \rightarrow 2 \text{Br}\cdot$	+193	+193
Chain propagation		
$\text{Br}\cdot + \text{CH}_4 \rightarrow \text{HBr} + \cdot\text{CH}_3$	+74	+78
$\cdot\text{CH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{Br}\cdot$	-100	small
Overall $\Delta H^0 =$	-26	

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IODINATION

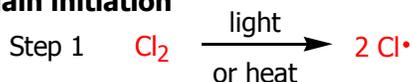
	ΔH° (kJ/mol)	E_{act} (kJ/mol)
Chain initiation		
$I_2 \rightarrow 2 I^\bullet$	+151	+151
Chain propagation		
$I^\bullet + CH_4 \rightarrow HI + \bullet CH_3$	+142	+140
$\bullet CH_3 + I_2 \rightarrow CH_3I + I^\bullet$	-89	small
Overall $\Delta H^\circ =$	+53	

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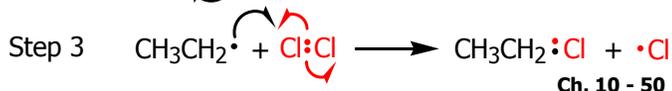
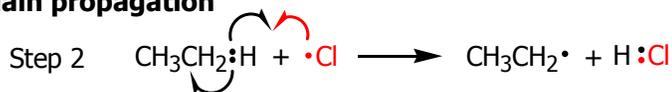
6. Halogenation of Higher Alkanes

❖ Mechanism for radical halogenation of ethane

Chain initiation

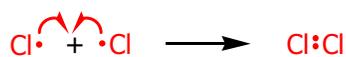
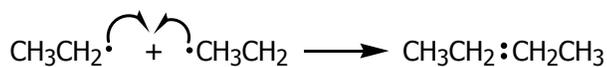
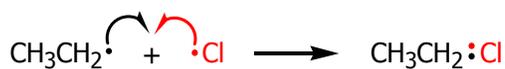


Chain propagation

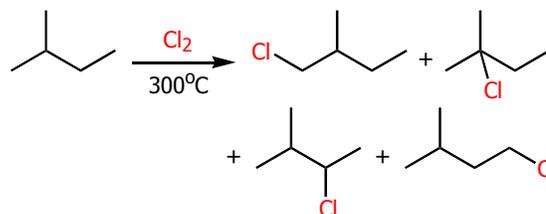
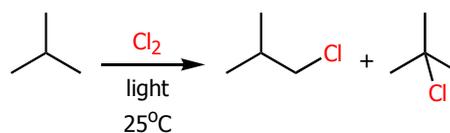
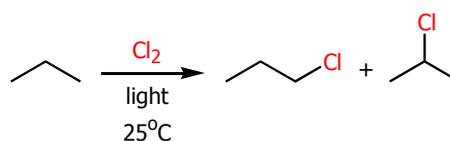


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Chain termination



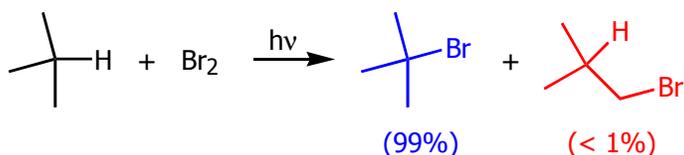
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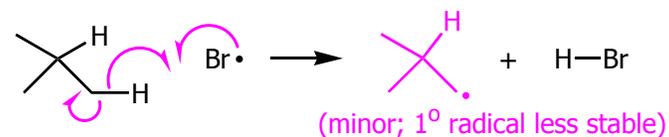
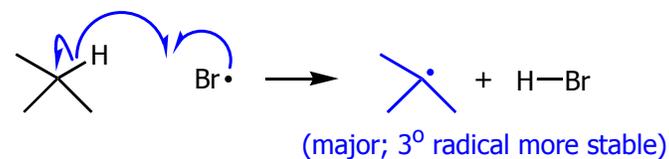
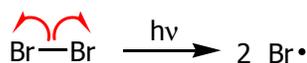
6A. Selectivity of Bromine

❖ Bromination is slower than chlorination because the 1st propagation step is more endothermic (overall still exothermic). As a result, bromination is *more selective* than chlorination



