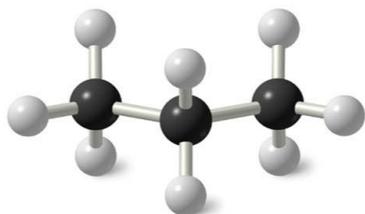


Carbon Compounds and polymers

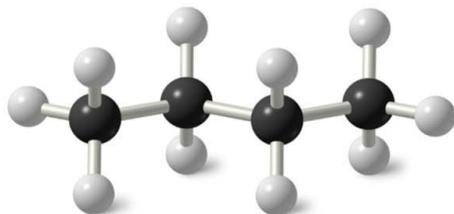
◆ Shapes of Alkanes

“Straight-chain” alkanes have a zig-zag orientation when they are in their most straight orientation

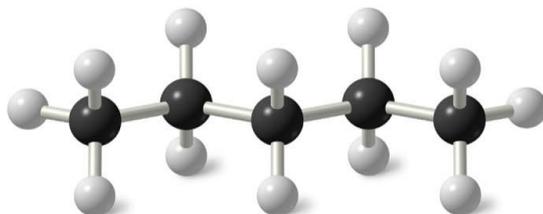
H Straight chain alkanes are also called unbranched alkanes



Propane
 $\text{CH}_3\text{CH}_2\text{CH}_3$ or 

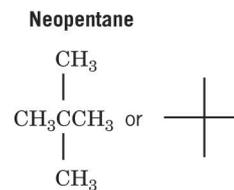
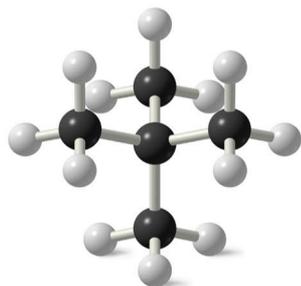
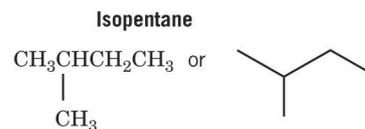
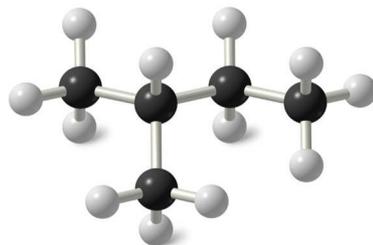
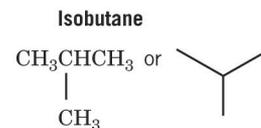
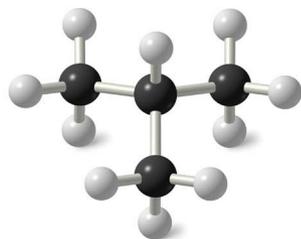


Butane
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ or 



Pentane
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or 

⌋ **Branched alkanes have at least one carbon which is attached to more than two other carbons**



Constitutional isomers have different physical properties (melting point, boiling point, densities etc.)

H Constitutional isomers have the same molecular formula but different connectivity of atoms

Molecular Formula	Structural Formula	mp (°C)	bp (°C) ^a (1 atm)	Density ^b (g mL ⁻¹)	Index of Refraction ^c (<i>n</i> _D 20°C)
C ₆ H ₁₄	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	-95	68.7	0.6594 ²⁰	1.3748
C ₆ H ₁₄	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	-153.7	60.3	0.6532 ²⁰	1.3714
C ₆ H ₁₄	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	-118	63.3	0.6643 ²⁰	1.3765
C ₆ H ₁₄	$\begin{array}{c} \text{CH}_3\text{CH}-\text{CHCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	-128.8	58	0.6616 ²⁰	1.3750
C ₆ H ₁₄	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	-98	49.7	0.6492 ²⁰	1.3688

^aUnless otherwise indicated, all boiling points given in this book are at 1 atm or 760 torr.

^bThe superscript indicates the temperature at which the density was measured.

^cThe index of refraction is a measure of the ability of the alkane to bend (refract) light rays. The values reported are for light of the D line of the sodium spectrum (*n*_D).

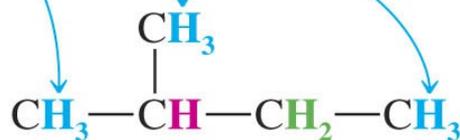
(The number of constitutional isomers possible for a given molecular formula increases rapidly with the number of carbons

Molecular Formula	Possible Number of Constitutional Isomers
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{30}H_{62}$	4,111,846,763
$C_{40}H_{82}$	62,481,801,147,341

◆ Classification of Hydrogen Atoms

Hydrogens take their classification from the carbon they are attached to

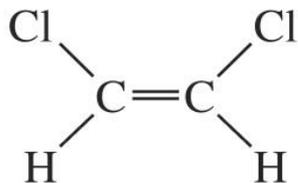
1° Hydrogen atoms



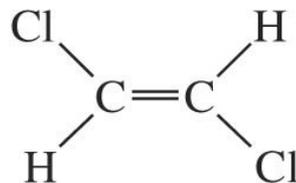
3° Hydrogen atom

2° Hydrogen atoms

- If two identical groups occur on the same side of the double bond the compound is **cis**
- If they are on opposite sides the compound is **trans**



cis-1,2-Dichloroethene



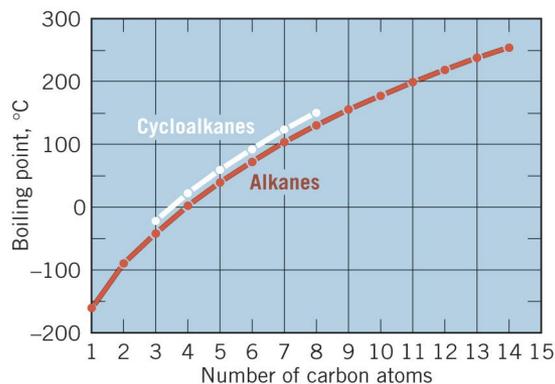
trans-1,2-Dichloroethene

- Several alkenes have common names which are recognized by IUPAC

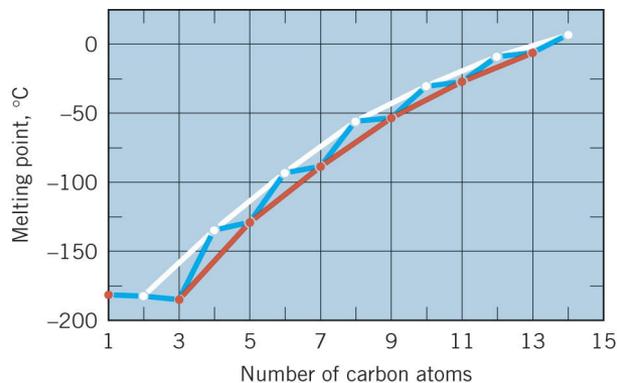
	$\text{CH}_2=\text{CH}_2$	$\text{CH}_3\text{CH}=\text{CH}_2$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}=\text{CH}_2 \end{array}$
IUPAC:	Ethene	Propene	2-Methylpropene
Common:	Ethylene	Propylene	Isobutylene

