Introduction to organic reactions

$$2 \, C_7H_5N_3O_6 \; + \; 21 \text{ ``O''} \; \rightarrow \; 14 \, CO_2 \; + \; 5 \, H_2O \; + \; 3 \, N_2$$

Extra Credit Announcement

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Thursday, March 10th, 2016
12:00 NOON – 1:00 PM

Romita Auditorium, Ryan Library, Iona College
New Rochelle, New York

Outline

- Introduction to organic reactions and reaction mechanisms
- 1 electron (radical) chemistry
- 2 electron chemistry
  - Addition, substitution, elimination, rearrangement reactions
  - Polar functional groups, nucleophiles, electrophiles
- Equilibria
- Free energy
- Reaction rates & Reaction coordinate diagrams

Reaction mechanisms

- A step by step visual depiction of electron movement - using **"arrow pushing"** to describe bond formation and cleavage – leading to a overall chemical reaction

- Best depicted mechanisms are simple and **"elegant"**

- **Reaction rates** are not described by arrow pushing, but are included in a complete reaction mechanism

THE ART OF WRITING

REASONABLE

ORGANIC REACTION

MECHANISMS

ROBERT B. GROSSMAN
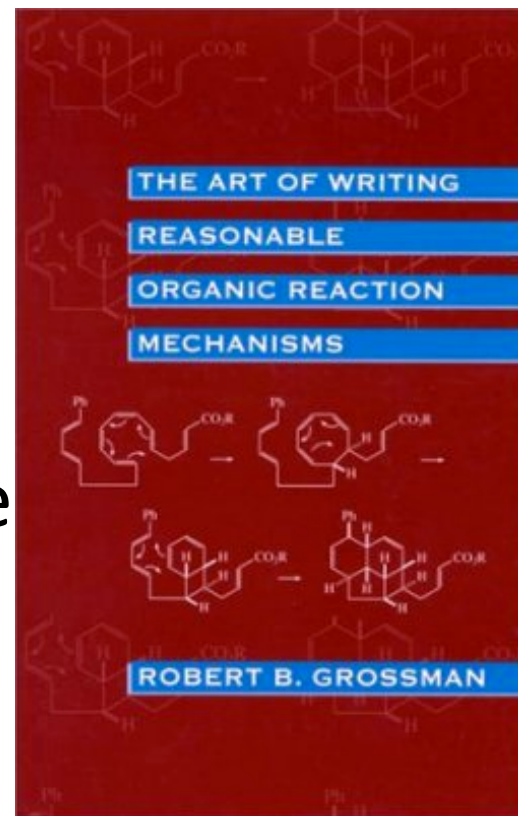
All Chemical Reaction Mechanisms are Classified into Three Basic Types

1. **Homolytic** (symmetrical bond breaking/making)
   – aka radical mechanisms or **one-electron chemistry**

2. **Heterolytic** (asymmetric bond breaking/making)
   - aka polar mechanisms or **two-electron chemistry**

3. **Pericyclic** reactions have *concerted* mechanisms, typically *rearrangements* with cyclic *transition states*.

$X = CR_2, NR, O$
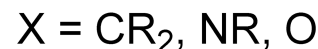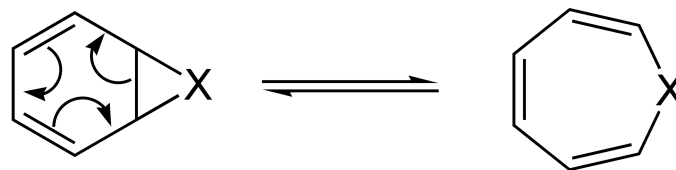
Homolytic (Radical) mechanisms

- Radicals "live fast and die young" – they are *highly reactive* and thus *short lived*

- Bond cleavage and bond formation are *both* possible

- Mechanistically represented by *single-headed arrows*

- Arrows represent movement of *one electron* (a radical or "free" radical)

- Molecules containing radicals are *neutral*

- Radicals are *unpaired electrons* in an orbital

- Biological occurrences include biosynthesis of prostaglandins and anti-oxidant activity (e.g. resveratrol from red wine)

- Polymer synthesis (polystyrene, polypropylene, PVC, surfactants, elastomers, carbon nanotubes, transparent PTMA solar cells
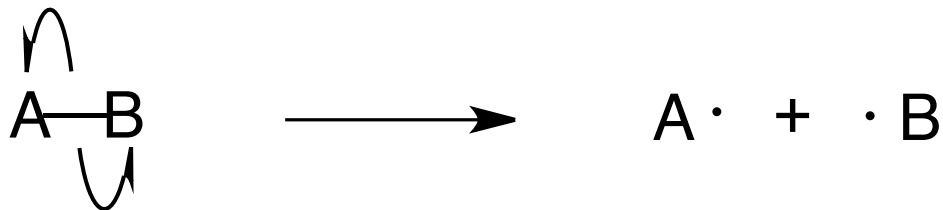

Micky Dora, "free radical" 1965
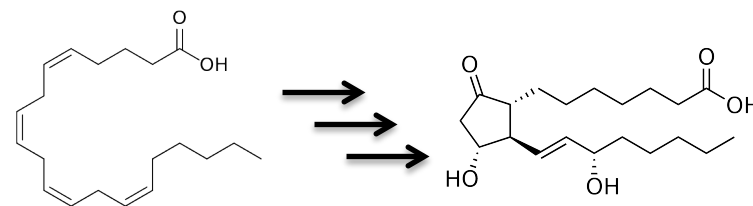

Prostaglandin biosynthesis

Polypropylene chairs

Homolytic Bond *Cleavage*

A—B $\longrightarrow$ A· + ·B

- Mechanistically represented by single-headed arrows
- One bonding e- stays with each product (bond cleavage)
- Radicals are neutral species
- Carbon atoms left with an odd number of e-s (7)
- Results in unpaired e-s in an orbital
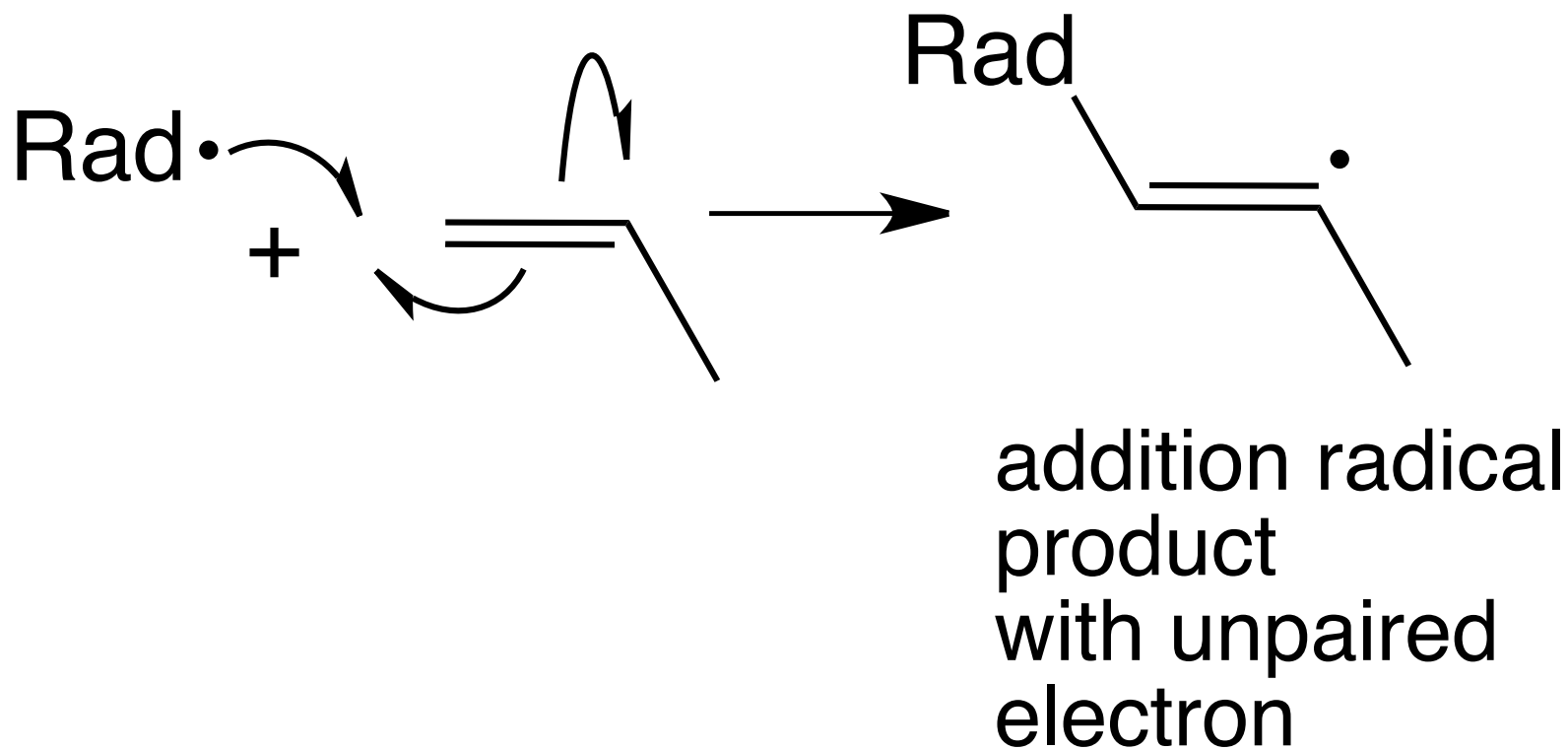- Radicals are highly reactive

Homolytic Bond *Formation*

A· + ·B = A· ·B ⟶ AB = A:B = A—B
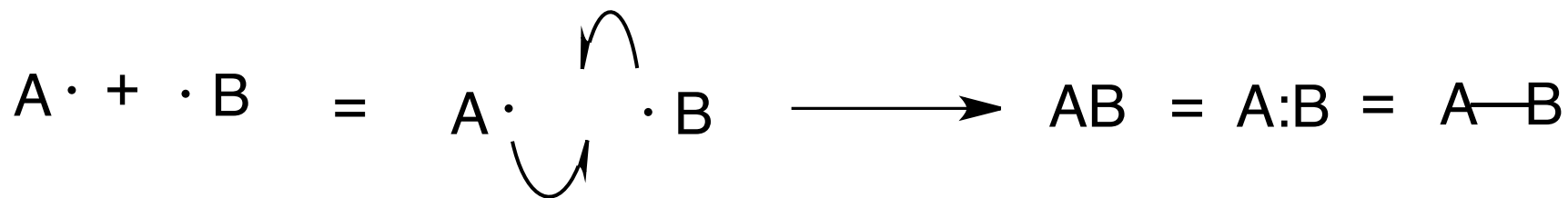
- One bonding electron derived from each reactant
- Result = formation of a new bond

Types of Homolytic Reactions

- Addition Reactions
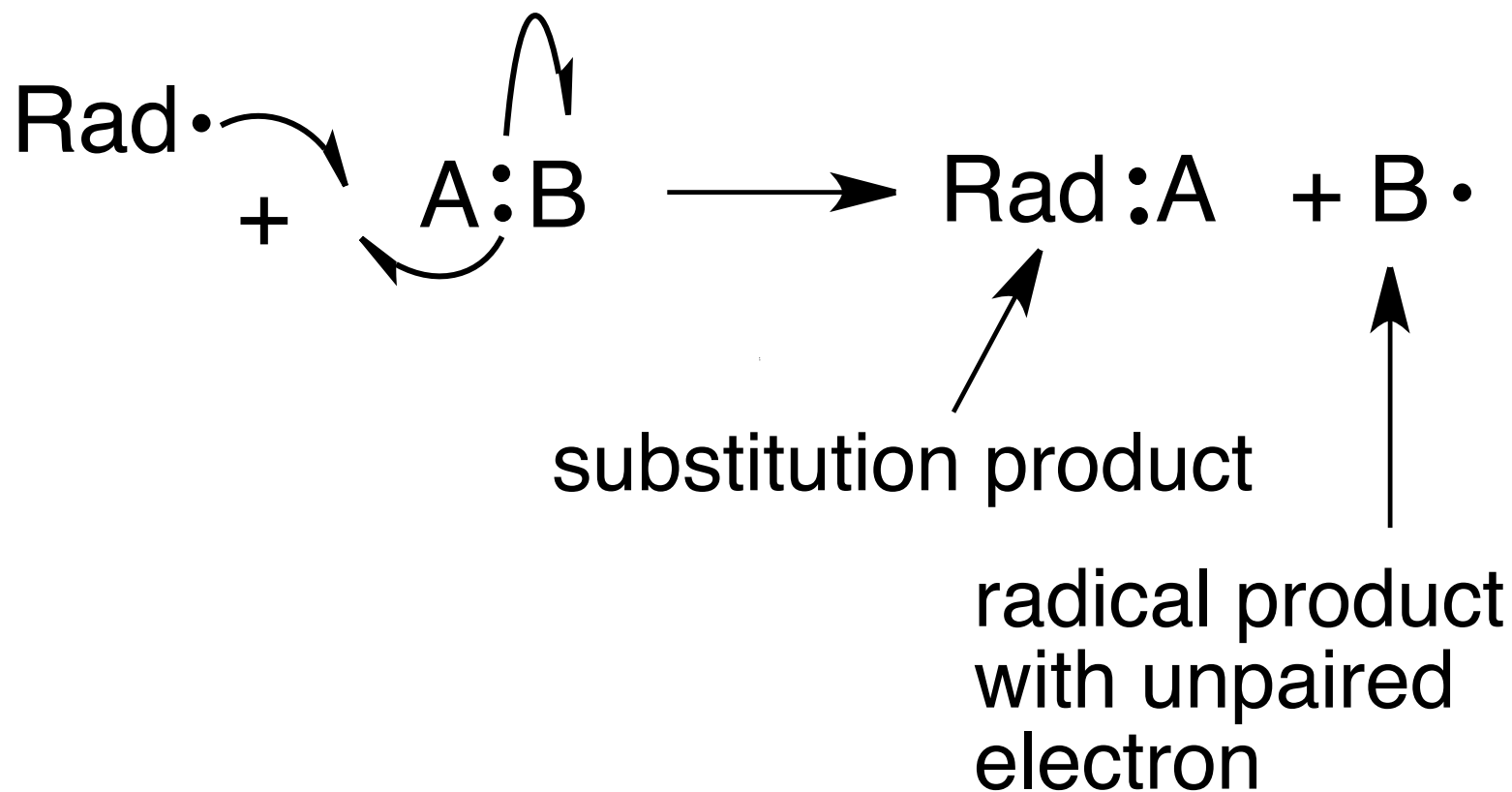- Substitution Reactions
- Chain Reactions

Radical *Addition*:
General Reaction Mechanism

Rad• + ⟶ Rad

addition radical
product
with unpaired
electron

Radical *Substitution*:
General reaction mechanism

Rad• + A:B → Rad:A + B•

substitution product

radical product
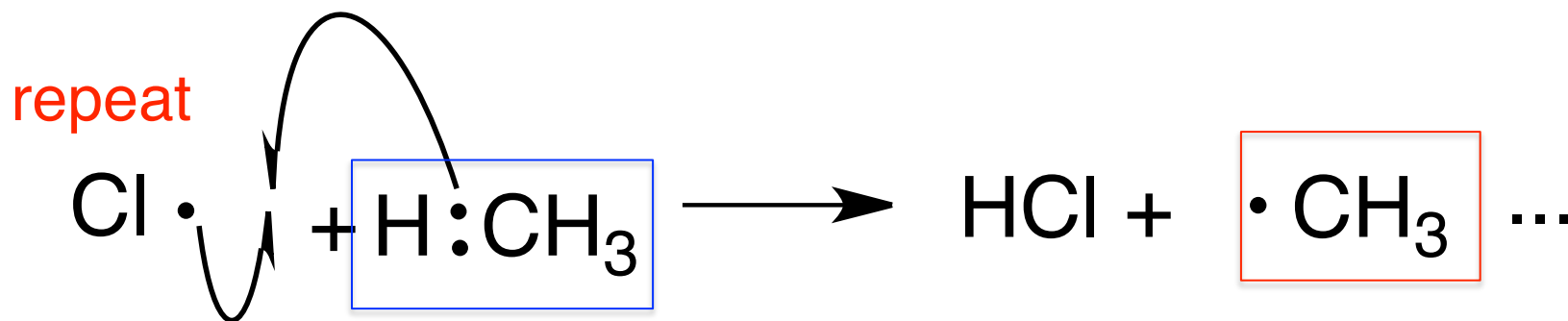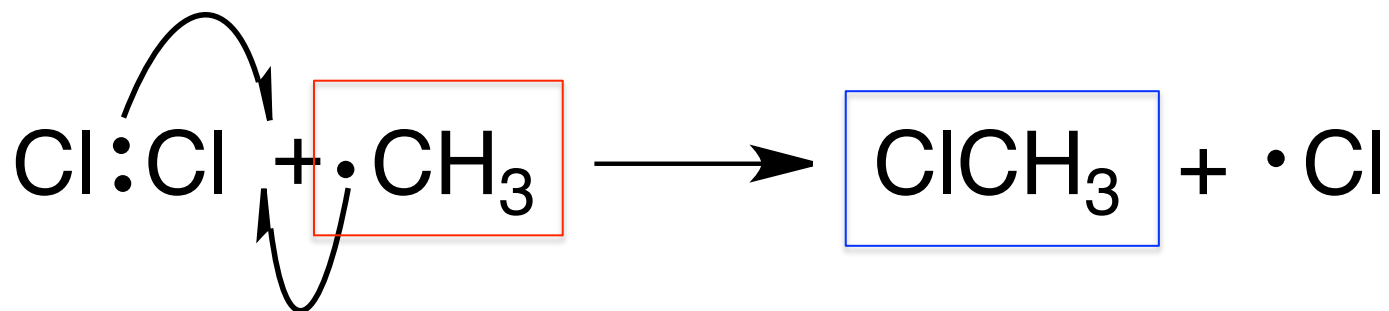with unpaired
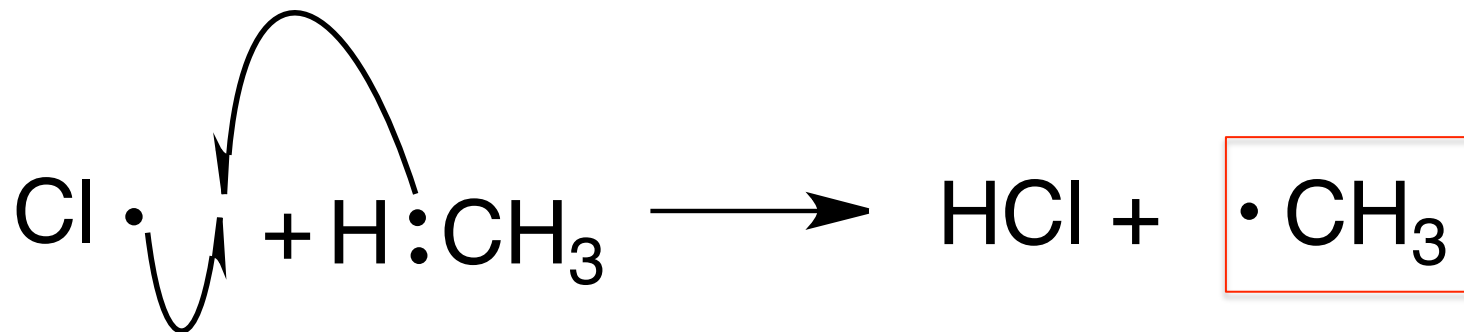electron