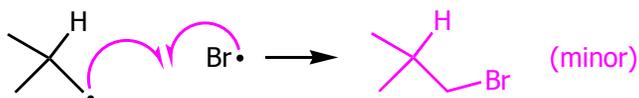
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❖ Mechanism

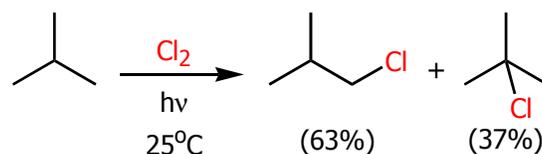
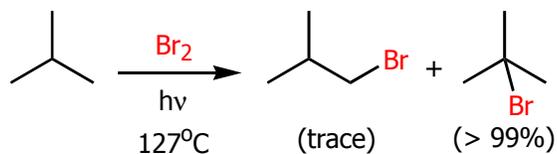


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❖ Mechanism

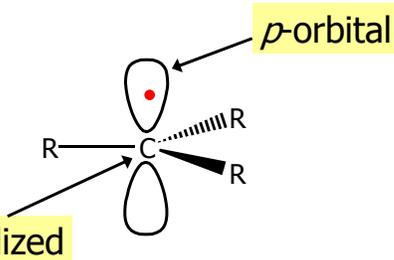


Ch. 10 - 55



Ch. 10 - 56

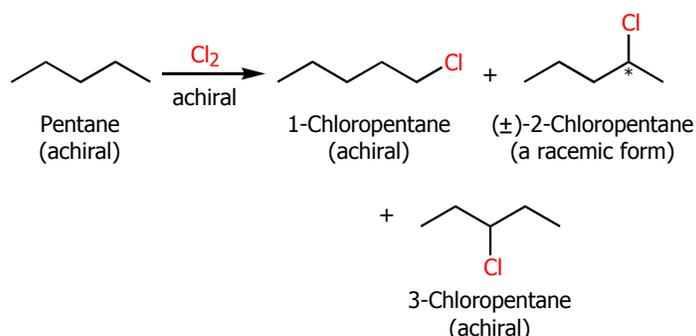
7. The Geometry of Alkyl Radicals



❖ Planar, similar to carbocation

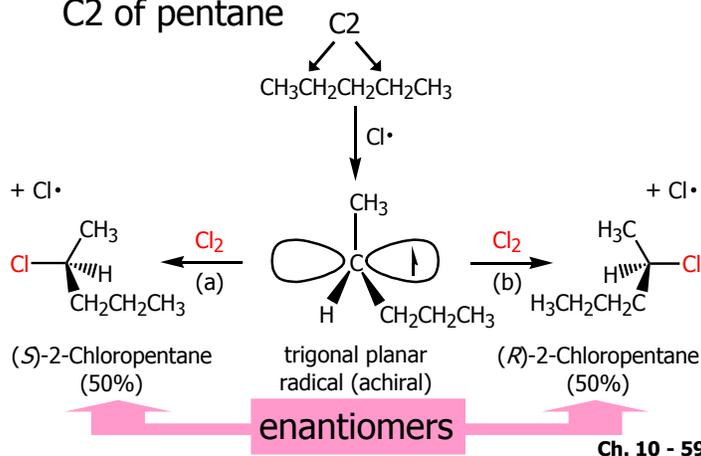
Ch. 10 - 57

8. Reactions That Generate Tetrahedral Chirality Centers



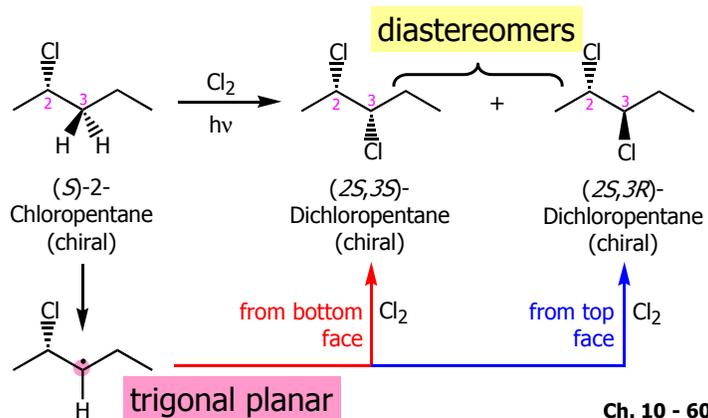
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❖ The Stereochemistry of chlorination at C2 of pentane