◆ Physical Properties of Alkanes and Cycloalkanes

- Boiling points of unbranched alkanes increase smoothly with number of carbons



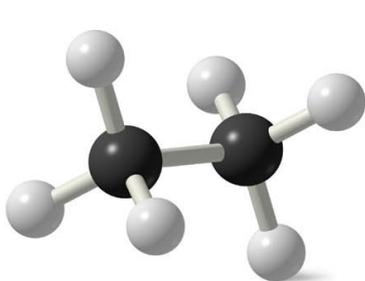
- Melting points increase in an alternating pattern according to whether the number of carbon atoms in the chain is even or odd



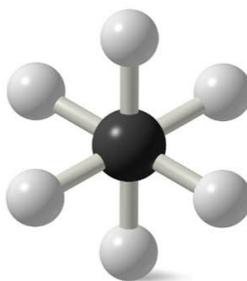
◆ Sigma Bonds and Bond Rotation

- ↳ Ethane has relatively free rotation around the carbon-carbon bond
- ↳ The staggered conformation has C-H bonds on adjacent carbons as far apart from each other as possible

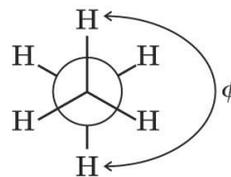
H The drawing to the right is called a Newman projection



(a)

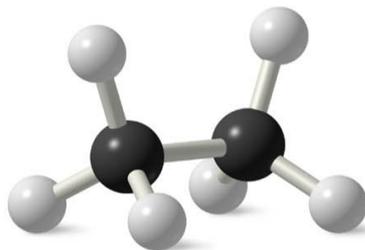


(b)

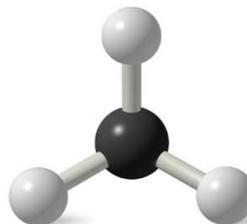


The dihedral angle (ϕ) between these hydrogens is 180° .

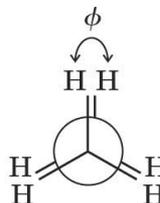
- ↳ The eclipsed conformation has all C-H bonds on adjacent carbons directly on top of each other



(a)

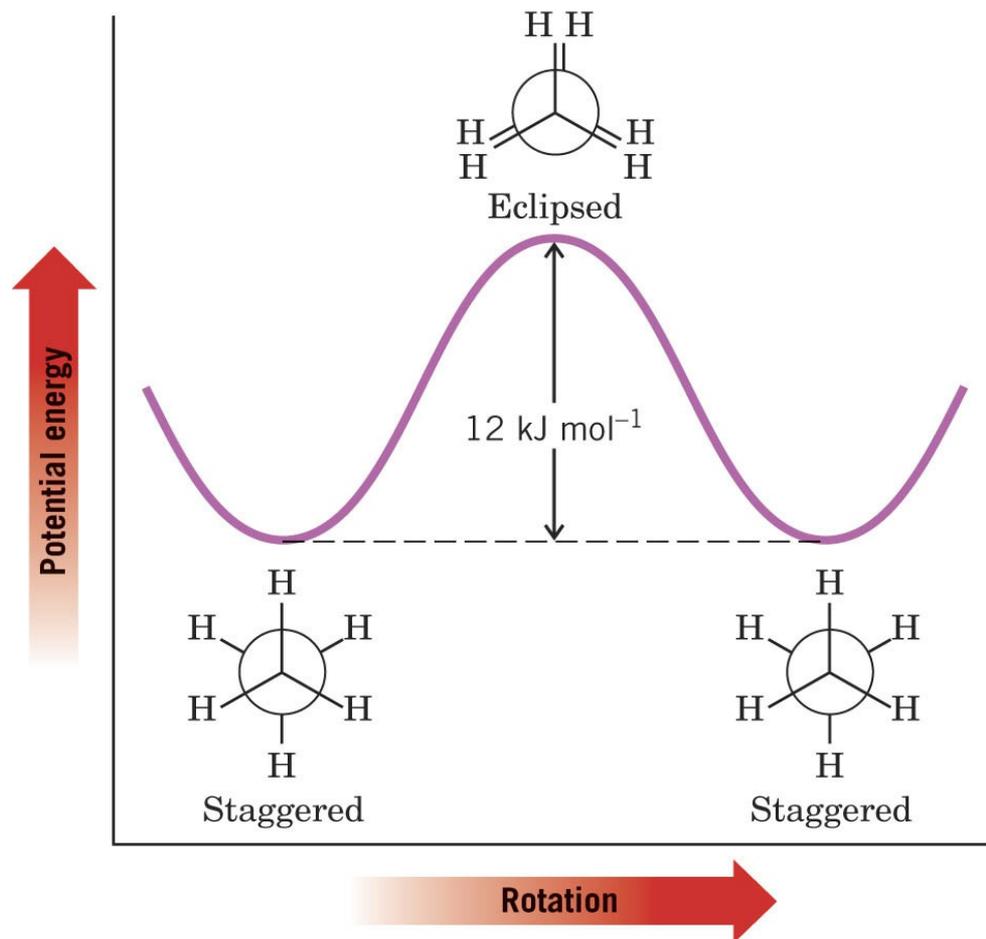


(b)



The dihedral angle (ϕ) between these hydrogens is 0° .

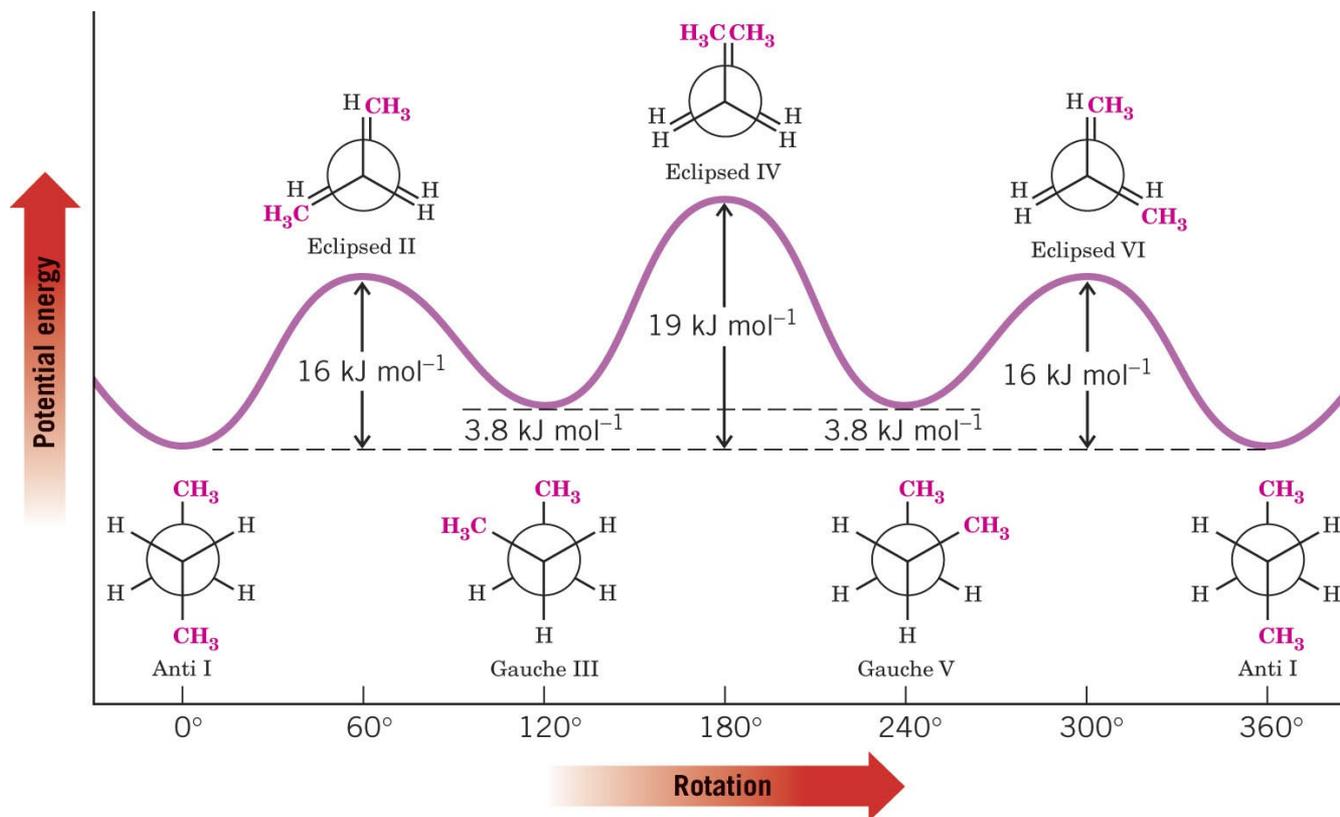
The potential energy diagram of the conformations of ethane shows that the staggered conformation is more stable than eclipsed by 12 kJ mol^{-1}