Chain Reactions

- Three steps: *initiation*, *propagation*, *termination*

- Used to produce *solvents* (e.g. DCM, chloroform) and *polymers* (polyethylene grocery bags, polystyrene foams, surfboards!, PVC pipes, etc.)
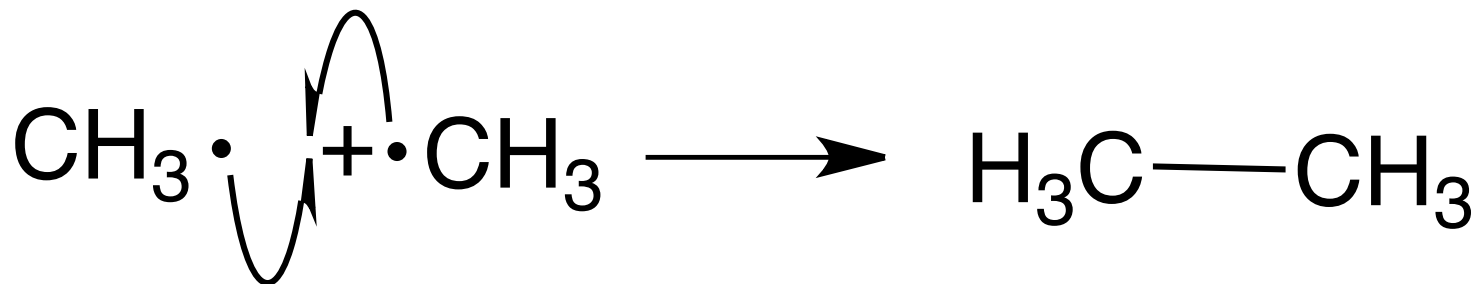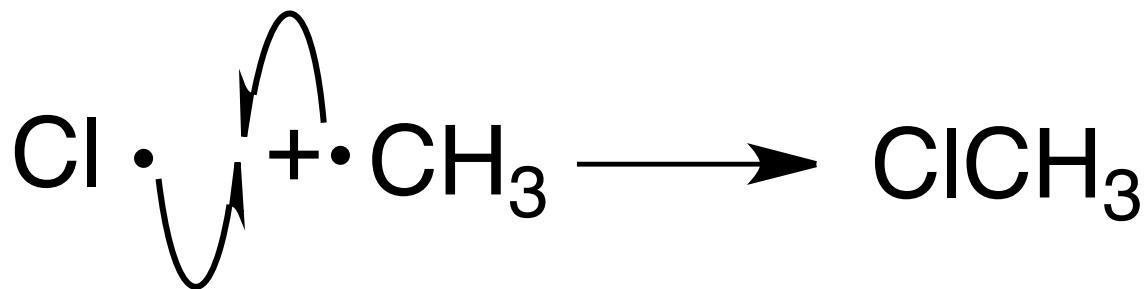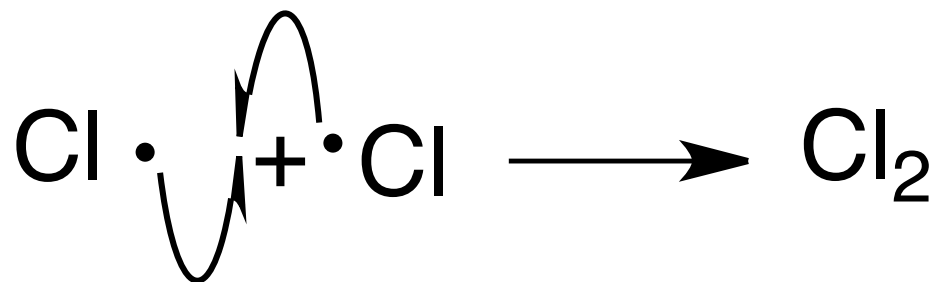
Radical Chain Reaction:
Part 1: Initiation

$$Cl{:}Cl \xrightarrow{h\nu} 2\ Cl\cdot$$
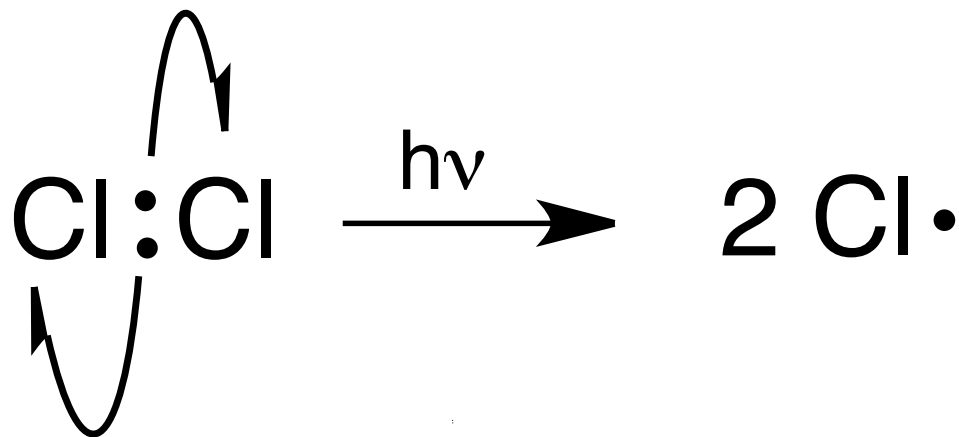
- Weak Cl-Cl bond (243 kJ/mol) is broken by irradiation at < 495 nm
- Only a small number of Cl_2 molecules / radicals actually form in this process, yet the process is still industrially efficient
- Other initiators used for other applications (e.g. peroxides, persulfates, azo compounds)

Radical Chain Reaction:
Part 2: Propagation

$Cl \cdot \quad + H:CH_3 \quad \longrightarrow \quad HCl + \quad \boxed{\cdot CH_3}$

$Cl:Cl \quad + \boxed{\cdot CH_3} \quad \longrightarrow \quad \boxed{ClCH_3} + \cdot Cl$

repeat

$Cl \cdot \quad + \boxed{H:CH_3} \quad \longrightarrow \quad HCl + \quad \boxed{\cdot CH_3} \quad \ldots$

Radical Chain Reaction:
Part 3: Termination

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

$$Cl \cdot + \cdot CH_3 \longrightarrow ClCH_3$$

$$CH_3 \cdot + \cdot CH_3 \longrightarrow H_3C \text{—} CH_3$$

In all cases, two radicals combine to form a stable product

Heterolytic (Polar) Reactions Mechanisms

- Represented by double headed arrows
- Two electron chemistry
- Much more common
- Unsymmetrical bond breakage or formation
- Results in polar species bearing (+) and (-) charges
- When two bonding e-s stay with product = -ve charge
- When two bonding e-s migrate = +ve charge
- Leads to even number of electrons in carbon orbitals (carbocations = 6, and carbanions = 8)

# All Chemical Reactions are Classified into Four Basic Types

1. **Addition** – two reactants come together and no atoms are wasted. "Good atom economy"

2. **Substitution** – when two reactants exchange atoms to give give two new products

3. **Elimination** – essentially the opposite as an addition reaction whereby reactant splits into two products

4. **Rearrangement** – when a single reactant undergoes a reorganization of bonds and atoms to yield an isomeric product

Polar Reactions

- Neutrally charged organic compounds often have "polarized" electron density

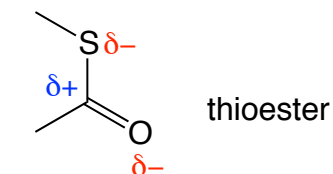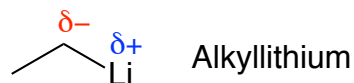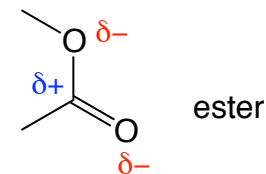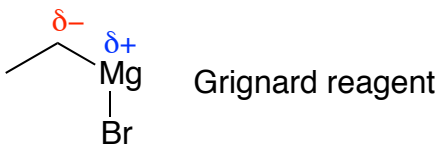Often due to *Electronegativity Difference* between atoms:

- N, O, Halogen = more electronegative than C
- Metals = less electronegative than C
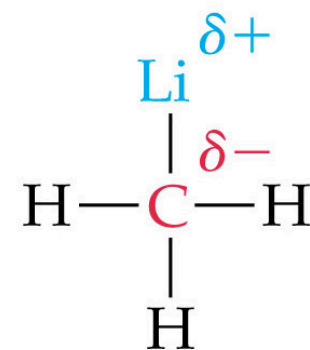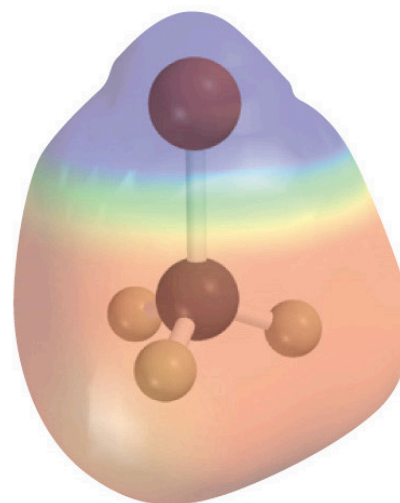
Methyl lithium has an electron rich carbon atom with a partial negative charge ($\delta-$) known as a "nucleophile"

The lithium atom has a partial positive charge ($\delta+$)

Polarity Patterns in Common Functional Groups
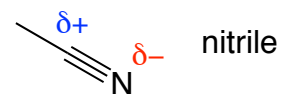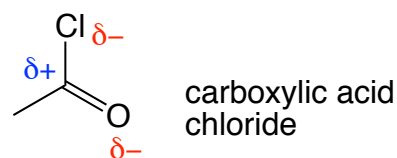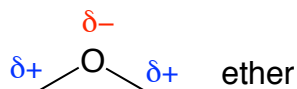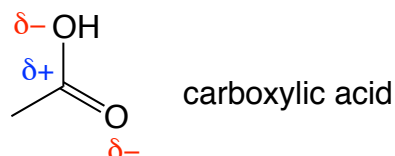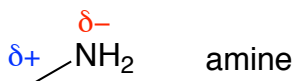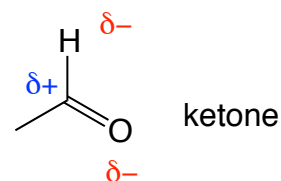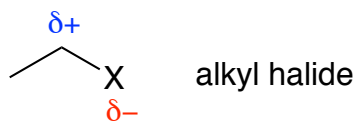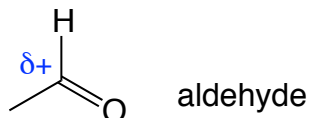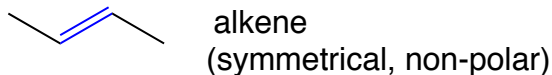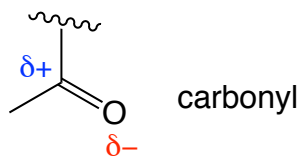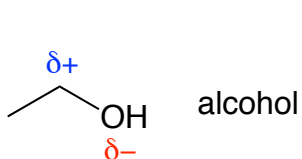
$\delta+$ = electrophilic site
= electron acceptor site
= Lewis acidic site

$\delta-$ = nucleophilic site
= electron donor site
= Lewis basic site

Polarizability

- Different than a polar bond; it is a dynamic quality of a specific atom
- Measure of the *response* of a atom in a molecule to an external electric field
- *Influenced* by interactions between solvent or polar molecules nearby
- e- distribution around the atom and (by extension) the molecule *changes*
- ***Larger atoms* with more loosely held e-'s are *more "polarizable"***
- ***Smaller atoms* with fewer, tightly held e-'s are *less "polarizable"***

For example:

C, S and I all have same Pauling electronegativity (2.5) so we would expect non-polar C-S and C-I bonds

However, because S and I are larger and polarizable than carbon, polar bonds result and $\delta+$ carbon atom becomes "*electrophilic*"

$\delta-$ OH $\delta-$ SH $\delta-$ Cl $\delta-$ I
$\delta+$ $\delta+$ $\delta+$ $\delta+$
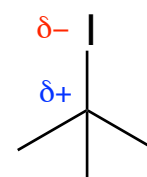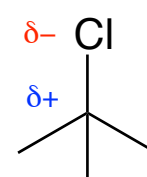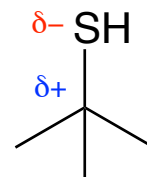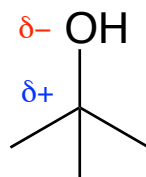
Electronegativity
C = 2.5
O = 3.5
S = 2.5
Cl = 3.0
I = 2.5

Why is this important for heterolytic reactions?

- Fundamental characteristic of heterolytic organic reactions is that e- rich sites react with e- poor sites
- *Bond making*: an e- rich atom donates an e-pair to an e- poor atom
- *Bond breaking*: when one atom leaves with both e-s from the former bond

(Nu:) Nucleophiles vs. Electrophiles (E)

- "Nucleus loving" (The nucleus is +vely charged)
- Has a negatively polarized, e- rich atom
- Forms new bonds by donating e-s
- Can either be neutral or negatively charged
- Neutral nucleophiles (ammonia NH_3, water H_2O) have lone pairs
- Negatively charged nucleophiles (hydroxide ion OH^-, chloride ion Cl^-) have lone pairs
- Typically Lewis *bases* (e- donors)

- "Electron loving"
- Positively charged, electron poor atom
- Forms bonds by accepting e-s from nucleophile
- Can be neutral of positively charged
- Neutral electrophiles (carbonyl compounds, alkyl halides)
- Positively charged electrophiles (hydronium ion, carbocations)
- Typically Lewis *acids* (e-

Interaction between nucleophiles and electrophiles

B : + A $\longrightarrow$ A——B
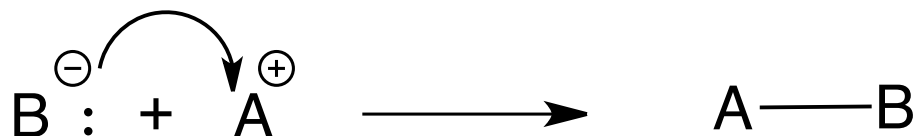
nucleophile   **electrophile**   electrons that moved from B:⁻ to A⁺
(electron rich)   (electron poor)   are now located in *new covalent bond*

* Note direction of electron movement (arrow pointing) from rich to poor

The Nucleophile *can be negatively charged or neutral*
    if negatively charged, it becomes neutral
    if neutral, it become positively charged

negatively charged
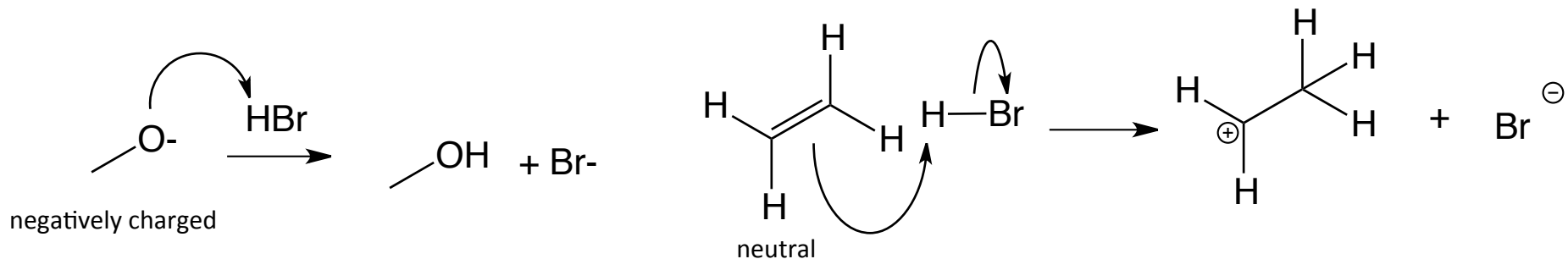
neutral

The Electrophile *can be positively charged or neutral*
    if positively charged, it becomes neutral
    if neutral, it becomes negatively charged

positively charged

neutral
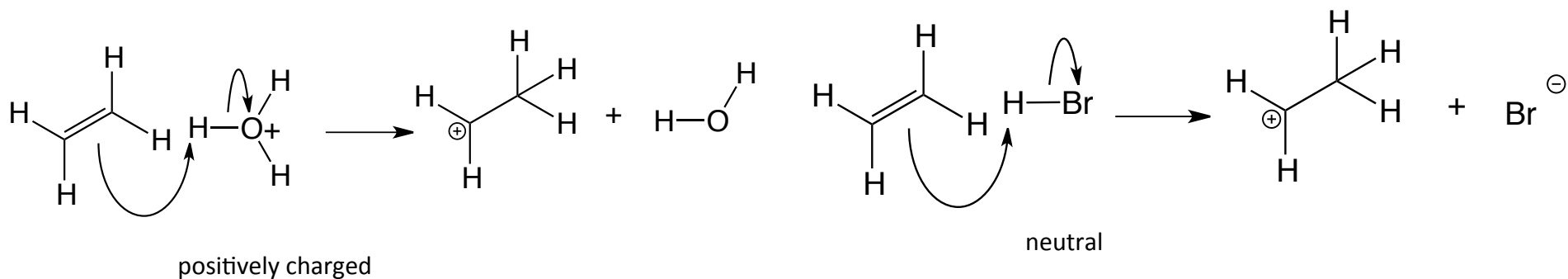
Heterolytic mechanisms

B:⁻ + A⁺ ⟶ A:B
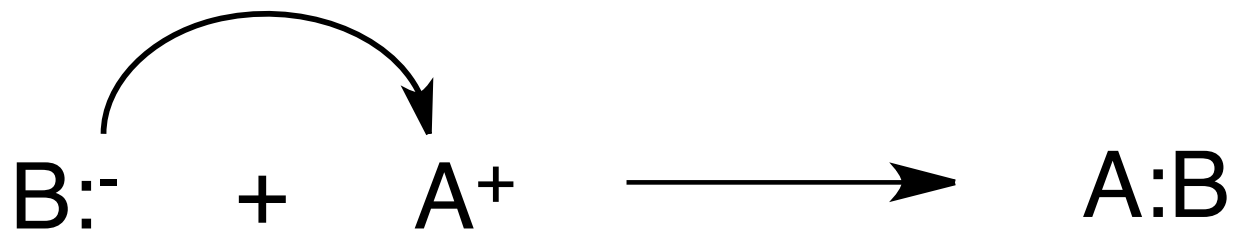
Heterolytic bond formation