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8A. Generation of a Second Chirality Center in a Radical Halogenation



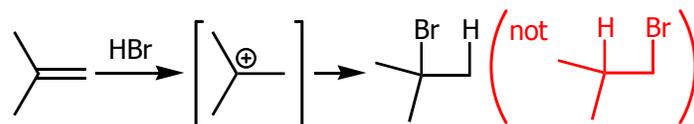
Ch. 10 - 60

❖ Note that other products are formed, of course, by chlorination at other carbon atoms

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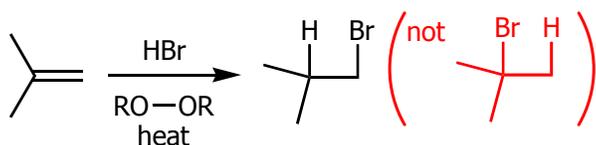
9. Radical Addition to Alkenes: The Anti-Markovnikov Addition of Hydrogen Bromide

- ❖ Anti-Markovnikov addition of HBr to alkenes – peroxide effect
 - Addition of HBr to alkenes usually follows **Markovnikov's rule**



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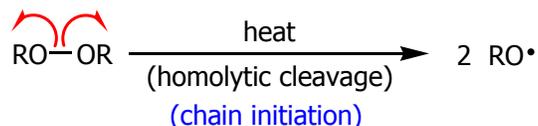
- In the presence of peroxides (RO-OR), **anti-Markovnikov addition** is observed



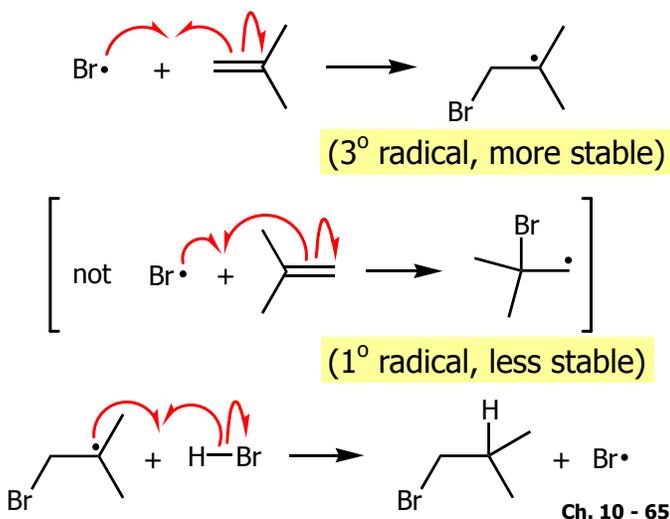
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❖ Mechanism

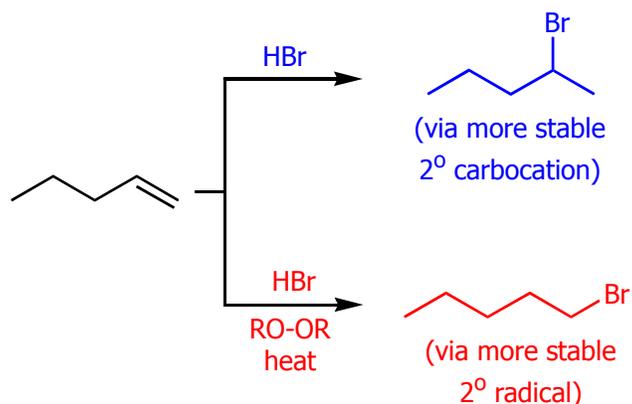
- Via a radical mechanism



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❖ Synthetic application



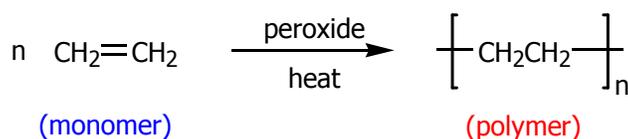
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❖ Hydrogen bromide is the only hydrogen halide that gives anti-Markovnikov addition when peroxides are present