◆ Conformational Analysis of Butane

Rotation around C₂-C₃ of butane gives six important conformations

H The gauche conformation is less stable than the anti conformation by 3.8 kJ mol⁻¹ because of repulsive van der Waals forces between the two methyls



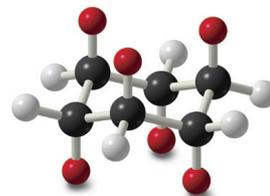
◆ Conformations of Cyclohexane

↳ The chair conformation has no ring strain

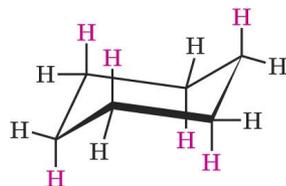
H All bond angles are 109.5° and all C-H bonds are perfectly staggered



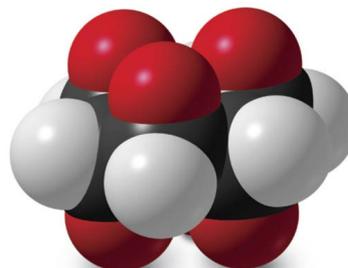
(a)



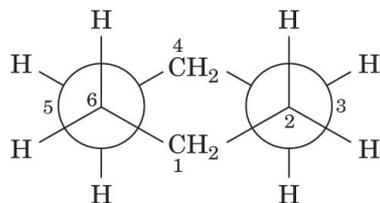
(b)



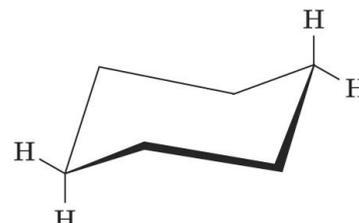
(c)



(d)

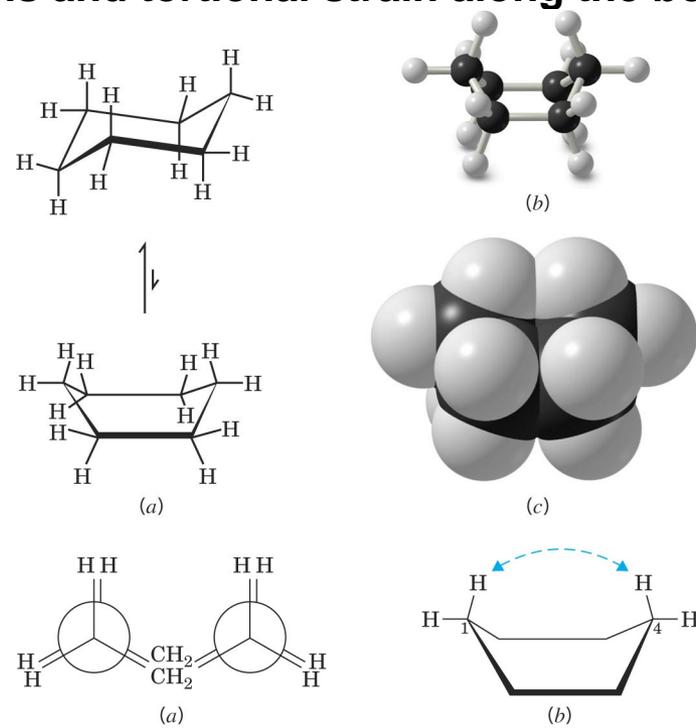


(a)



(b)

The boat conformation is less stable because of flagpole interactions and torsional strain along the bottom of the boat

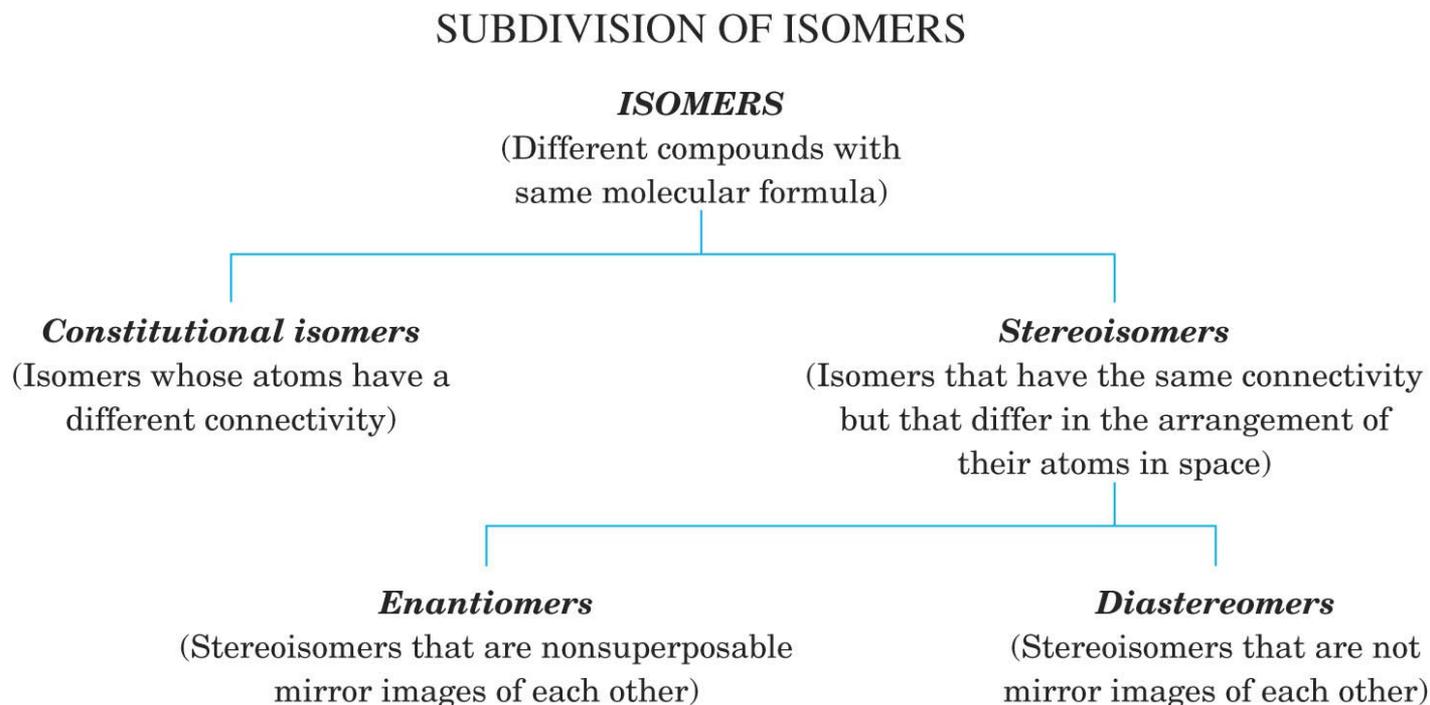


The twist conformation is intermediate in stability between the boat and the chair conformation