A:B ⟶ A⁺ + B:⁻
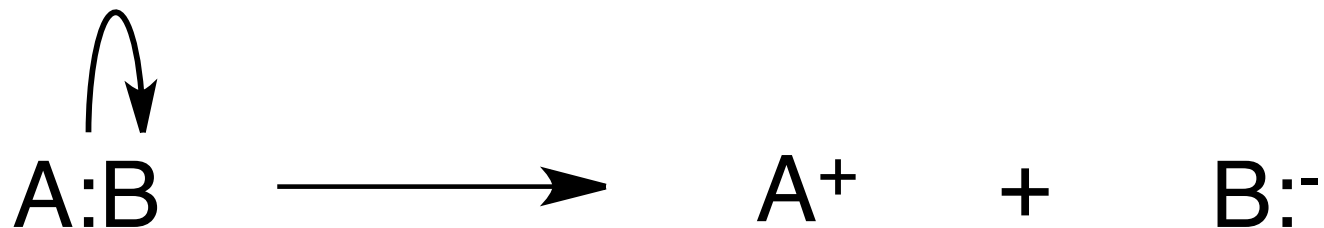
Heterolytic bond cleavage

The art of drawing reasonable reaction mechanisms

Electrons must move from a nucleophilic source (Nu:) to an electrophilic sink (E)

Nucleophilic source must have electron pair available as a lone pair or in a multiple bond
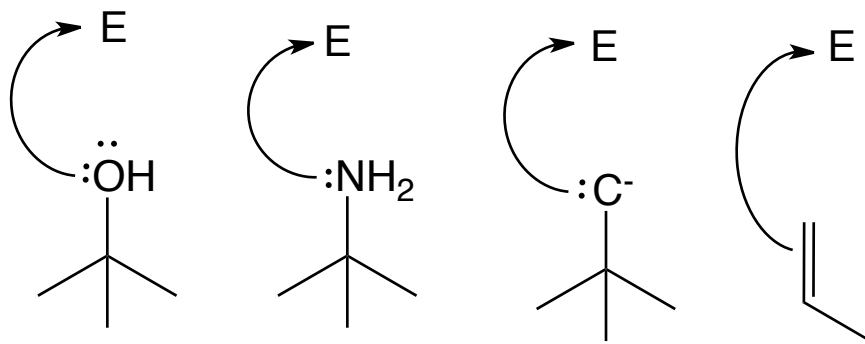
Electrophilic sink must have be able to accept a pair or electrons, either on a positively charged atom or an atom with partial positive charge (polarized bond)
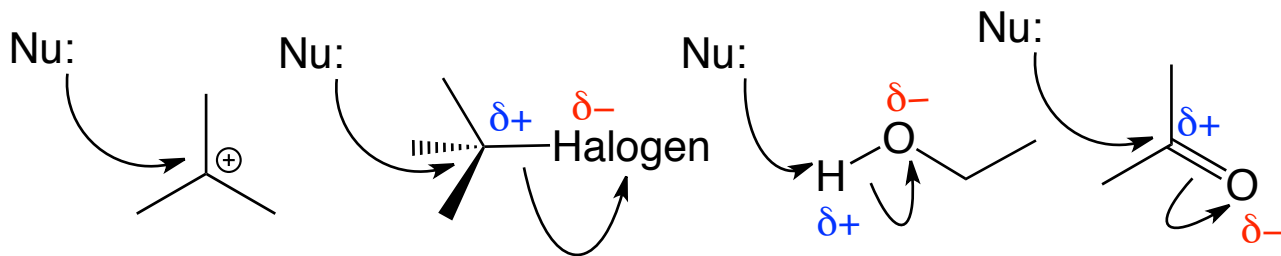
Follow the octet rule

- Moving electrons must be done so all atoms are left with 8 electrons (or 2 electrons for H), or appropriate + or – charges (i.e. protons, carbocations, carbanions)

- No second row atom (C, N, O) can be left with 10 electrons (or 4 for H)

- If an electron pair moves to an atom that already has an octet (or 2 electrons if H) then another electron pair must move simultaneously away from that atom to maintain the octet

Addition reactions
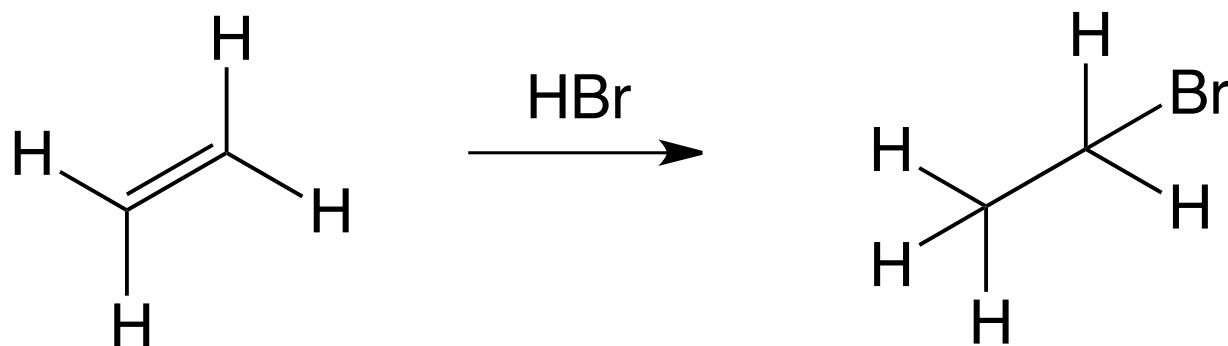
- Good "atom economy" – 2nd Principal of Green Chemistry
- Atom economy asks "what atoms of the reactants are incorporated into the final desired product(s) and what atoms are wasted?" [1]
- The opposite of elimination reactions

[1]The Atom Economy-A Search for Synthetic Efficiency; Barry M. Trost; *Science* 1991, (254), pp 1471-1477.

Electrophilic addition of HBr to ethylene
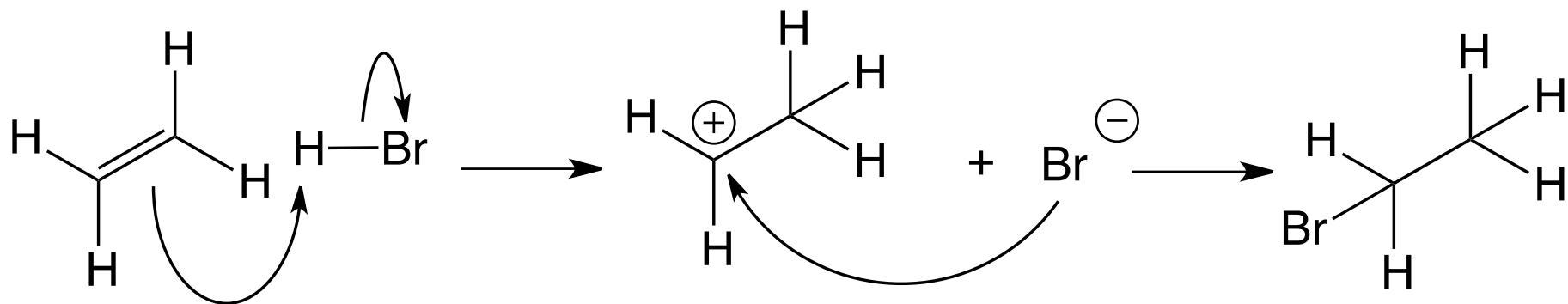
- Ethylene is nucleophile
- HBr is electrophile

- Two electrons move onto bromine giving bromide ion
- Ethane carbocation has a vacant p-orbital
- Bromide "attacks" carbocation

- Addition product

Electrophilic addition reaction of ethylene and HBr

HBr = strong acid
H^+ is good electrophile

Br^- = electron rich, good nucleophile

nucleophilic alkene

electrophilic carbocation with vacant p orbital easily attacked by bromide ion

addition product
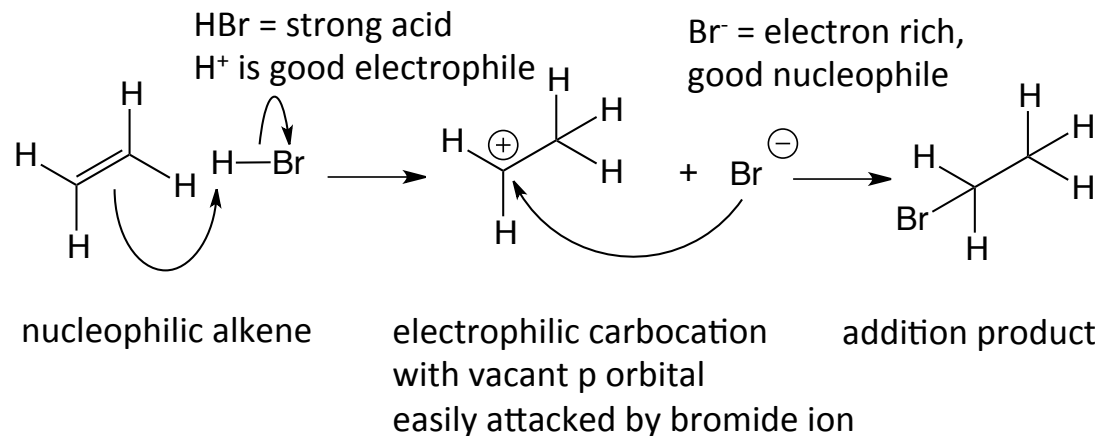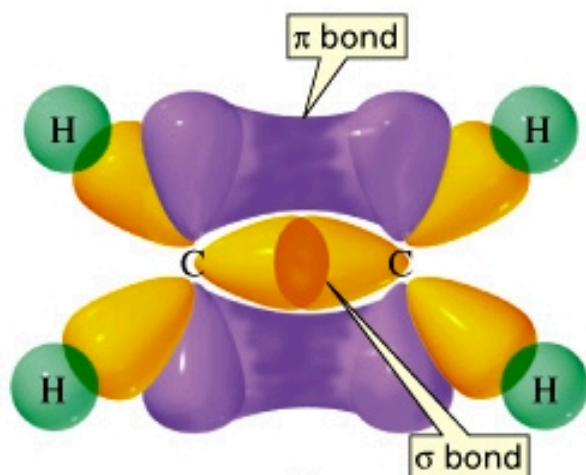
Alkane (C-C and C-H single bonds) electrons in sigma bonds, close to nucleus, non-polar, inert

Alkenes (C=C double bonds) have greater e- density (4 instead of 2 e-s), are accessible (i.e. pi bond located above and below plane of sp^2, trigonal planar molecule), and are further from nucleus.

Therefore, alkene double bonds can react as nucleophiles

Elimination Reactions
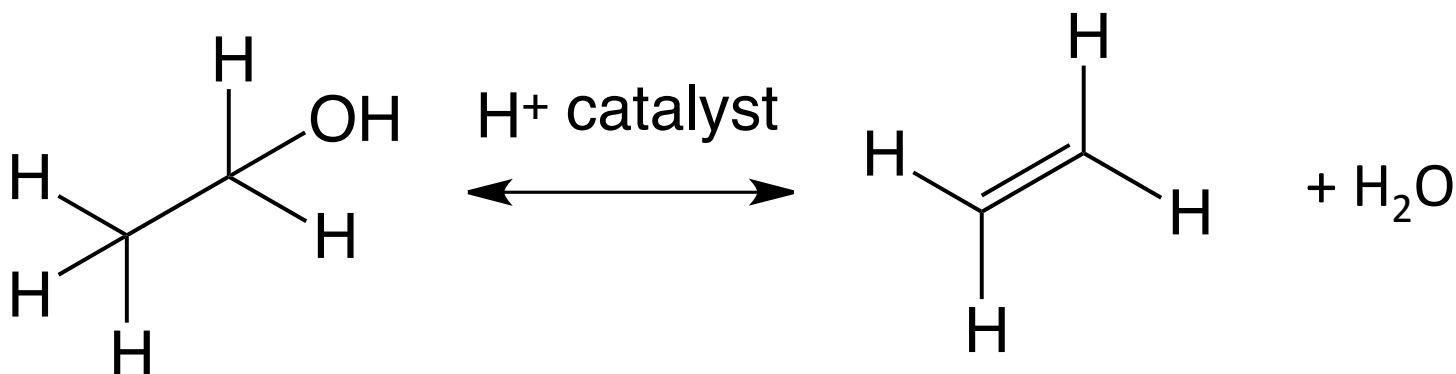
- Reactant splits into two products, one is usually small (i.e. HBr or H_2O)
- Occur by three different mechanisms (E1, E2, E1cB)
- Often equilibrium reactions
- Considered the opposite of addition reactions

E1 Elimination
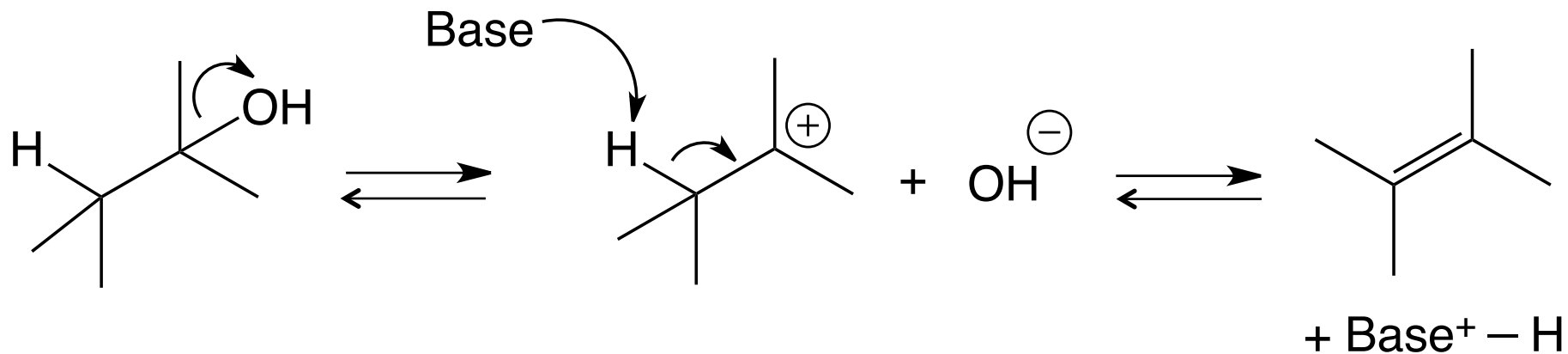
- C-OH bond breaks

- Carbocation intermediate formed
- Base removes proton

- Alkene product

Substitution Reactions

Methyl acetate (ester)

$+$ H_2O $\longrightarrow$

Acetic acid (carboxylic acid)

$+$ CH_3OH
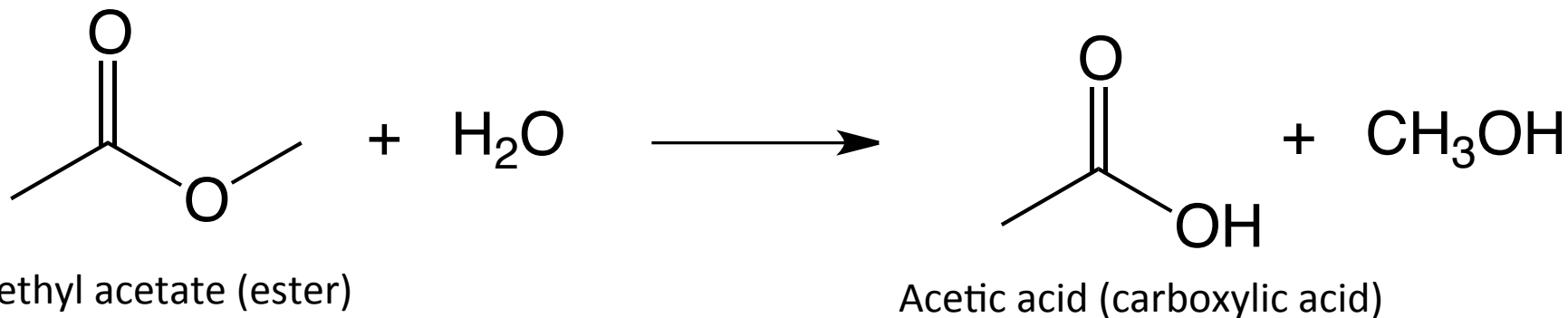
- One functional group of a compound is replaced by another function group
- Classified as either bimolecular or unimolecular depending on specific mechanism involved
- Carbocation, carbanion or radical intermediates
- Aliphatic or aromatic substrates
- Many occur in biological systems (e.g. fat metabolism)