❖ Hydrogen fluoride, hydrogen chloride, and hydrogen iodide *do not* give anti-Markovnikov addition even when peroxides are present

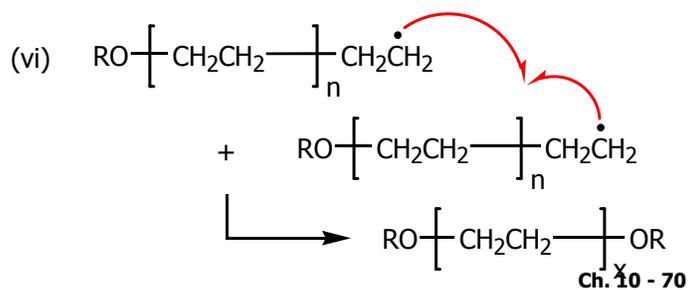
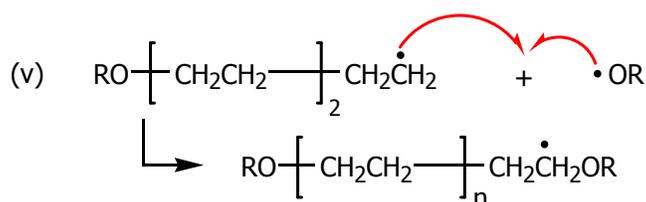
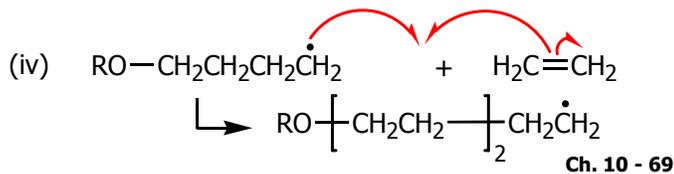
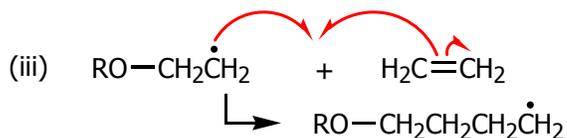
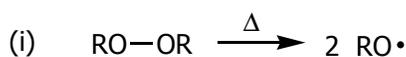
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10. Radical Polymerization of Alkenes: Chain-Growth Polymers

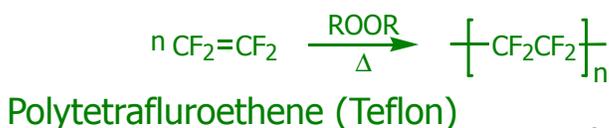
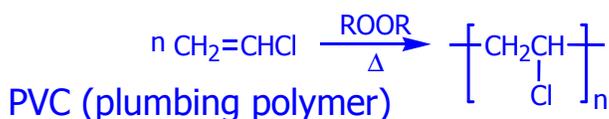
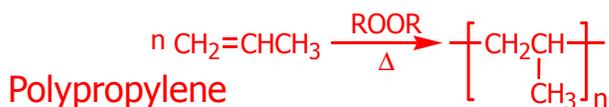


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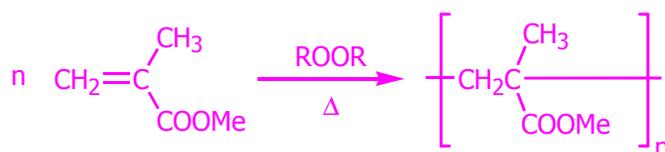
❖ Via radical mechanism



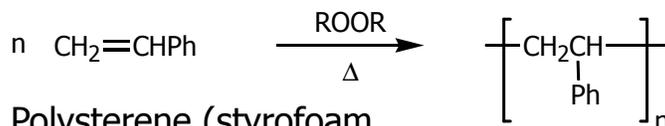
❖ Other common polymers



❖ Other common polymers



Polymethyl methacrylate
(windshield, contact lenses)



Polystyrene (styrofoam,
coffee cup, etc.)

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 **END OF CHAPTER 10** 

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