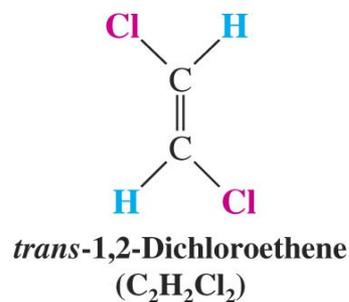
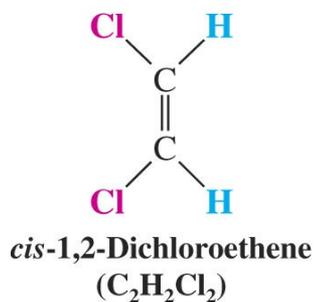
◆ Isomerism: Constitutional Isomers and Stereoisomers

- Stereoisomers are isomers with the same molecular formula and same connectivity of atoms but different arrangement of atoms in space

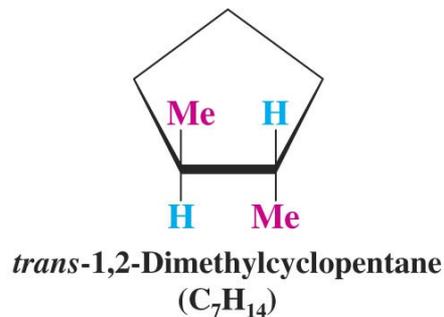
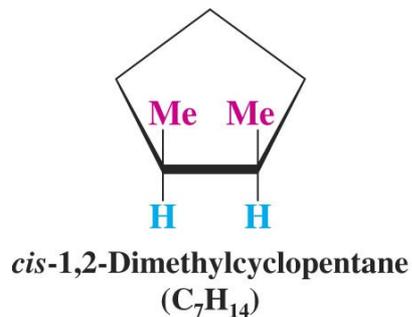


- **Enantiomers:** stereoisomers whose molecules are nonsuperposable mirror images
- **Diastereomers:** stereoisomers whose molecules are not mirror images of each other

↳ Example: cis and trans double bond isomers



↳ Example: cis and trans cycloalkane isomers

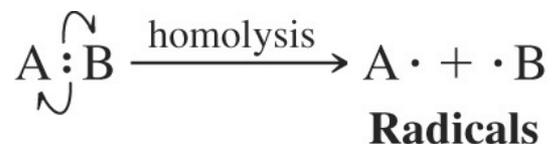


◆ Introduction

Homolytic bond cleavage leads to the formation of radicals (also called free radicals)

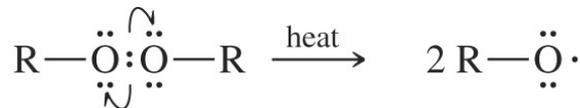
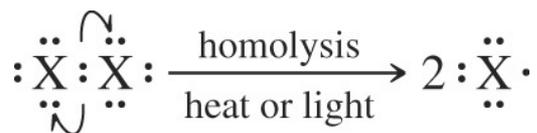
Radicals are highly reactive, short-lived species

H Single-barbed arrows are used to show the movement of single electrons



● Production of Radicals

Homolysis of relatively weak bonds such as O-O or X-X bonds can occur with addition of energy in the form of heat or light



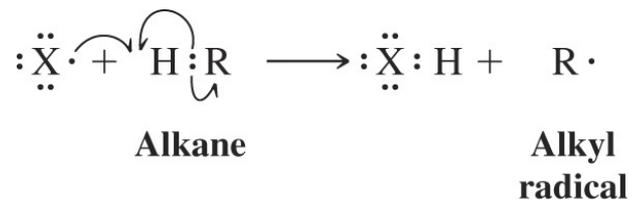
Dialkyl peroxide

Alkoxy radicals

● Reactions of Radicals

Radicals tend to react in ways that lead to pairing of their unpaired electron

^H Hydrogen abstraction is one way a halogen radical can react to pair its unshared electron

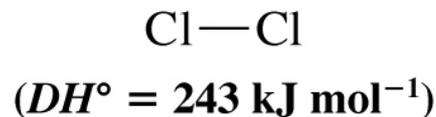
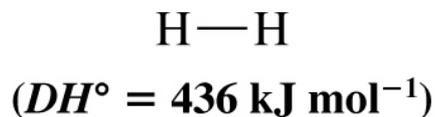


◆ Homolytic Bond Dissociation Energies

- Atoms have higher energy (are less stable) than the molecules they can form
 - The formation of covalent bonds is exothermic
- Breaking covalent bonds requires energy (*i.e.* is endothermic)



- The homolytic bond dissociation energy is abbreviated DH°



- **Homolytic Bond Dissociation Energies and Heats of Reaction**

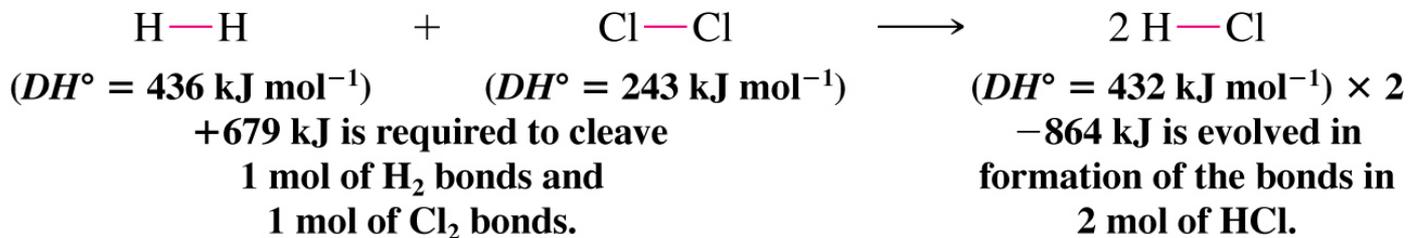
- ⌋ Homolytic Bond Dissociation energies can be used to calculate the enthalpy change (ΔH°) for a reaction

- ⌋ DH° is positive for bond breaking and negative for bond forming

- ⌋ **Example**

- H This reaction below is highly exothermic since ΔH° is a large and negative

- H ΔH° is not dependant on the mechanism; only the initial and final states of the molecules are considered in determining ΔH°



$$\Delta H^\circ = (-864 \text{ kJ} + 679 \text{ kJ}) = -185 \text{ kJ} \quad \text{for 2 mol HCl produced}$$