S$_N$2 substitution reaction

(R)-2-bromobutane

(S)-2-butanol
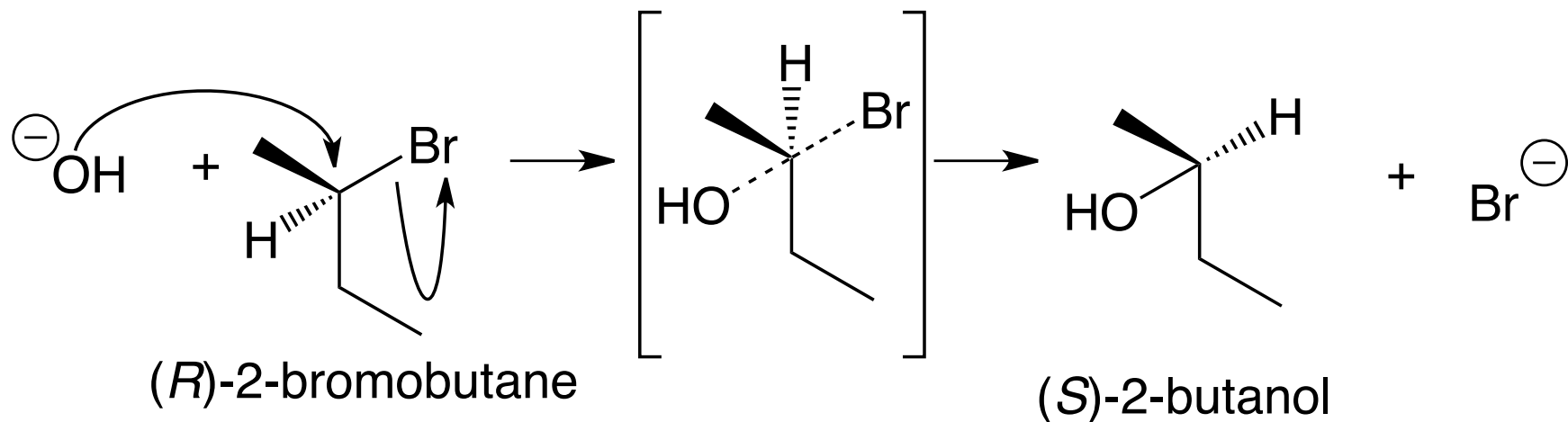
- Nucleophilic OH- attacks the electrophilic carbon atom

- Planar transition state where C-OH bond is forming while C-Br bond is breaking

- Product has *inverted* stereochemistry

Rearrangement Reactions
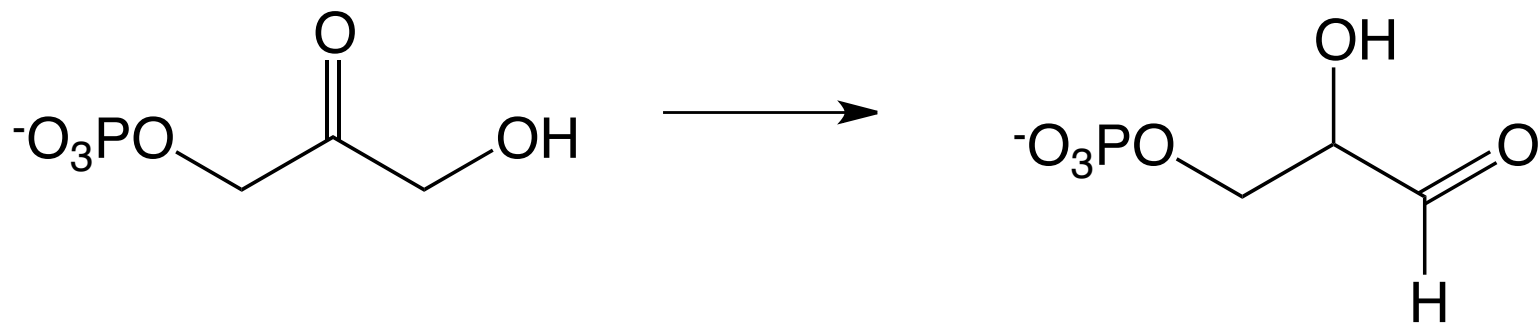
dihydroxyacetone phosphate   glyceraldehyde-3-phosphate

- Broad class of organic reactions where carbon skeleton is rearranged to give a constitutional (structural) isomer

- Not well described by "arrow pushing"

- Often involving orbital interactions (i.e. pericyclic reactions)

- Examples include 1,2-rearrangements, pericyclic reactions and olefin metathesis

Rearrangement reaction: 1,2-hydride shift
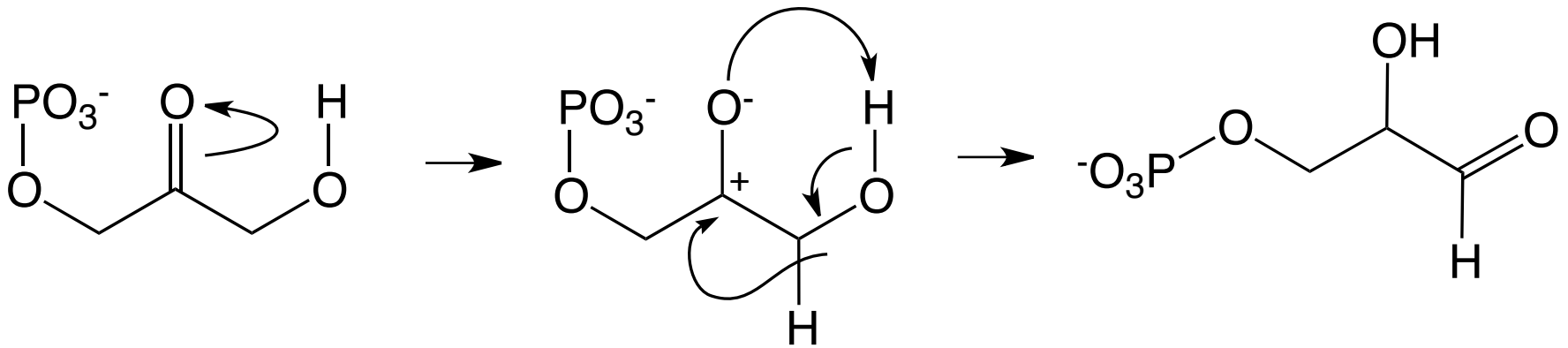
- Electrons of ketone double bond migrate to form alkoxide/ carbocation intermediate

- Alkoxide oxygen abstracts proton from alcohol
- Electrons collapse to form aldehyde
- Hydride ion shifts to carbonyl carbon atom

- Rearrangement product

Polar bonds resulting from interaction of functional groups with Brønsted _**acids**_

Methanol C is _somewhat_ electron poor due to bonding with electronegative oxygen atom

H—O $\delta-$

C $\delta+$

H H H

H—A

→

H—O+—H

C $\delta+$

H H H

+ A $^{\ominus}$:
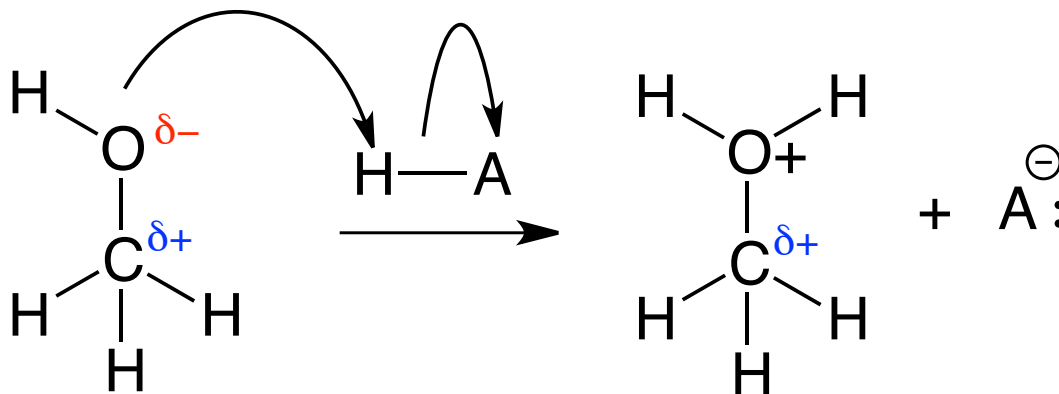
Upon protonation with acid, methanol C is _very_ electron poor because electrons of C-O bond are also needed by two O-H bonds

As a result, C is much more _**electrophilic**_

Polar bonds resulting from interaction of functional groups with Brønsted **_bases_**

Methanol O is _somewhat_ **nucleophilic** due to 2 lone pairs
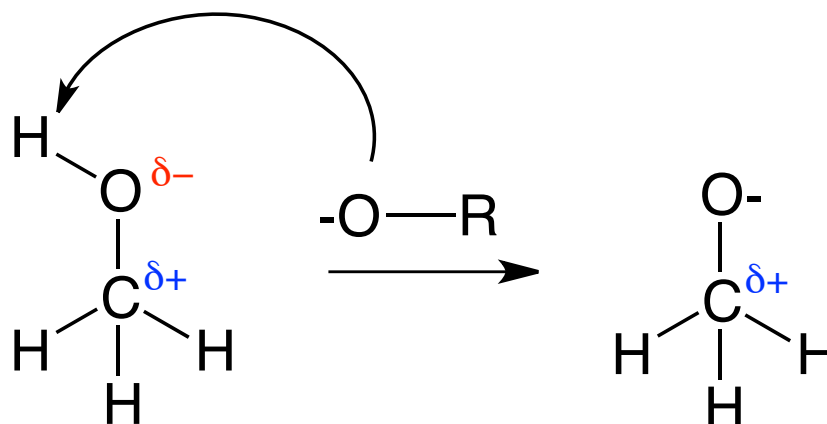
Methoxide ion O is _very_ **nucleophilic** due to 3 lone pairs

Course Updates

- Homework notebooks DUE next week (3/16)
- Quiz 3 (in class) next week (3/16) on chapters 6 & 7
- No class on March 30
- Green Chemistry presentation topics + abstracts DUE March 30 (Title + 1 paragraph abstract)
- Extra Credit Tomorrow at Iona College 12-1pm

Equilibria

All chemical reactions can proceed in either the forward or reverse direction

For the general reaction:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

K_{eq} = The equilibrium constant. Dictates the direction of the equilibrium and is determined experimentally:
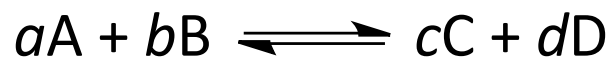
$K_{eq} > 1$ reaction proceeds forward
$K_{eq} = 1$ reaction contains equal mix of reactant and product
$K_{eq} < 1$ reaction proceeds in reverse

$$K_{eq} = \frac{[\text{C}]^c \, [\text{D}]^d}{[\text{A}]^a \, [\text{B}]^b}$$

Stoichiometry
Concentration

For practical purposes,
If $K_{eq} > 10^3$ then there are
no detectable products in the
reaction mixture (< 0.1%)

What determines the magnitude of K_{eq}?

For a reaction to proceed, the free energy of the products must be lower (more stable), than the free energy of the reactants.

In terms of a chemical reaction, this change in Energy is called "Gibbs Free Energy" (ΔG)

$\Delta G = G_{products} - G_{reactants}$

$-\Delta G$ = energy is released from chemical system to the surroundings (a.k.a. *energy released* = exergonic reaction)

$+\Delta G$ = energy is absorbed by chemical system from surroundings (a.k.a. *energy required* = endergonic reaction)

ΔG^o = Standard free energy change (1 atm, 298K,

1.0 M solute concentrations

Relationship between Equilibria and Free Energy

Equilibrium constants (K_{eq}) and standard free energy changes (ΔG^o) *both measure whether a reaction is favorable,* and they are related:

$$\Delta G^o = -RT\; ln\; K_{eq}$$

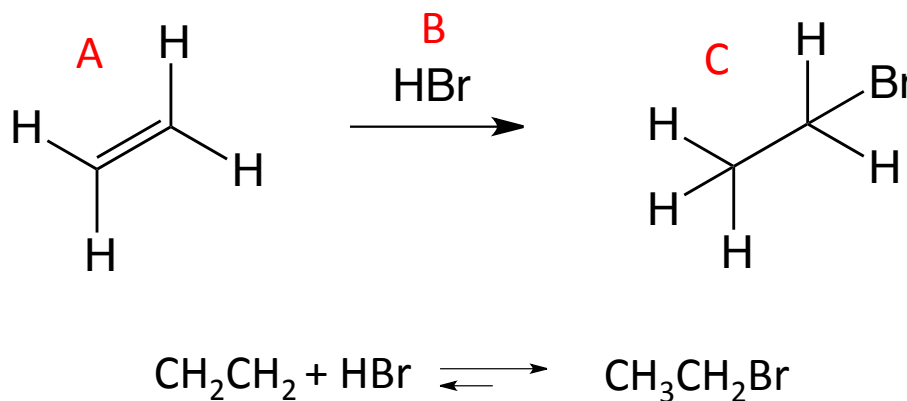where: R = 8.314 J / (K mol)

T = Temperature Kelvin

$ln\; K_{eq}$ = natural logarithm of K_{eq}

Reaction of ethylene with HBr

$$K_{eq} = \frac{[C]^c}{[A]^a\,[B]^b}$$

$$= \frac{[CH_3CH_2Br]}{[CH_2CH_2]\,[HBr]} = 7.1 \times 10^7$$

A   B   C

HBr

$CH_2CH_2 + HBr \rightleftharpoons CH_3CH_2Br$

$\Delta G^o = -RT\,ln\,K_{eq}$

$= -[8.314\ J/(K\ mol)]\,(298K)\,(18.08)$

$= -44{,}800\ J/mol = \textit{-44.8 kJ/mol}$

The reaction is exergonic (energy releasing) under standard conditions

This is to say the reaction is "favorable" under standard conditions

Relationship between Thermodynamic Principals and Free Energy

ΔG is comprised of three terms:

Enthalpy (ΔH) = bond energy (heat provided by chemicals)

Temperature (T) = heat provided by chemist

Entropy (ΔS) = molecular randomness energy (temperature dependent)

Related through the equation:

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

Enthalpy (ΔH)

- a.k.a heat of reaction
- Often larger and more dominant term in ΔG equation
- Essentially the <u>difference in bond energies</u> between reactants and products
- But also takes into account resonance, strain and solvation energies

Exothermic = -ΔH = products more stable than reactants
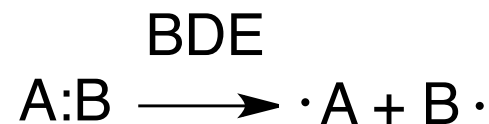Endothermic = +ΔH = reactants more stable than products

Bond Dissociation Energies (KJ/mol)

ΔH = (Total BDE of products – Total BDE of reactants)

Measured in a calorimeter

Bonds form = energy released
Bonds break = energy consumed

$$A{:}B \xrightarrow{\text{BDE}} \cdot A + B \cdot$$

H—H	436[a]	C—H	410	N—H	390	O—H	460	F—F	159[a]
H—C	410	C—C	350	N—C	300	O—C	350	Cl—Cl	243[a]
H—F	570[a]	C—F	450	N—F	270	O—F	180	Br—Br	193[a]
H—Cl	432[a]	C—Cl	330	N—Cl	200	O—Cl	200	I—I	151[a]
H—Br	366[a]	C—Br	270	N—Br	240	O—Br	210	S—F	310
H—I	298[a]	C—I	240	N—I	—	O—I	220	S—Cl	250
H—N	390	C—N	300	N—N	240	O—N	200	S—Br	210
H—O	460	C—O	350	N—O	200	O—O	180	S—S	225
H—S	340	C—S	260	N—S	—	O—S	—		

Multiple covalent bonds[b]

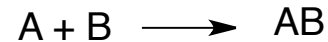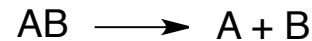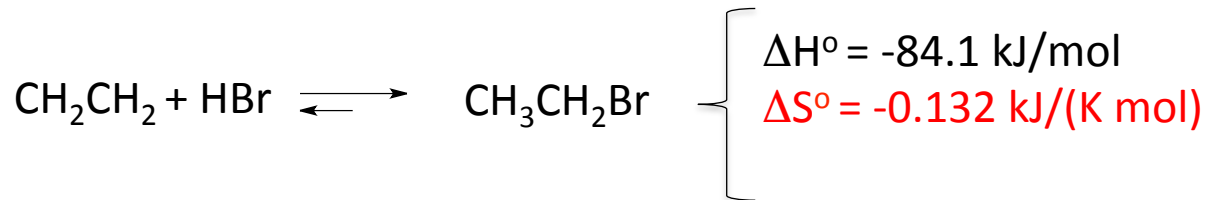| C=C	611	C≡C	835	C=O	732	O=O	498[a]	N≡N	945[a]

[a] Exact value

Entropy (ΔS)

- Measure of the amount of disorder or randomness of a system
- Temperature dependent in the Gibbs equation
- Not typically a large number
- Determined experimentally
- Nature prefers high entropy (disorder)

+ΔS = randomness increases

-ΔS = randomness decreases

$$AB \longrightarrow A + B$$

$$A + B \longrightarrow AB$$

Thermodynamics of HBr Addition to Ethylene

$$CH_2CH_2 + HBr \rightleftharpoons CH_3CH_2Br$$

$\Delta H^o = -84.1$ kJ/mol
$\Delta S^o = -0.132$ kJ/(K mol)

- *Negative entropy term because randomness decreases*
- *Notice the large temperature influence on ΔG*

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

$= -84.1$ kJ/mol $- (298$ K $* -0.132$ kJ/K mol$)$
$= -84.1$ kJ/mol $- (-39.3$ kJ/mol$)$

$\Delta G^o = -44.8$ kJ/mol

# Difference between Equilibrium and Rate

K_{eq} tells only how much product is possible, but does ***not*** tell how fast it is made

Some reaction are very slow, even under favorable conditions.