A·B → A· + B·			
Bond Broken (shown in red)	kJ mol ⁻¹	Bond Broken (shown in red)	kJ mol ⁻¹
H—H	436	(CH ₃) ₂ CH—Br	298
D—D	443	(CH ₃) ₂ CH—I	222
F—F	159	(CH ₃) ₂ CH—OH	402
Cl—Cl	243	(CH ₃) ₂ CH—OCH ₃	359
Br—Br	193	(CH ₃) ₂ CHCH ₂ —H	422
I—I	151	(CH ₃) ₃ C—H	400
H—F	570	(CH ₃) ₃ C—Cl	349
H—Cl	432	(CH ₃) ₃ C—Br	292
H—Br	366	(CH ₃) ₃ C—I	227
H—I	298	(CH ₃) ₃ C—OH	400
CH ₃ —H	440	(CH ₃) ₃ C—OCH ₃	348
CH ₃ —F	461	C ₆ H ₅ CH ₂ —H	375
CH ₃ —Cl	352	CH ₂ =CHCH ₂ —H	369
CH ₃ —Br	293	CH ₂ =CH—H	465
CH ₃ —I	240	C ₆ H ₅ —H	474
CH ₃ —OH	387	HC≡C—H	547
CH ₃ —OCH ₃	348	CH ₃ —CH ₃	378
CH ₃ CH ₂ —H	421	CH ₃ CH ₂ —CH ₃	371
CH ₃ CH ₂ —F	444	CH ₃ CH ₂ CH ₂ —CH ₃	374
CH ₃ CH ₂ —Cl	353	CH ₃ CH ₂ —CH ₂ CH ₃	343
CH ₃ CH ₂ —Br	295	(CH ₃) ₂ CH—CH ₃	371
CH ₃ CH ₂ —I	233	(CH ₃) ₃ C—CH ₃	363
CH ₃ CH ₂ —OH	393	HO—H	499
CH ₃ CH ₂ —OCH ₃	352	HOO—H	356
CH ₃ CH ₂ CH ₂ —H	423	HO—OH	214
CH ₃ CH ₂ CH ₂ —F	444	(CH ₃) ₃ CO—OC(CH ₃) ₃	157
CH ₃ CH ₂ CH ₂ —Cl	354	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}_6\text{H}_5\text{CO} - \text{OCC}_6\text{H}_5 \end{array}$	139
CH ₃ CH ₂ CH ₂ —Br	294	CH ₃ CH ₂ O—OCH ₃	184
CH ₃ CH ₂ CH ₂ —I	176	CH ₃ CH ₂ O—H	431
CH ₃ CH ₂ CH ₂ —OH	395	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C} - \text{H} \end{array}$	364
CH ₃ CH ₂ CH ₂ —OCH ₃	355		
(CH ₃) ₂ CH—H	413		
(CH ₃) ₂ CH—F	439		
(CH ₃) ₂ CH—Cl	355		

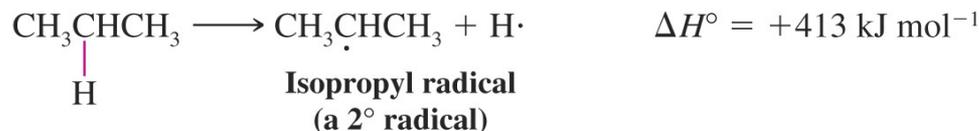
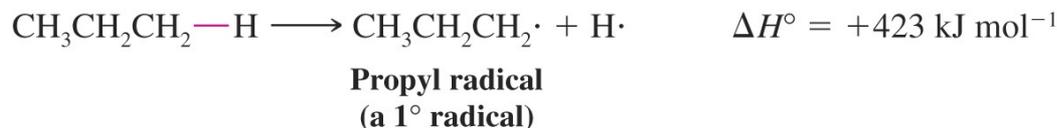
^aData compiled from the *National Institute of Standards (NIST) Standard Reference Database Number 69*, July 2001 Release, accessed via *NIST Chemistry WebBook* (<http://webbook.nist.gov/chemistry/>) and the *CRC Handbook of Chemistry and Physics*, 3rd Electronic Edition (updated from content in the 81st print edition), accessed via *Knovel Engineering and Scientific Online References* (<http://www.knovel.com>). DH° values were obtained directly or calculated from heat of formation (H_f) data using the equation $DH^\circ[\text{A—B}] = H_f[\text{A}] + H_f[\text{B}\cdot] - H_f[\text{A—B}]$.

- **Homolytic Bond Dissociation Energies and the Relative Stabilities of Radicals**

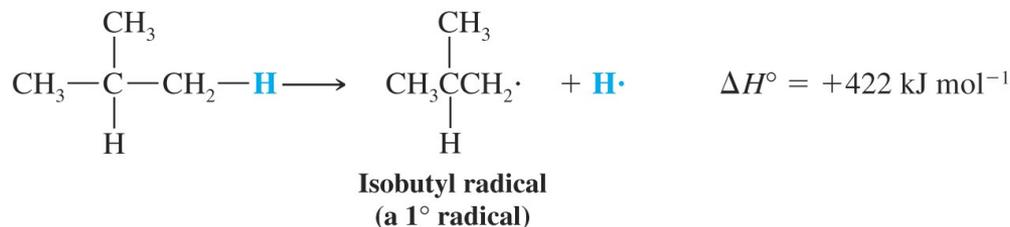
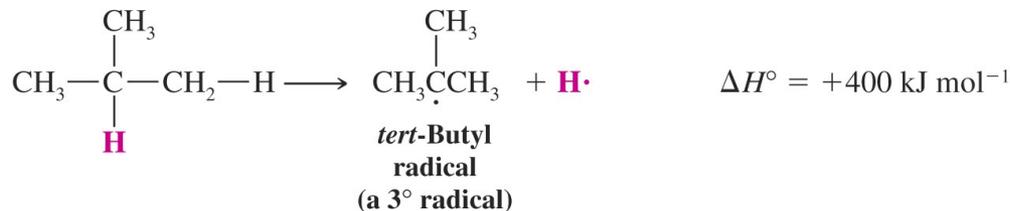
- ⌋ The formation of different radicals from the same starting compound offers a way to estimate relative radical stabilities

- ⌋ **Examples**

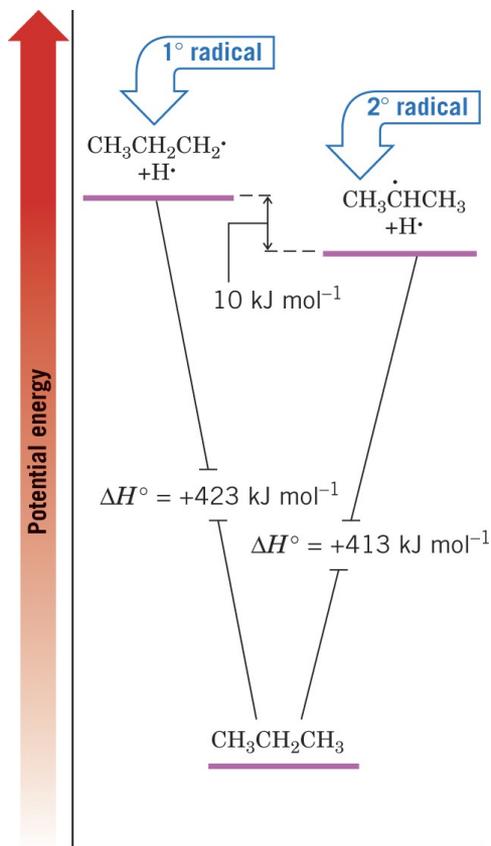
- H The propyl radical is less stable than the isopropyl radical



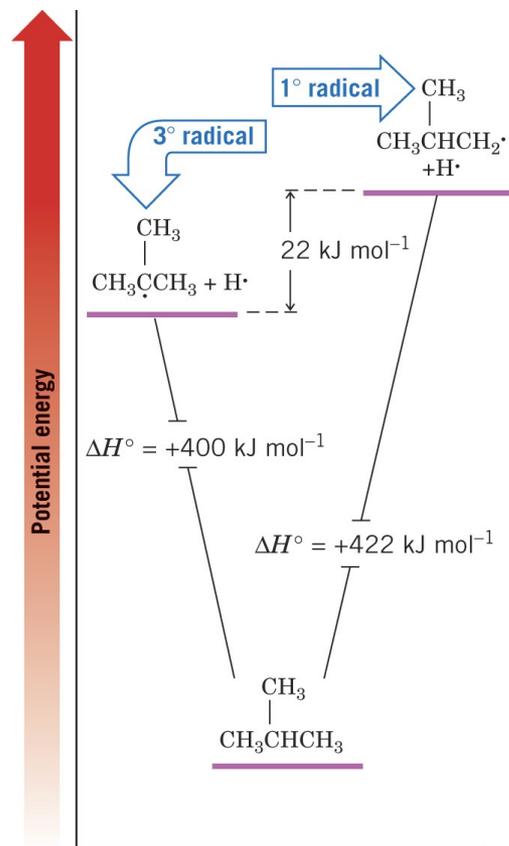
- H Likewise the *tert*-butyl radical is more stable than the isobutyl radical



The energy diagrams for these reactions are shown below



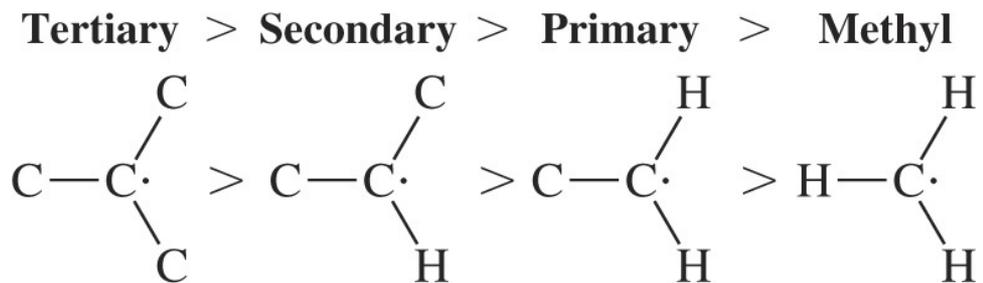
(a)



(b)

(**Stabilities of radicals:**

- H The most substituted radical is most stable
- H Radicals are electron deficient, as are carbocations, and are therefore also stabilized by hyperconjugation



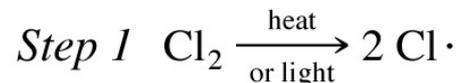
◆ Chlorination of Methane: Mechanism of Reaction

↳ The reaction mechanism has three distinct aspects:
Chain initiation, chain propagation and chain termination

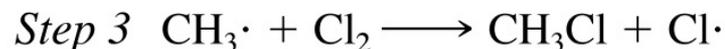
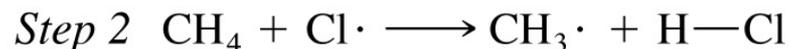
↳ Chain initiation

- H Chlorine radicals form when the reaction is subjected to heat or light
- H Chlorine radicals are used in the chain propagation steps below

Chain Initiation



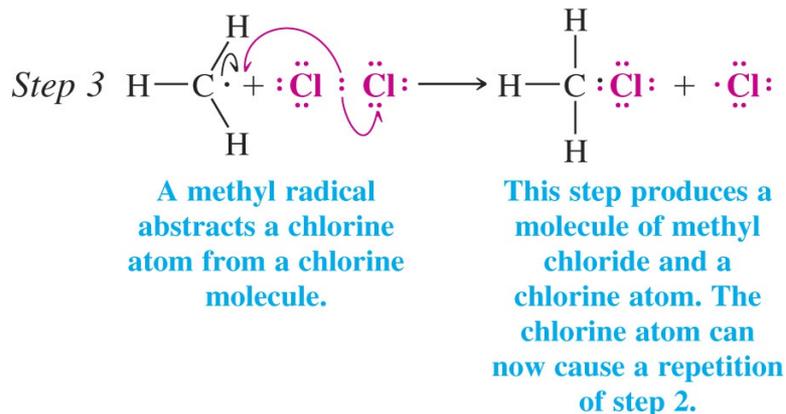
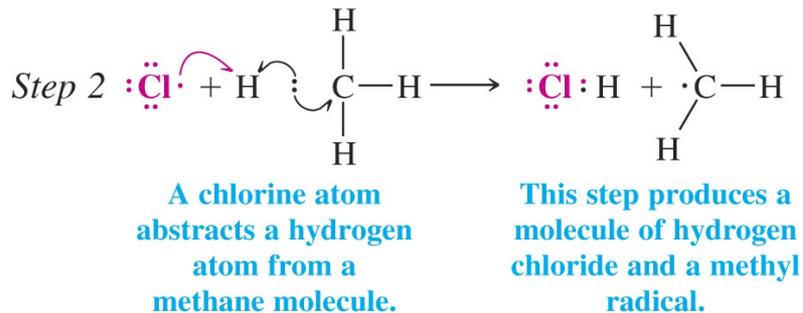
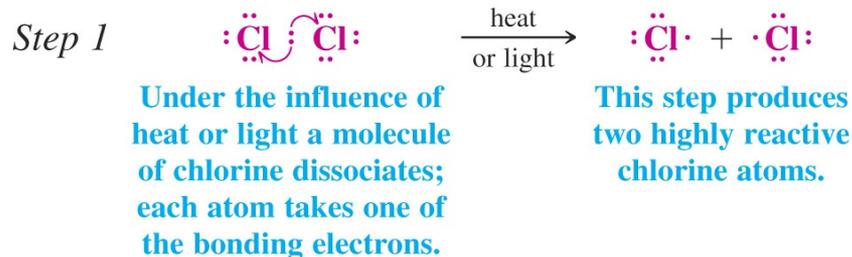
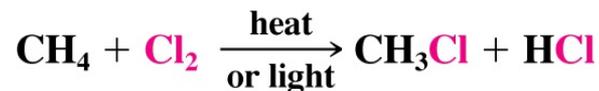
Chain Propagation



↳ Chain propagation

- H A chlorine radical reacts with a molecule of methane to generate a methyl radical
- H A methyl radical reacts with a molecule of chlorine to yield chloromethane and regenerate chlorine radical
- H A chlorine radical reacts with another methane molecule, continuing the chain reaction
- H A single chlorine radical can lead to thousands of chain propagation cycles