Gasoline is stable at RT because reaction rate with oxygen is slow. When sparked (higher T) the reactants are quickly converted to products

Reaction Coordinate Diagrams

- Used to visualize the progress of a reaction with respect to energetics <u>and rate</u>
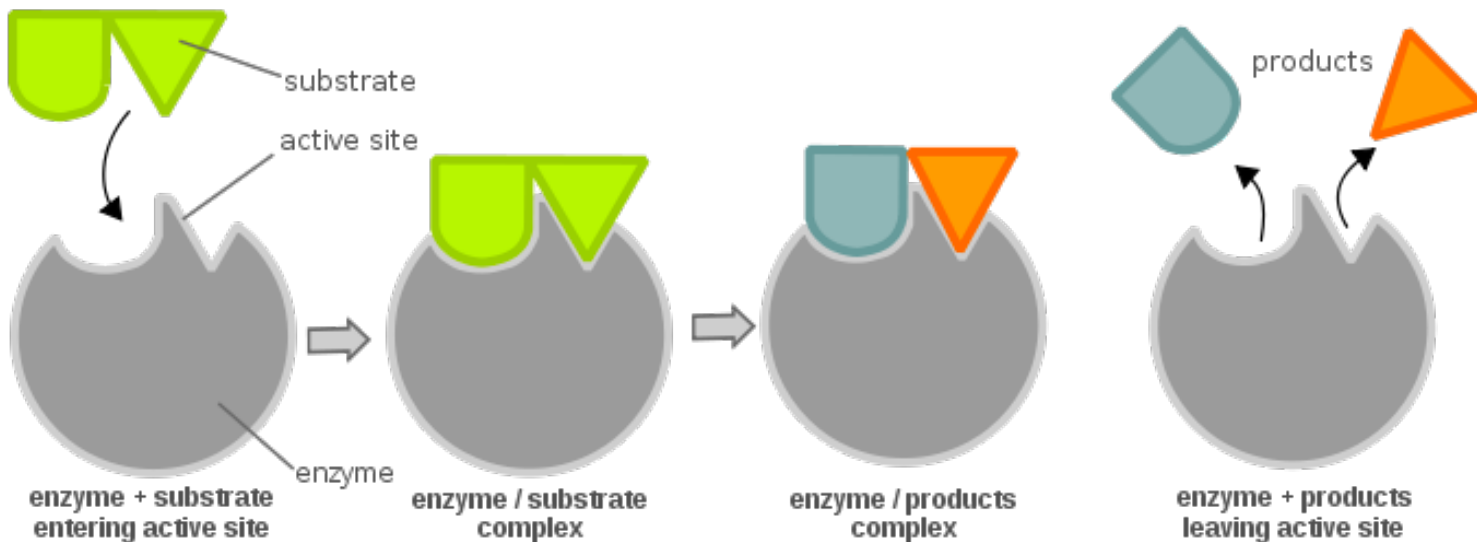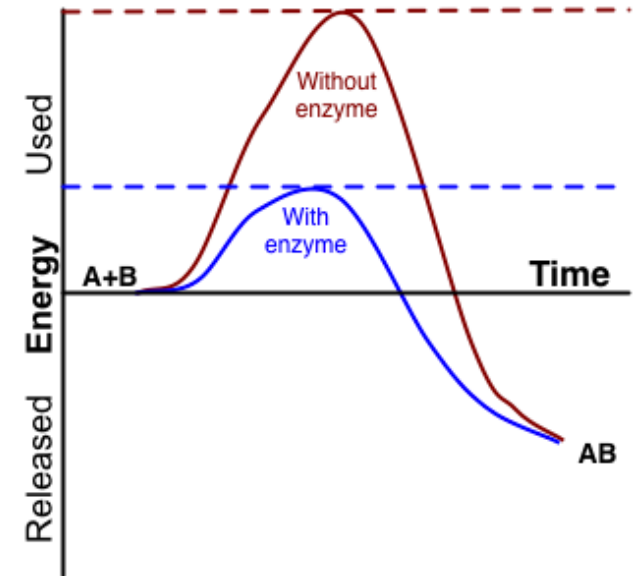- Can be used to show differences in reaction progress with catalyst present
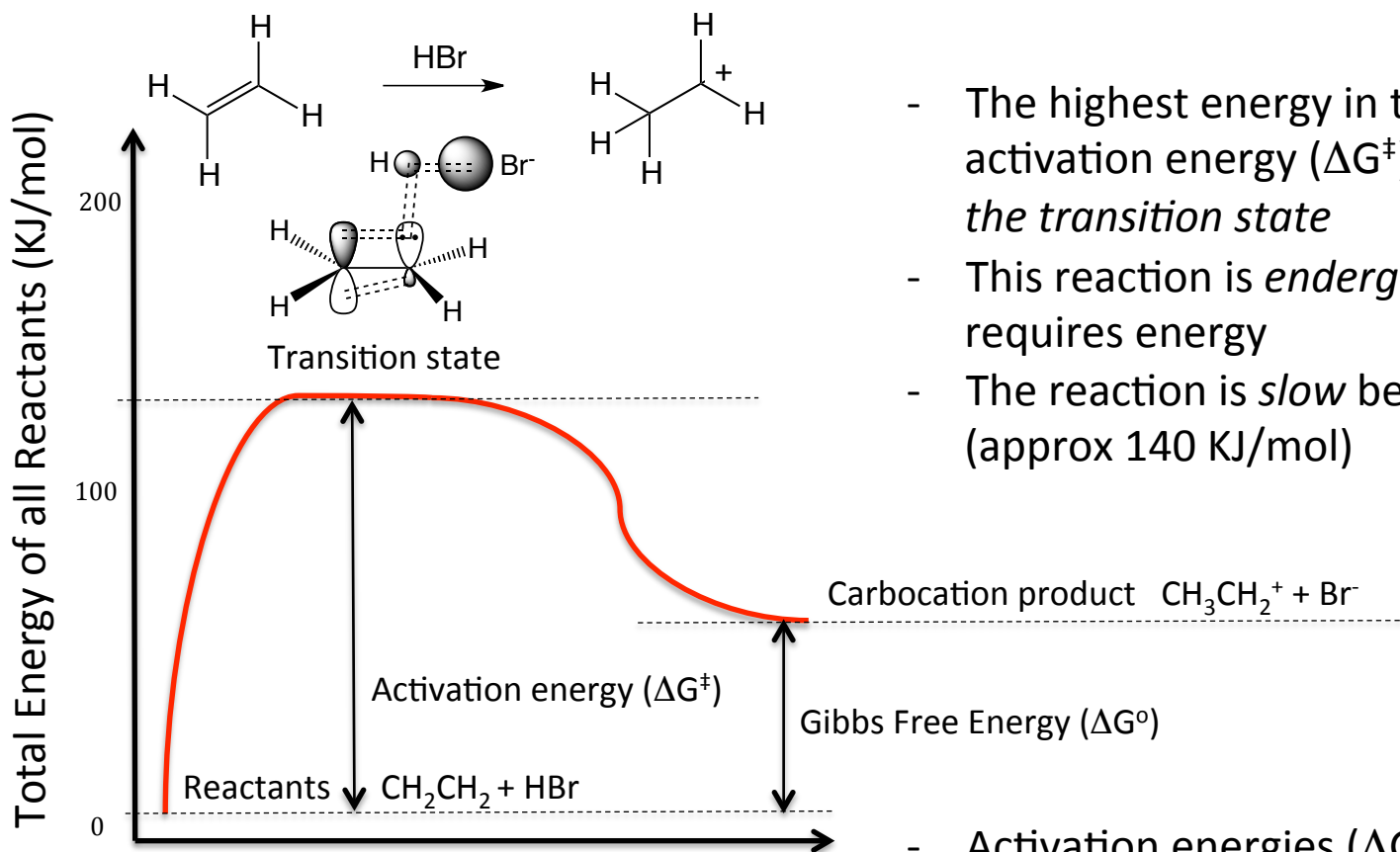
- The highest energy in the reaction is the activation energy ($\Delta G^{\ddagger}$) which signifies *the transition state*
- This reaction is *endergonic* ($+\Delta G^o$), it requires energy
- The reaction is *slow* because $\Delta G^{\ddagger}$ is large (approx 140 KJ/mol)

Carbocation product $CH_3CH_2^+ + Br^-$

Gibbs Free Energy (ΔG^o)

Activation energy ($\Delta G^{\ddagger}$)

Transition state

Reactants $CH_2CH_2 + HBr$

Total Energy of all Reactants (KJ/mol)

200

100

0

- Activation energies ($\Delta G^{\ddagger}$)
  - < 80KJ/mol take place at RT
 - > 80 KJ/mole require heat

Catalyzed reactions

- Catalysts lower the activation energy of a reaction
- Many different types of catalysts: acid, base, metal, solid (heterogeneous), solid (homogeneous), microporous (Zeolites), redox, etc.
- Enzymes are proteins that act as catalysts in cells (or *in vitro*)

enzyme + substrate entering active site

enzyme / substrate complex

enzyme / products complex

enzyme + products leaving active site

Transition state analogs

- Chemicals (typically pharmaceuticals) with structures that resemble the transition state of a substrate molecule in an enzyme-catalyzed reaction

- Could act as inhibitors or activators of enzyme

- Often the structures are derived from natural sources (a.k.a. natural products) because taking advantage of millions of years of enzyme-substrate co-evolution
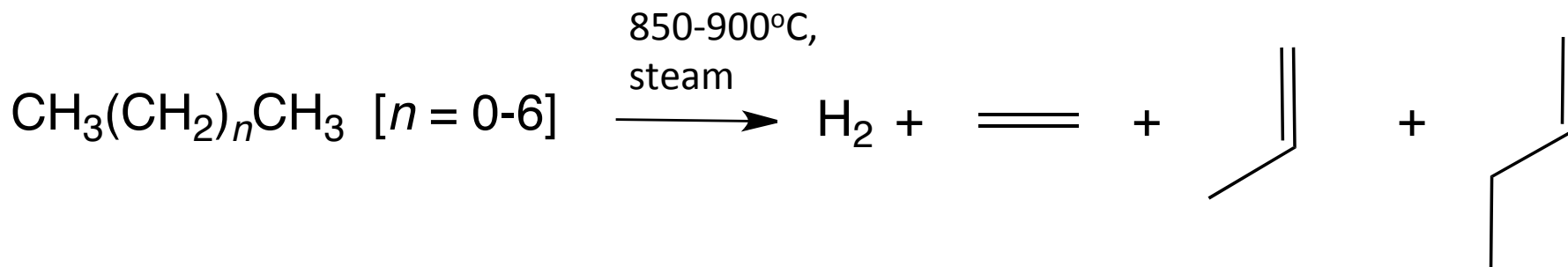

Carsten Müssig eLiS UP
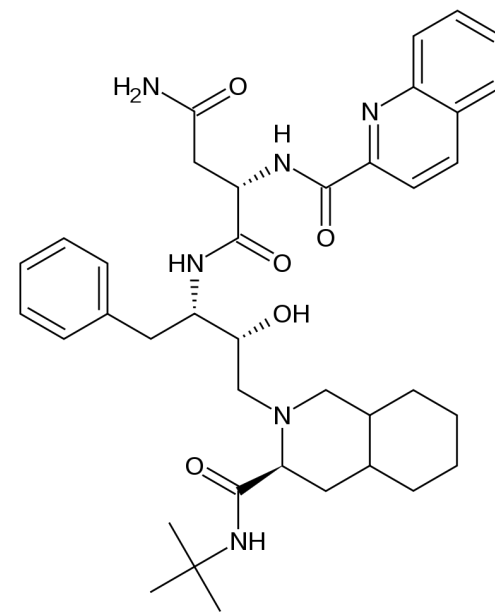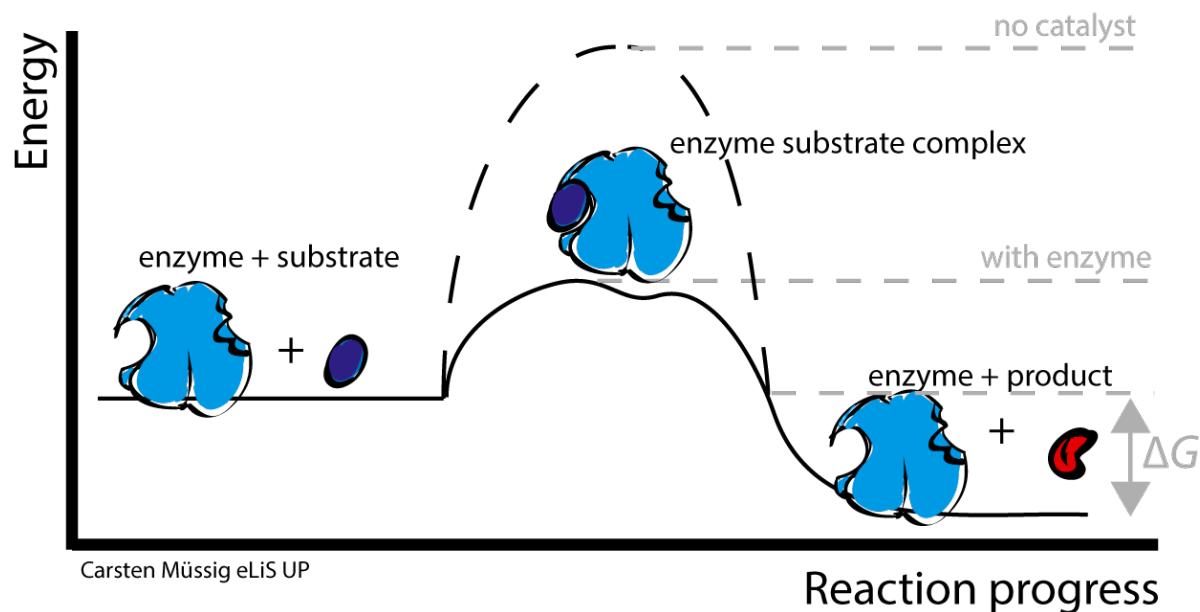
Saquinavir – an HIV protease inhibitor

Chemistry of Alkenes

- Intro to alkenes
  - Alkene nomenclature
  - Calculating Degrees of Unsaturation Solving For Unknowns
  - Alkene stability
  - Carbocation structure and stability
  - Electrophilic addition reactions
  - Synthetic polymers and biopolymers

Steam cracking of alkanes: produces alkenes

$$CH_3(CH_2)_nCH_3 \quad [n = 0\text{-}6] \xrightarrow{\substack{850\text{-}900^oC, \\ \text{steam}}} H_2 + \diagup\!\!\!\!\diagup \;+\; \diagup\!\!\!\!\diagup \;+\; \diagup\!\!\!\!\diagup$$

- Complex mechanism involving radical reactions
- *Energetics driven by entropy (S) since many smaller molecules created from larger hydrocarbon chain*
- Carbon-carbon BDE = 370 kJ/mol
- High temperatures contribute to a favorable reaction via (TΔS)

Naming alkenes

- Same as naming alkanes with the ending "ene"
- Numbering priority given to double bond rather than nearest branch point (if there's a tie, use nearest branch point)
- Indicate the position of the double bond by giving the number of the first alkene carbon, and placing that number directly before parent name
- If multiple double bonds present use diene, triene, tetraene, etc.
- Slight variation because of 1993 IUPAC rules
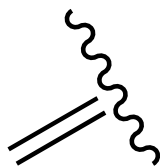
Some examples
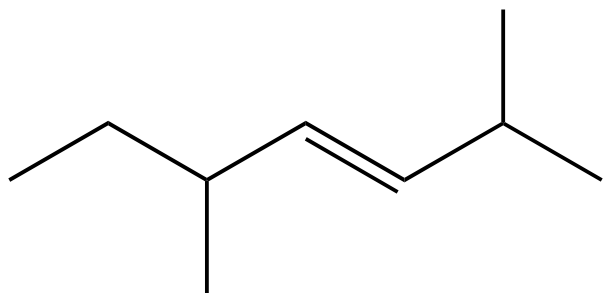
old: 2,5-dimethyl-3-heptene

new: 2,5-dimethylhept-3-ene
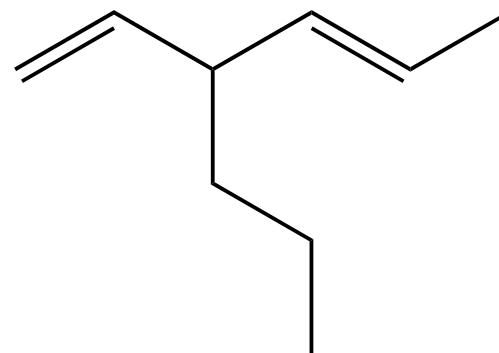
old: 3-propyl-1,4-hexadiene

new: 3-propylhexa-1,4-diene

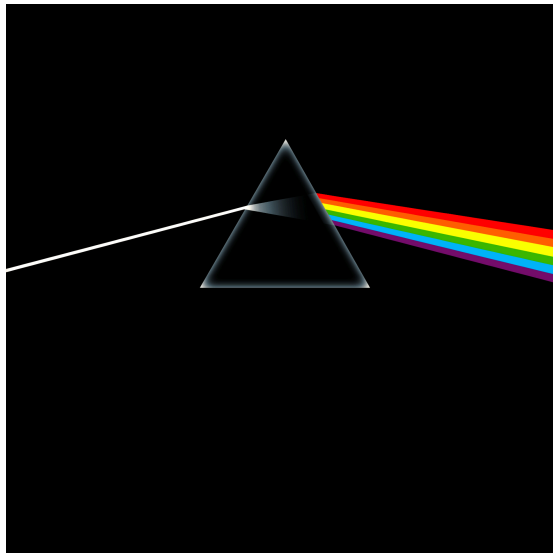# Noteworthy nomenclature
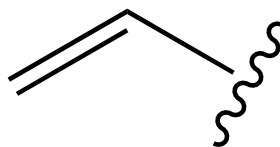
methylene group   vinyl group   allyl group
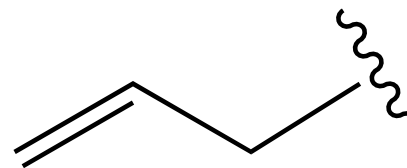
Noteworthy vinyl groups
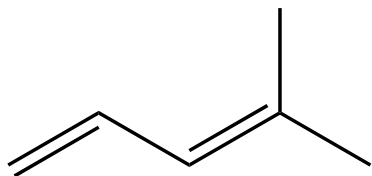
Degrees of unsaturation

- Alkanes are "saturated" with H atoms and obey the formula C_nH_{2n+2}
- Alkenes are "unsaturated"
- Rings and double bonds each remove 2H from a formula (2H atoms = 1° of unsaturation)
- Solving unknown structures requires calculation of a compound's "number of degrees of unsaturation"
- Heteroatoms (halogens, oxygen, nitrogen) must also be accounted for in calculation

Example:
MW of unknown hydrocarbon = 82 amu

- Corresponds to MF of C_6H_{10} = [(12 x 6) + (10 x 1)]
- Therefore, the MW 82 sample has *2 degrees of unsaturation* (H_{14} - H_{10} = H_4 = ***2 H_2***)
- Since there are no heteroatoms, the possibilities are:
  - Two double bonds
  - One ring and one double bond
  - Two rings
  - One triple bond
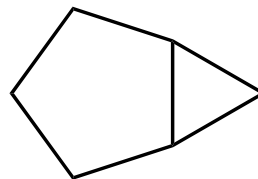- We still do not know structure, but this is pertinent information

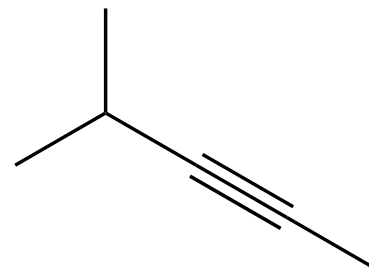# Possible structures for MW 82 hydrocarbon

4-methylpenta-1,3-diene   cyclohexene   bicyclo[3.1.0]hexane   4-methylpent-2-yne
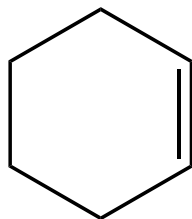
Calculating degrees of unsaturation: Compounds containing halogens

- Halogen substituent (X) acts as a replacement for hydrogen (H)

- Therefore, X + H = equivalent hydrocarbon formula from which degree of unsaturation can be found

- For example, $C_4H_6Br_2 = C_4H_8$

- Fully saturated C4 compound = $C_4H_{2(4)+2} = C_4H_{10}$

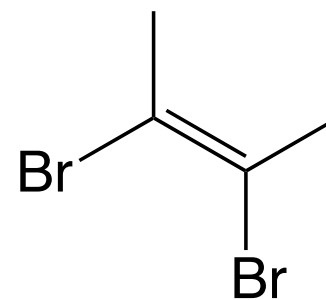- $H_{10} - H_8 = H_2 = $ **$1 H_2$** = 1 degree of unsaturation

Possible structures, exact masses and MWs for $C_4H_6Br_2$
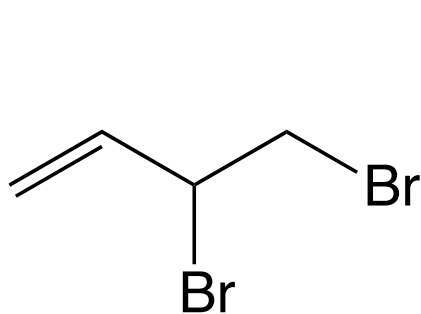
Chemical Formula: $C_4H_6Br_2$
Exact Mass: 211.88
Molecular Weight: 213.90
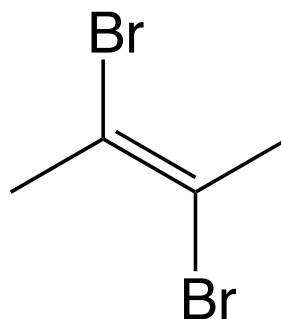
Chemical Formula: $C_4H_6Br_2$
Exact Mass: 211.88
Molecular Weight: 213.90

Chemical Formula: $C_4H_6Br_2$
Exact Mass: 211.88
Molecular Weight: 213.90

Exact mass = accounts for lightest isotopes only (used for MW Formula calculator)
Molecular weight = accounts for all isotopes (and relative abundances)

Calculating degrees of unsaturation: Compounds containing oxygen

- Oxygen forms 2 bonds in neutral molecules, so formula of equivalent hydrocarbon is not affected and oxygen can thus be ignored in calculating degrees of unsaturation

- Substituting an oxygen (i.e. as an ether or an alcohol) does not change number of H atoms

- Example C_5H_8O is equivalent to C_5H_8 (both have 2 degrees of unsaturation)

- Same rule applies for sulfur

All compounds have 2 degrees of unsaturation
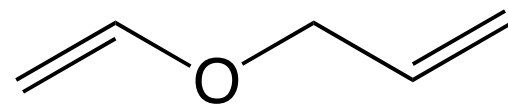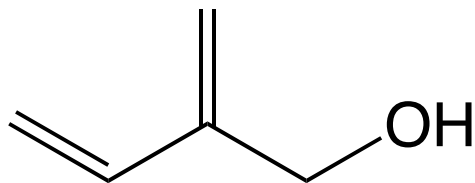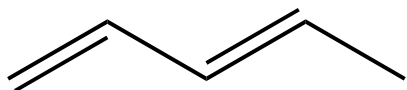
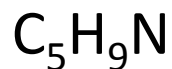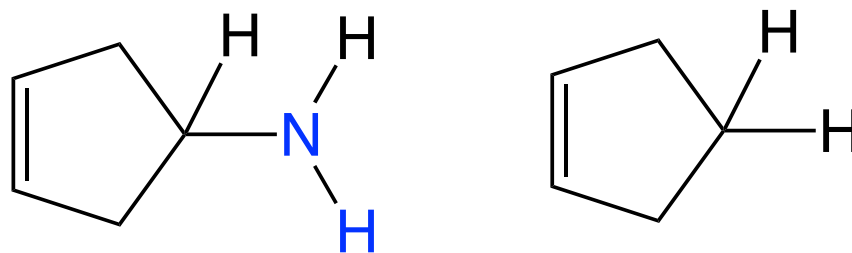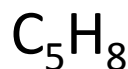# Calculating degrees of unsaturation: Compounds containing nitrogen

- Nitrogen a little trickier, it forms 3 bonds in neutral state, compounds containing N have one more H than related hydrocarbon

- Therefore, **subtract the total number of N from total number of H** to arrive at equivalent hydrocarbon formula.

- For example, the formula $C_5H_9N = C_5H_8$ and since fully saturated linear pentane is C_5H_{12} this compounds has 12H-8H = 4H *(2 degrees of unsaturation)*

C_5H_9N
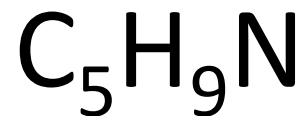
- Convince yourself by inserting a N into the hydrocarbon chain (as an amine)
  - C-C becomes C-NH-C
  - C-H becomes $C-NH_2$


C_5H_9N becomes C_5H_8

Summary for simplifying C_8H_8NOBr and calculating degrees of unsaturation

- Count halogens as hydrogens = C_8H_9NO
- Omit oxygen and sulfur = C_8H_9N
- Subtract total N from total H = C_8H_8
- Saturated hydrocarbon (octane) is C_nH_{2n+2} = C_8H_{18}
- Subtract unsaturated hydrogens from saturated hydrogens (C_8H_{18} - C_8H_8 = H_{10})
- Divide 10H atoms by 2 (because one degree = 2H)
- Degree of unsaturation therefore = 10/2
  = 5 degrees of unsaturation

Molecular formula calculator to determine unknown structures

- Once a high resolution "exact mass" is obtained (e.g. 314.469 g/mol)

- Use MF calculator program to search likely candidates

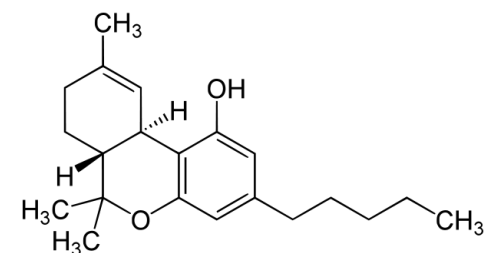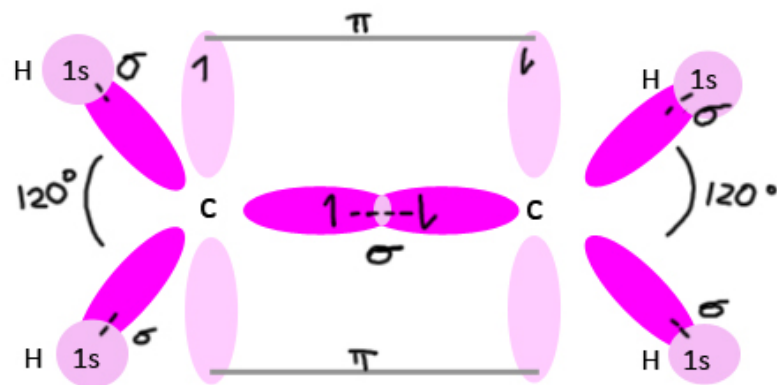- If these candidates do not have requisite number of degrees of unsaturation, disqualify them

http://www.chemcalc.org/mf_finder/mfFinder_em_new

Forensics Example
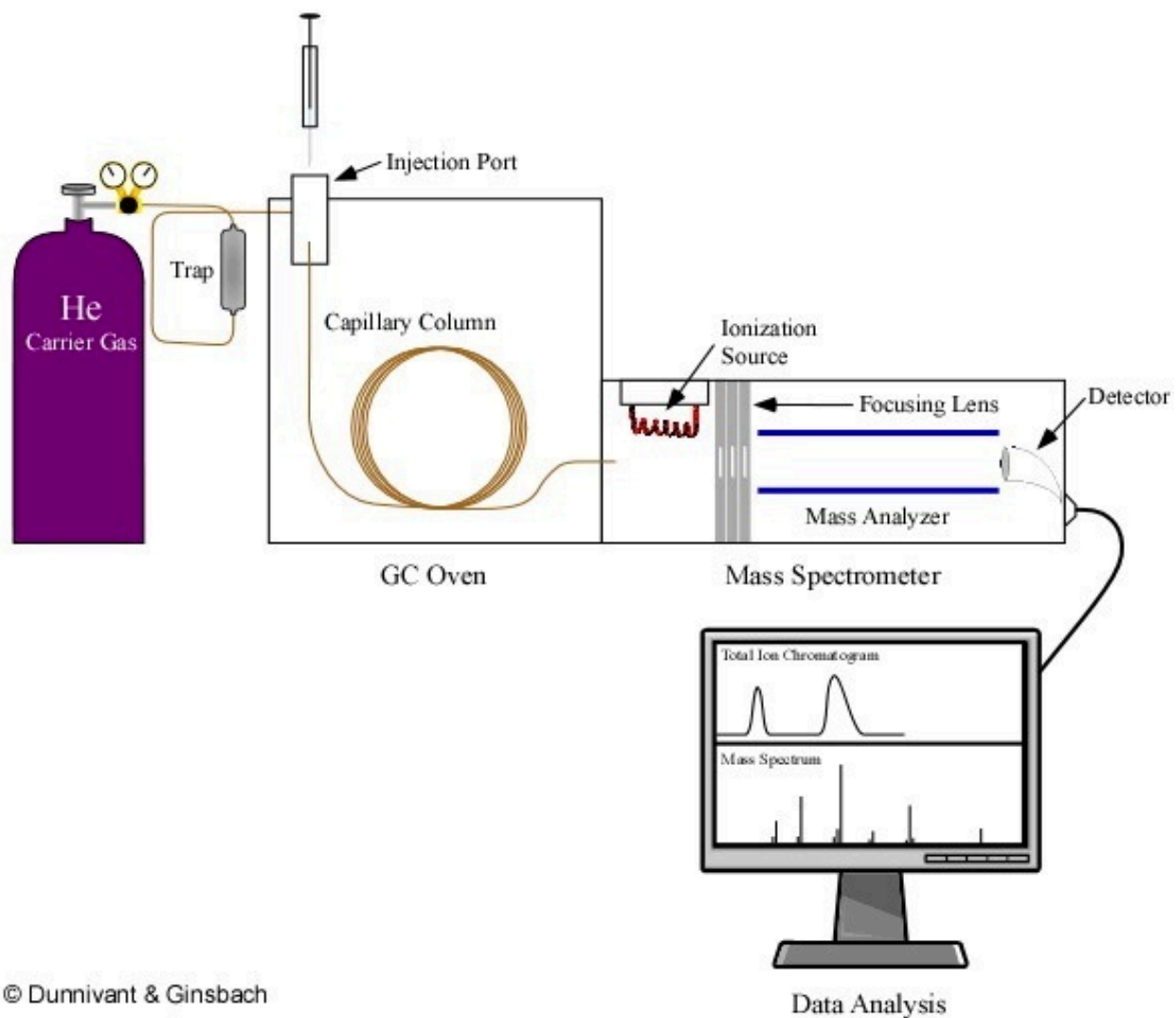
HRMS = 314.469

$C_{21}H_{30}O_2$

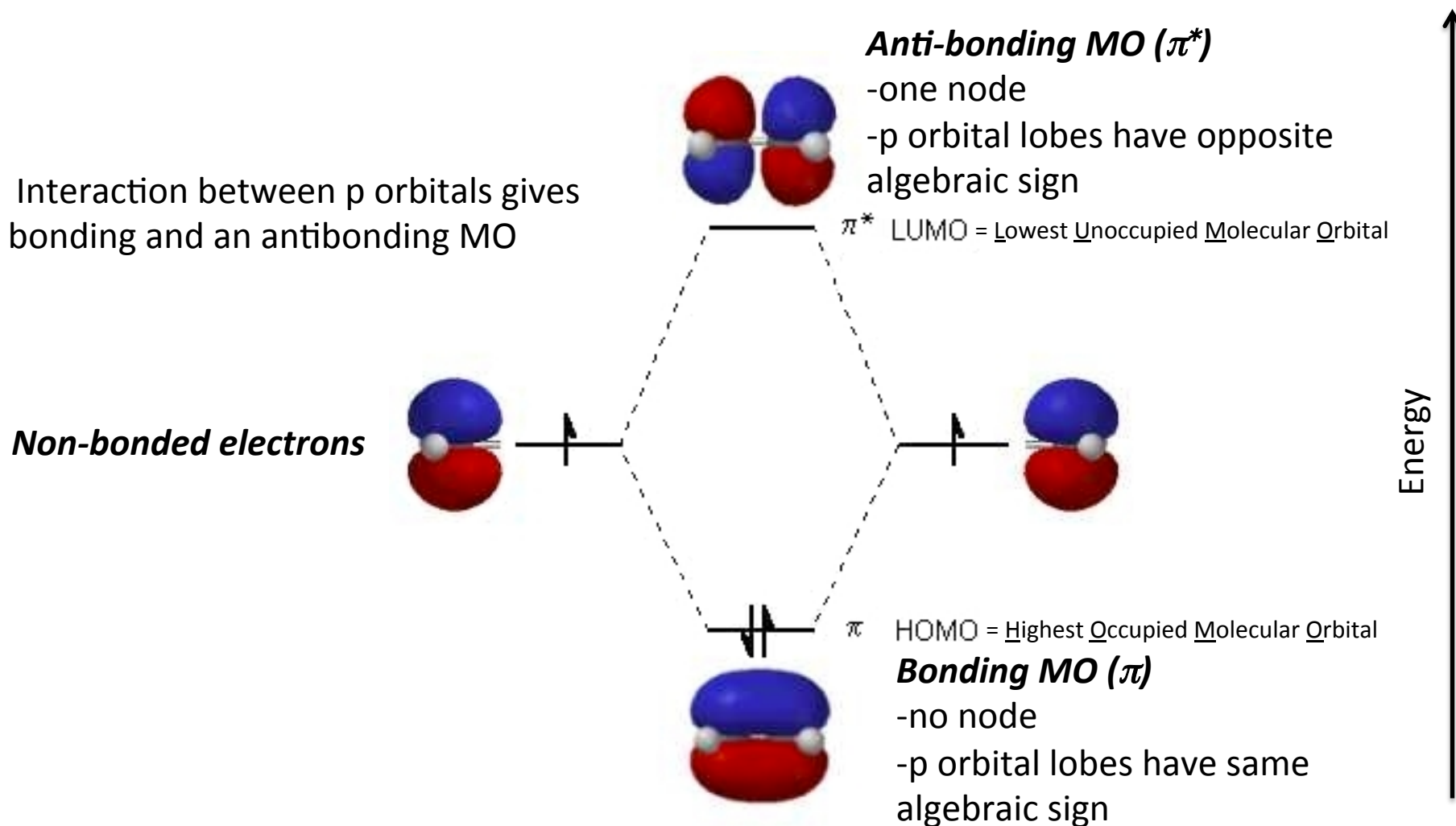7° unsaturation

© Dunnivant & Ginsbach

Review of Valence Bond (VB) theory

- Alkene carbons are sp^2 hybridized

- 3 equivalent hybrid atomic orbitals

- Sigma (σ) bond formed from two sp^2 orbitals' overlap

- Pi (π) bond formed from two p orbitals' overlap

- 120° bond angles, trigonal planar geometry

Review of Molecular Orbital (MO) Theory

Anti-bonding MO (π^*)

-one node

-p orbital lobes have opposite algebraic sign

π^* LUMO = Lowest Unoccupied Molecular Orbital

• Interaction between p orbitals gives a bonding and an antibonding MO

Non-bonded electrons

Energy

π HOMO = Highest Occupied Molecular Orbital

Bonding MO (π)

-no node

-p orbital lobes have same algebraic sign

Both theories, same resulting bond strength

- For rotation to occur at a double bond, must first break the π bond (350 kJ/mol)

- Contrast this to rotamers of ethane (12 kJ/mol for eclipsed conformation)

- Disubstituted alkenes (e.g. 2-butene) can occur as two cis/trans isomers

- These isomers are isolable

Stability of alkenes

- *cis-trans* conversion does not occur spontaneously, but can be obtained by treatment with heat or strong acid (this is how *trans*-fats are created…)