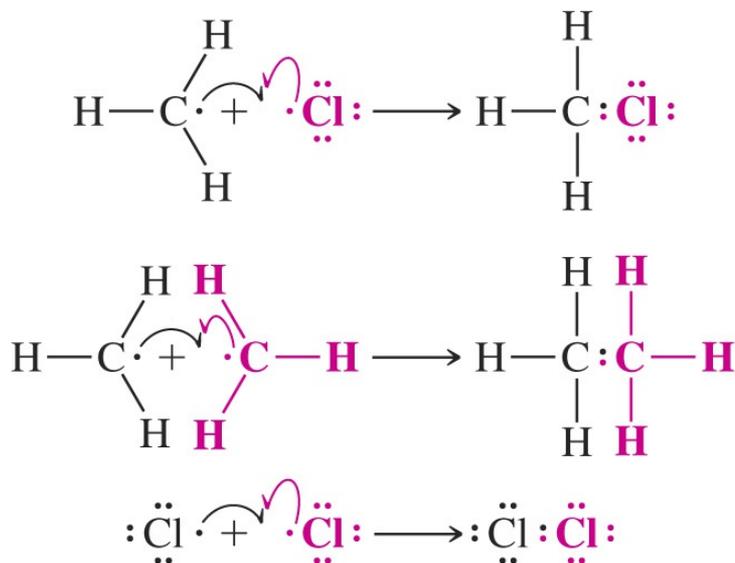
The entire mechanism is shown below



Chain reaction: a stepwise mechanism in which each step generates the reactive intermediate that causes the next cycle of the reaction to occur

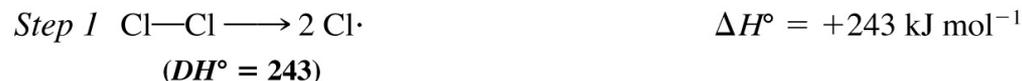
Chain termination

- Occasionally the reactive radical intermediates are quenched by reaction pathways that do not generate new radicals
- The reaction of chlorine with methane requires constant irradiation to replace radicals quenched in chain-terminating steps

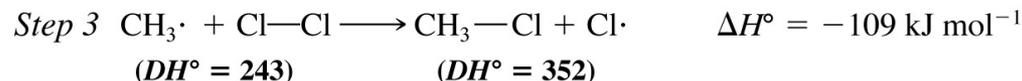
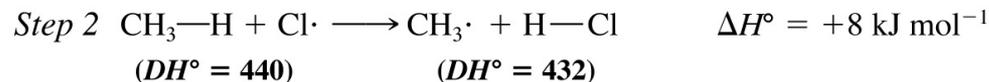


◆ Chlorination of Methane: Energy Changes

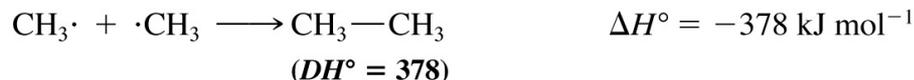
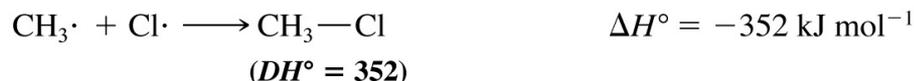
Chain Initiation



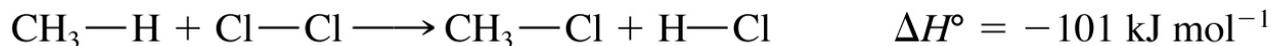
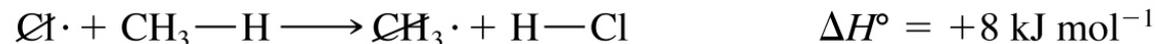
Chain Propagation



Chain Termination



(**The chain propagation steps have overall $\Delta H^\circ = -101 \text{ kJ mol}^{-1}$ and are highly exothermic**



- **The Overall Free-Energy Change: $\Delta G^\circ = \Delta H^\circ - T (\Delta S^\circ)$**

- ↳ In radical reactions such as the chlorination of methane the overall entropy change (ΔS°) in the reaction is small and thus it is appropriate to use ΔH° values to approximate ΔG° values

- H $\Delta G^\circ = -102 \text{ kJ mol}^{-1}$ and $\Delta H^\circ = -101 \text{ kJ mol}^{-1}$ for this reaction

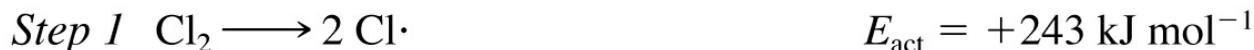
- **Activation Energies**

- ↳ When using enthalpy values (ΔH°) the term for the difference in energy between starting material and the transition state is the energy of activation (E_{act})

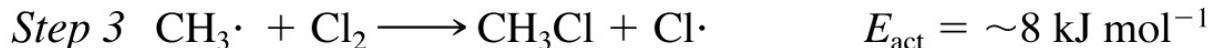
- H Recall when free energy of activation (ΔG°) values are used this difference is ΔG^\ddagger

- ↳ For the chlorination of methane the E_{act} values have been calculated

Chain Initiation



Chain Propagation

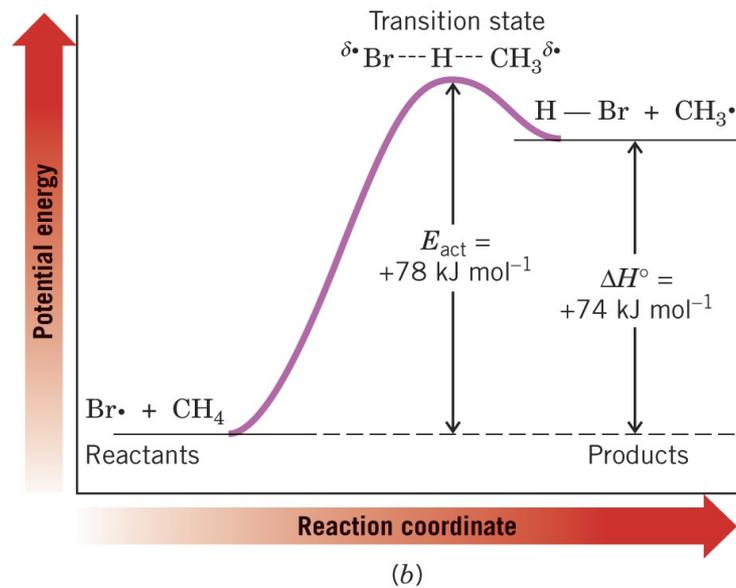
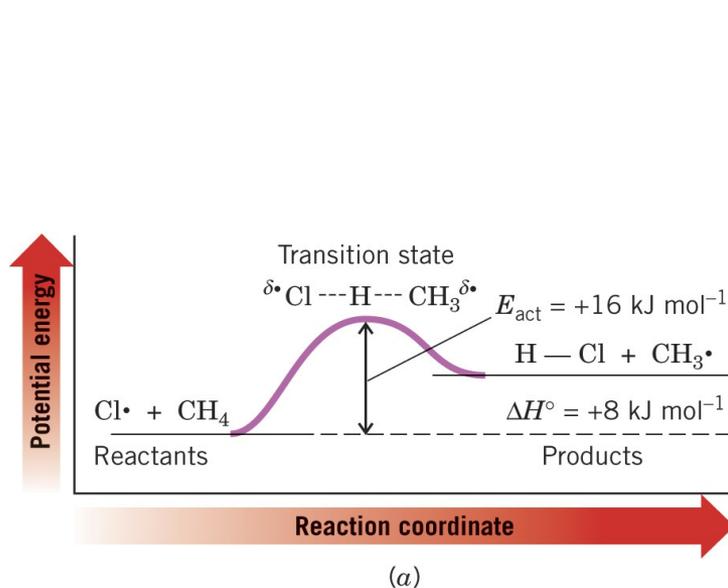