- *cis* isomer experiences higher **steric** strain

- ΔG^o = 2.8 kJ/mol (equilibrium favors *trans* isomer)

Trans isomer (76%)
2.8 kJ/mol more stable

Cis isomer (24%)
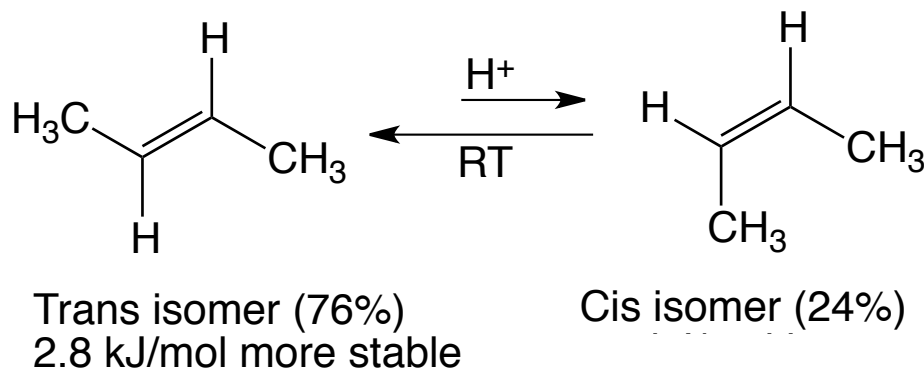
Hyperconjugation adds to alkene stability

Alkenes become more stable with increasing substitution

Increasing hyperconjugation

4° > 3° > 2° trans ~ 2° cis > 1°

Decreasing stability
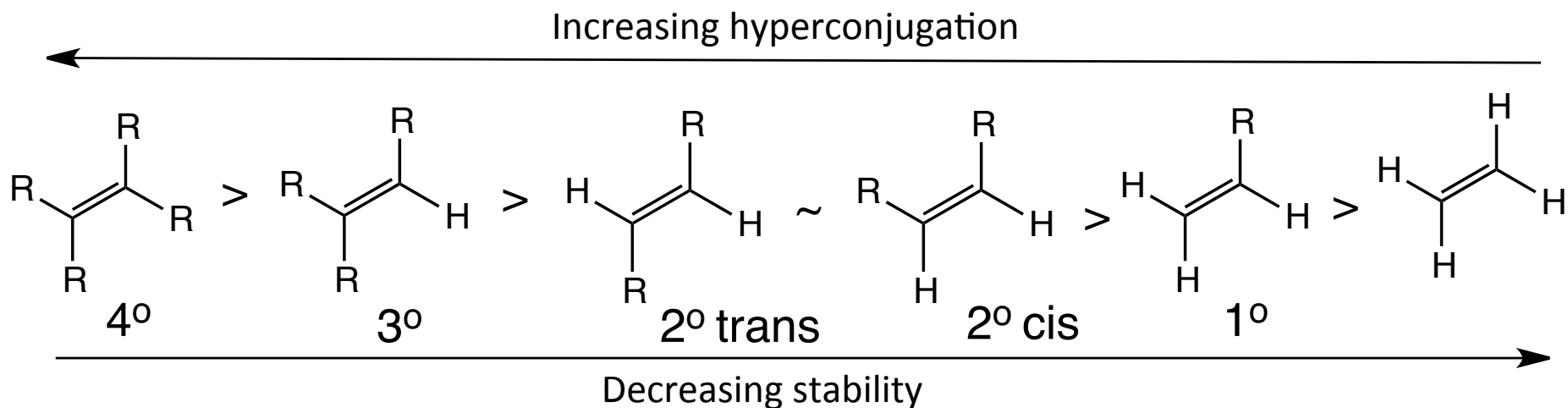
"Hyperconjugation" whereby a bonding MO extends over the 4 atom C=C-C-H grouping

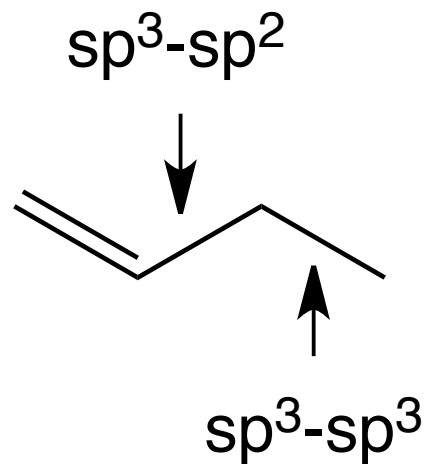*The more substituents present on the double bond, the more hyperconjugation and more stable the alkene*

monosubstituted alkene
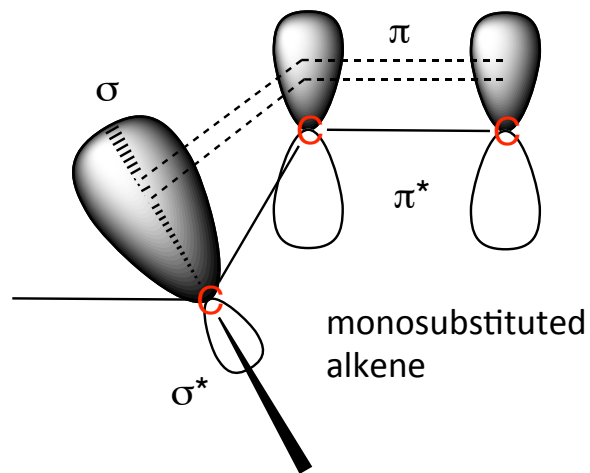
Bond strengths add to alkene stability

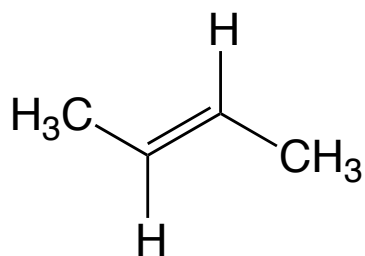- Bonds between sp^2 carbon and sp^3 carbon are stronger than bonds between sp^3 carbon and another sp^3 carbon

sp^3-sp^2

sp^3-sp^2

sp^3-sp^2

sp^3-sp^3
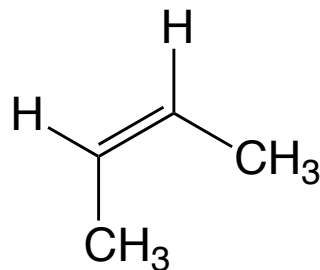
2-butene (more stable)
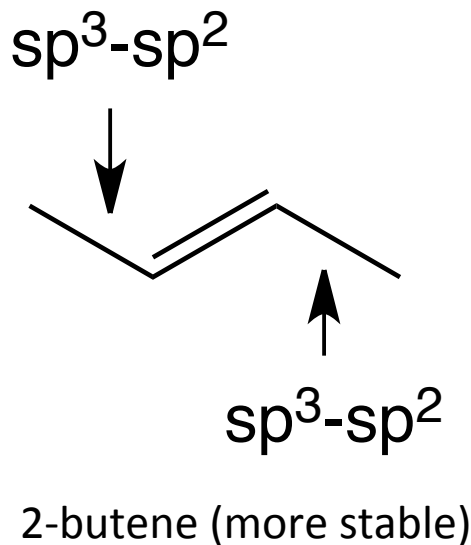
1-butene (less stable)

$\Delta H_{hydrog} = -116$ kJ/mol

$\Delta H_{hydrog} = -127$ kJ/mol

Stability of butene isomers
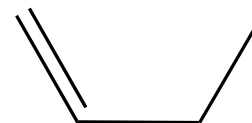

trans-2-butene
ΔH_{hydrog} = -116 kJ/mol

cis-2-butene
ΔH_{hydrog} = -120 kJ/mol
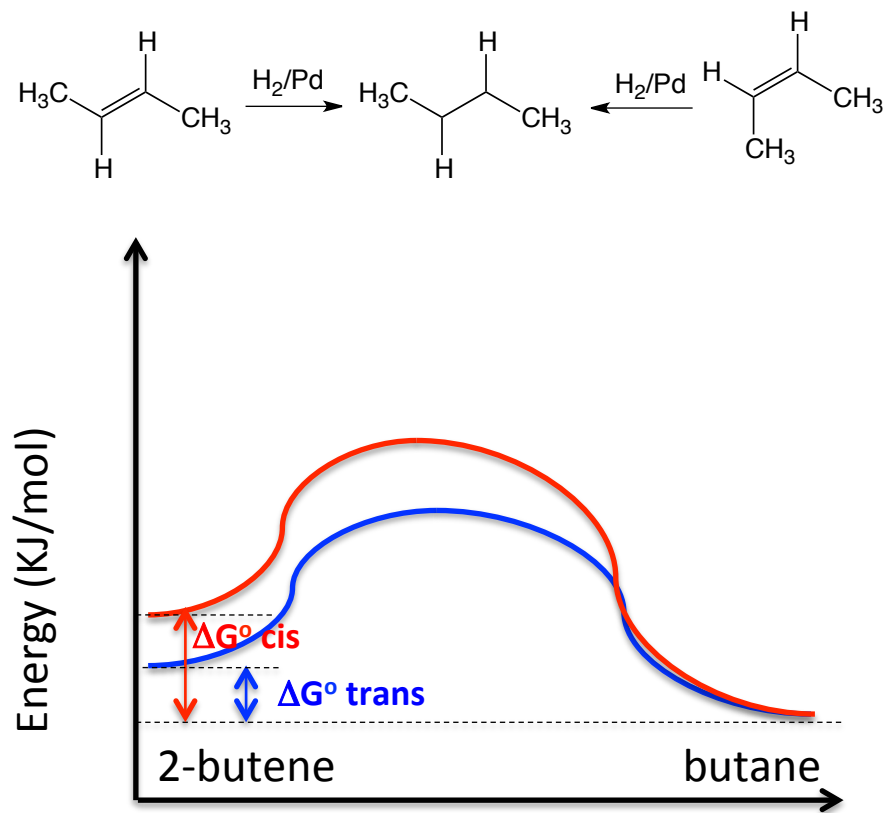
1-butene
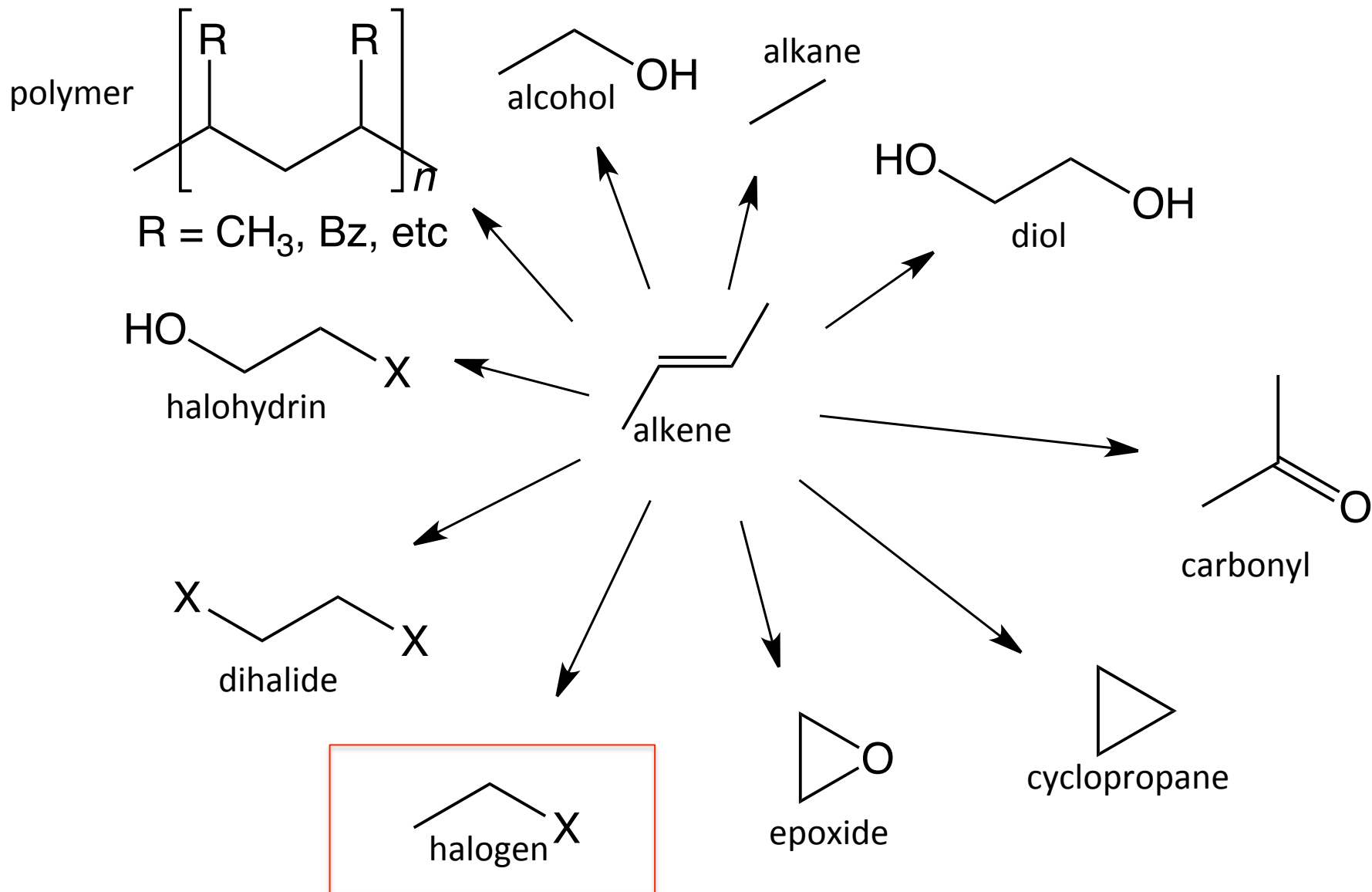ΔH_{hydrog} = -127 kJ/mol
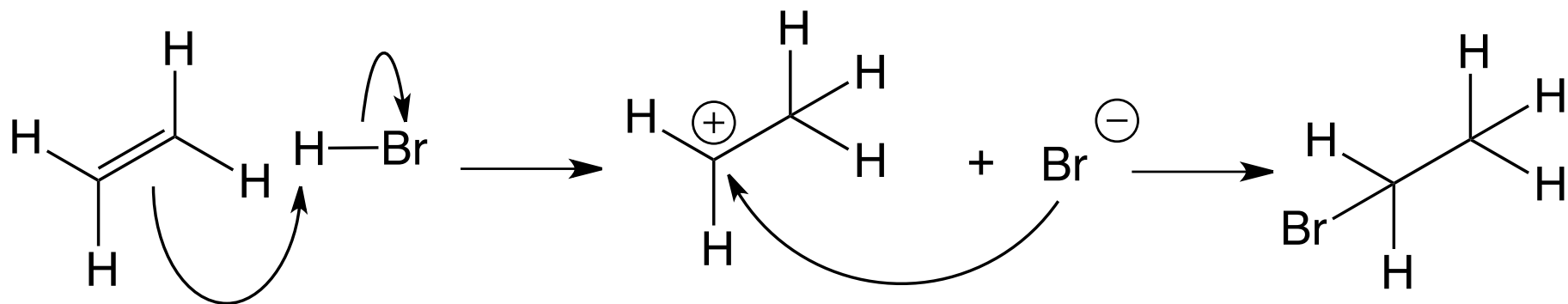
Heat of hydrogenation:
cis vs. trans butene

- Reaction coordinate diagram for hydrogenation shows ΔG^o of *cis* isomer is lower than that for *trans* isomer

- More energy released during hydrogenation of *cis* isomer because it is higher energy (less stable) to begin with

- ΔH_{hydrog} = Enthalpy (4 kJ/mol)

- ΔG^o = -2.8 kJ/mol

- Difference accounted for by:
  - Entropy (ΔS)