- Energy of activation values can be predicted

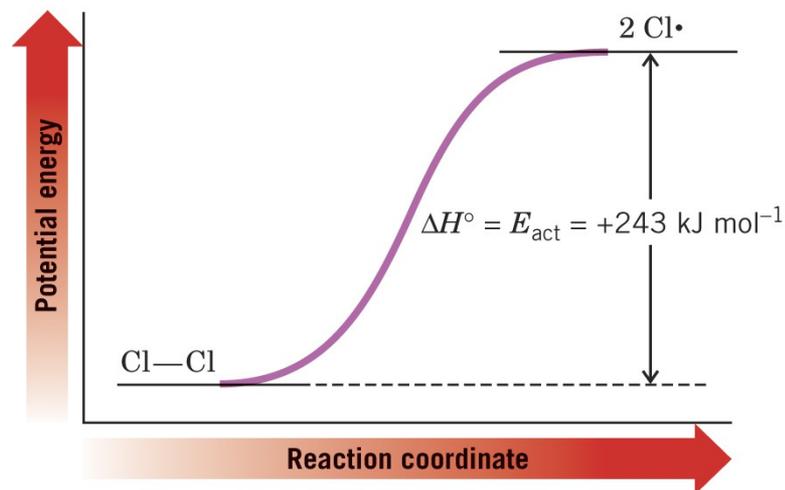
- ⌋ A reaction in which bonds are broken will have $E_{\text{act}} > 0$ even if a stronger bond is formed and the reaction is highly exothermic

- H Bond forming always lags behind bond breaking

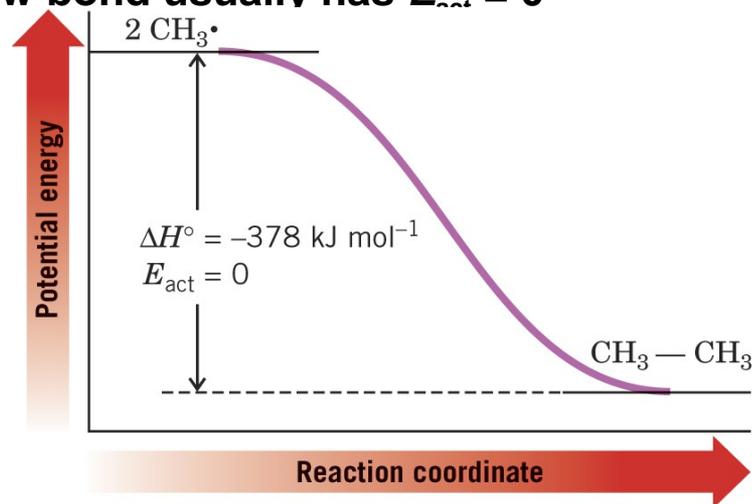
- ⌋ An endothermic reaction which involves bond breaking and bond forming will always have $E_{\text{act}} > \Delta H^\circ$



(A gas phase reaction in which only bond homolysis occurs has $\Delta H^\circ = E_{\text{act}}$

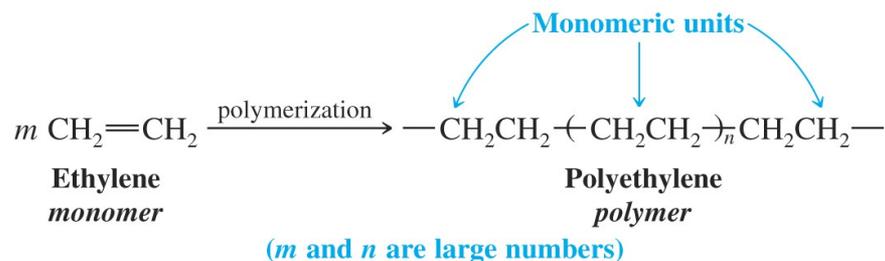


(A gas phase reaction in which small radicals combine to form a new bond usually has $E_{\text{act}} = 0$

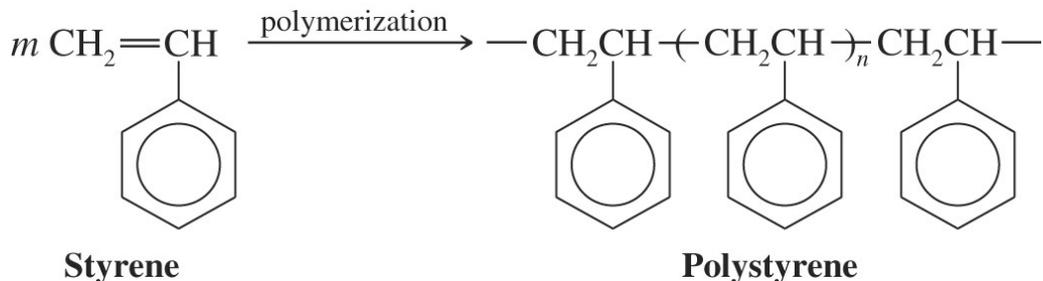


◆ Radical Polymerization of Alkenes: Chain-Growth Polymers

- Polymers are macromolecules made up of repeating subunits
 - The subunits used to synthesize polymers are called monomers
- Polyethylene is made of repeating subunits derived from ethylene
 - Polyethylene is called a chain-growth polymer or addition polymer

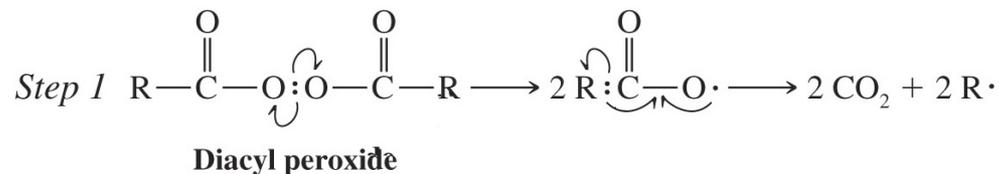


- Polystyrene is made in an analogous reaction using styrene as the monomer



- A very small amount of diacyl peroxide is added in initiating the reaction so that few but very long polymer chains are obtained

Chain Initiation



The diacyl peroxide dissociates and releases carbon dioxide gas. Alkyl radicals are produced, which in turn initiate chains.

- The propagation step simply adds more ethylene molecules to a growing chain

Chain Propagation



Chains propagate by adding successive ethylene units, until their growth is stopped by combination or disproportionation.

Monomer	Polymer	Names
$\text{CH}_2=\text{CHCH}_3$	$\text{-(CH}_2\text{-CH)}_n\text{-}$ CH_3	Polypropylene
$\text{CH}_2=\text{CHCl}$	$\text{-(CH}_2\text{-CH)}_n\text{-}$ Cl	Poly(vinyl chloride), PVC
$\text{CH}_2=\text{CHCN}$	$\text{-(CH}_2\text{-CH)}_n\text{-}$ CN	Polyacrylonitrile, Orlon
$\text{CF}_2=\text{CF}_2$	$\text{-(CF}_2\text{-CF}_2\text{)}_n\text{-}$	Polytetrafluoroethene, Teflon
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	$\text{-(CH}_2\text{-C)}_n\text{-}$ CH_3 CO_2CH_3	Poly(methyl methacrylate), Lucite, Plexiglas, Perspex