Products of alkene reactions

polymer

R = CH$_3$, Bz, etc

alcohol

alkane

diol

halohydrin

alkene

dihalide

carbonyl

cyclopropane

halogen

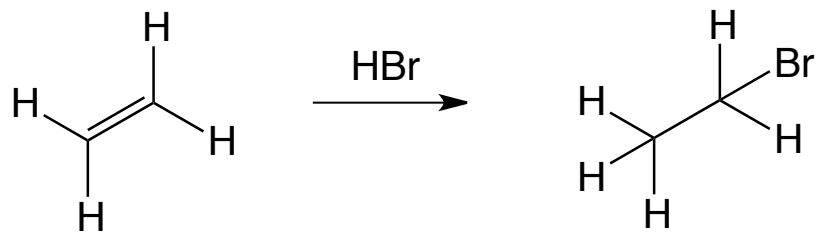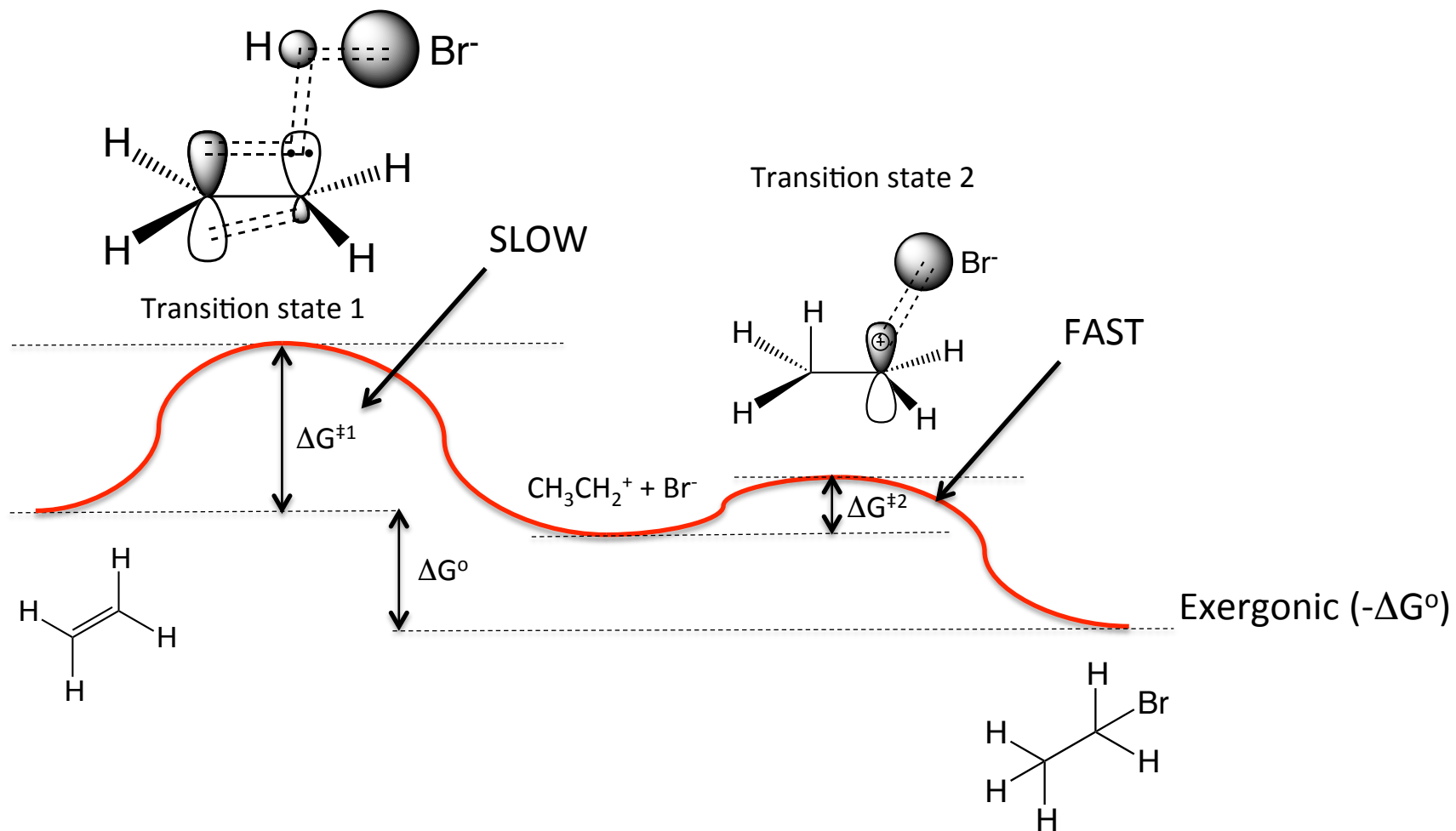epoxide

Electrophilic addition of HBr to ethylene

- Ethylene is nucleophile
- HBr is electrophile

- Two electrons move onto bromine giving bromide ion
- Ethane carbocation has a vacant p-orbital
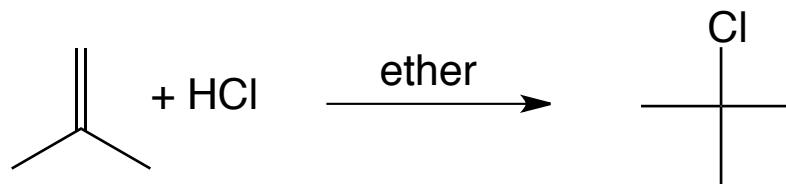- Bromide "attacks" carbocation

- Addition product

Total Energy of all Reactants (KJ/mol)

HBr

SLOW

Transition state 1

Transition state 2

FAST

$\Delta G^{\ddagger 1}$

$CH_3CH_2^+ + Br^-$

$\Delta G^{\ddagger 2}$

ΔG^o

Exergonic ($-\Delta G^o$)
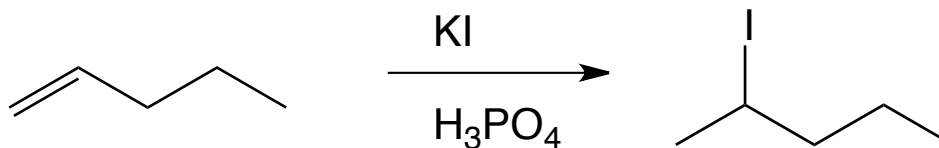
$H \ominus - \cdots Br^-$

Br^-

Additional examples of electrophilic addition reactions – similar mechanisms as HBr addition

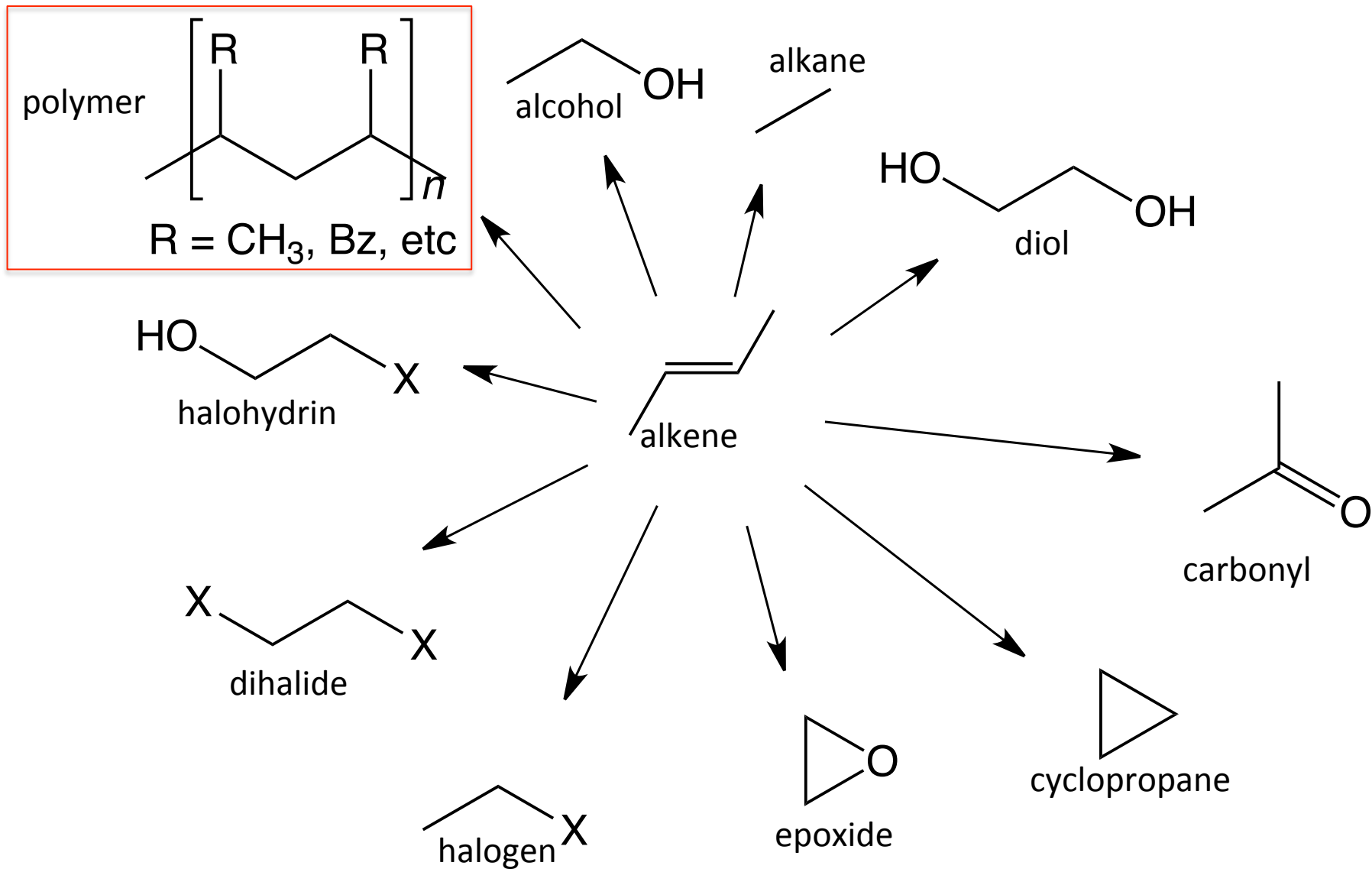Electrophilic addition reactions work with *HBr, HCl, HI and H$_2$O*

$$+ \; HCl \xrightarrow{\text{ether}}$$

KI + H$_3$PO$_4$ generates HI *in situ*

$$\xrightarrow[\text{H}_3\text{PO}_4]{\text{KI}}$$

Strong acid catalyst (H$_2$SO$_4$) is needed for addition of water

$$\xrightarrow[\text{H}_2\text{SO}_4 \; (\text{catalyst})]{\text{H}_2\text{O}}$$
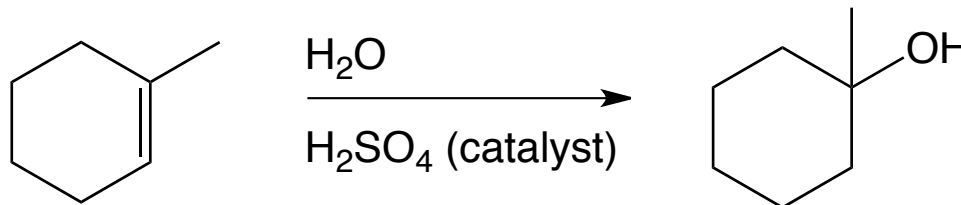
Products of alkene reactions

Radical initiated polymer synthesis

heat

2

+ 2 CO$_2$
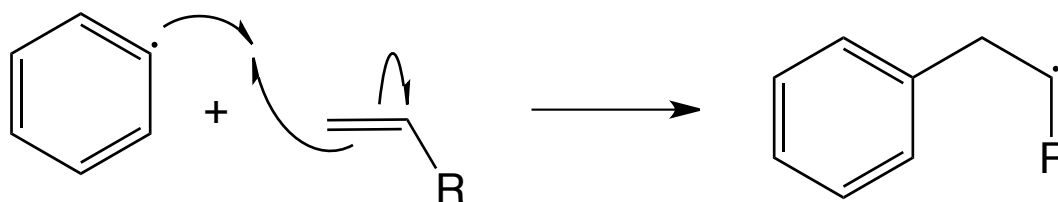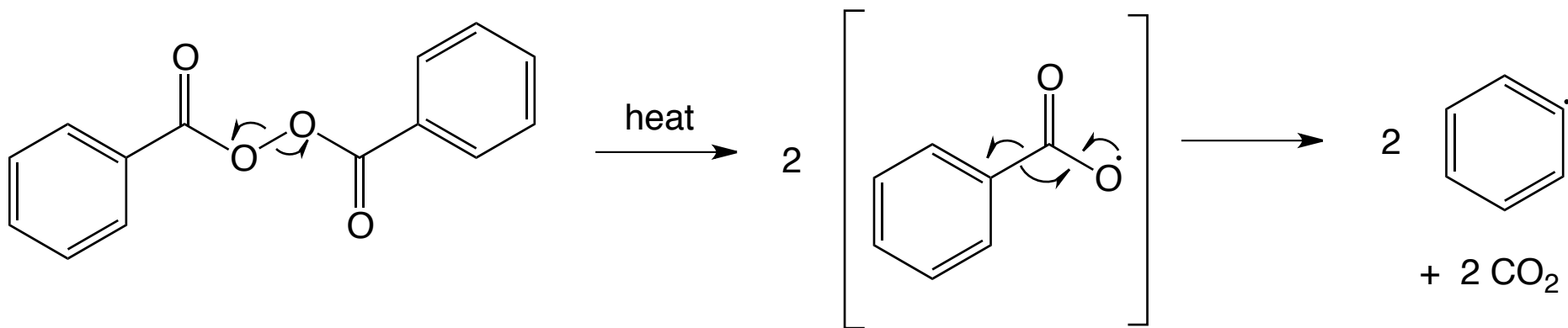
Initiation:

R =
H (polyethylene)
CH$_3$ (polypropylene)
C$_6$H$_5$ (polystyrene)

"vinyl monomers"

Propagation

R =
H (polyethylene)
CH$_3$ (polypropylene)
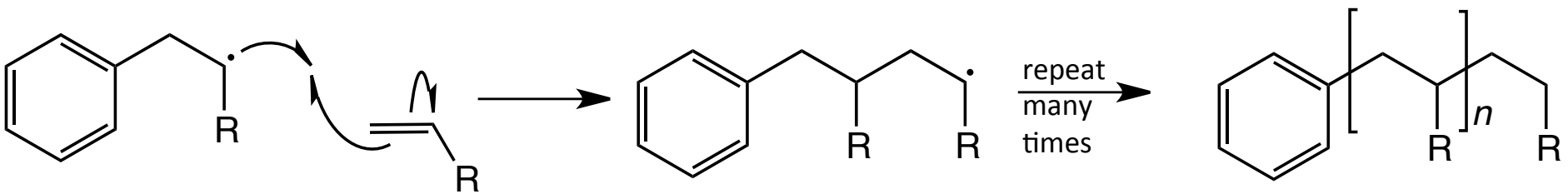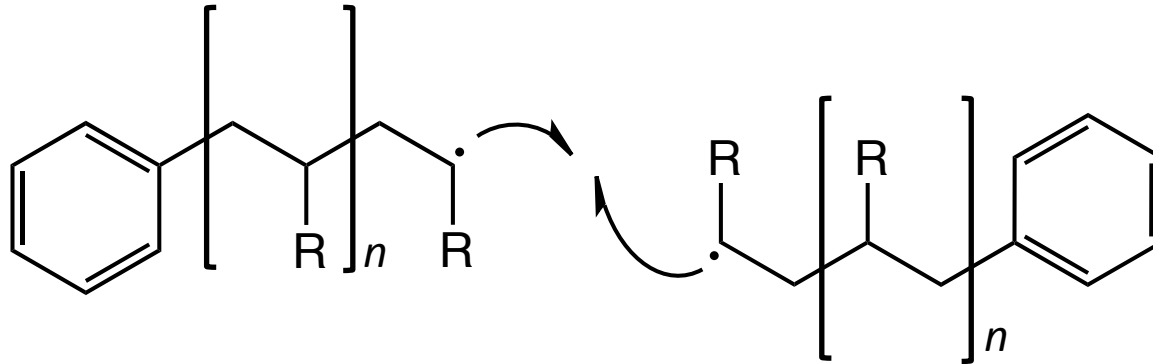C$_6$H$_5$ (polystyrene)

Polymers can contain hundreds of thousands of monomers, reaching molecular weights over 5 million amu!

Termination

R =

H (polyethylene) --- packaging, bottles

CH_3 (polypropylene) --- molding, rope, carpet

C_6H_5 (polystyrene) --- foam, molding (CD cases, disposable razors, "styrofoam")

Styrofoam[1] *= non-recyclable, non-biodegradable = lives 500 yrs in landfills!!!*

[1]http://www.livestrong.com/article/159954-facts-about-landfill-styrofoam/

Worldwide alkene production

- **Ethylene** = 127 million metric tons/yr
  ($d = 1.18$ kg/m^3)

Produces: Ethanol, ethylene glycol, ethylene dichloride, acetaldehyde, acetic acid, ethylene oxide, vinyl acetate, polyethylene, vinyl chloride
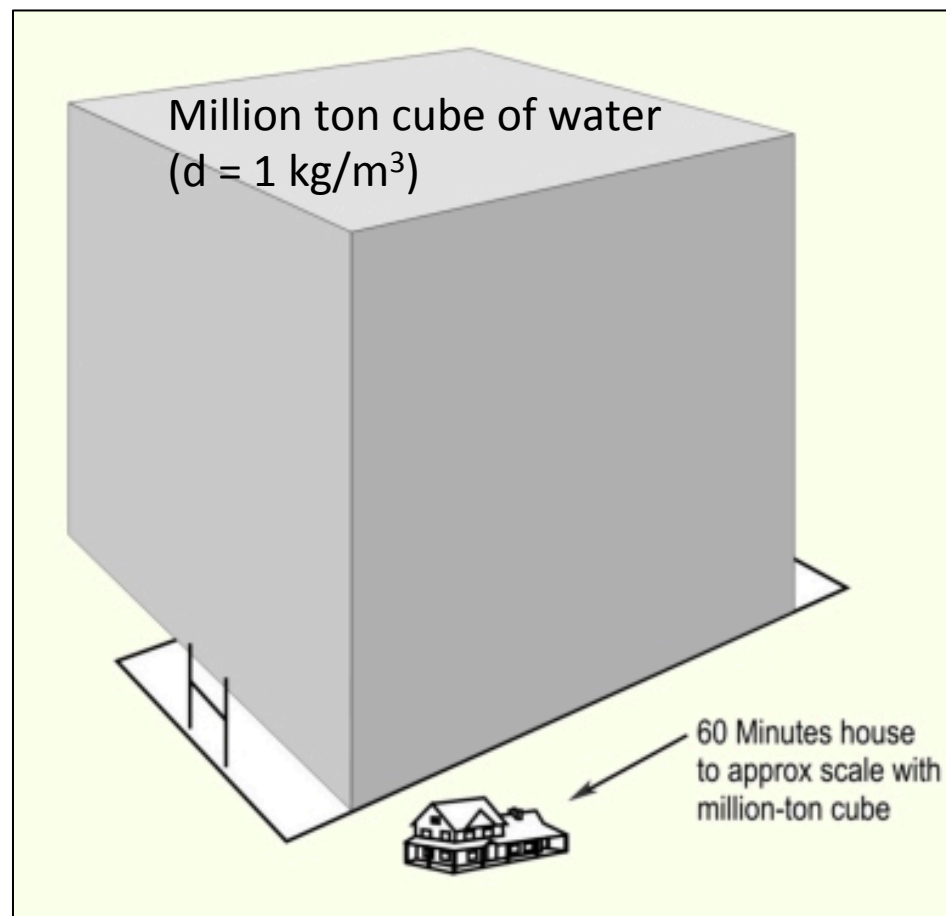
Polyethylene
$22.2B (2009)
6 million amu

- **Propylene** = 54 million metric tons/yr
  ($d = 1.81$ kg/m^3)

*Produces*: isopropyl alcohol, propylene oxide, polypropylene, cumene

Polypropylene
$77.4B (2012)

Million ton cube of water
($d = 1$ kg/m^3)

60 Minutes house to approx scale with million-ton cube

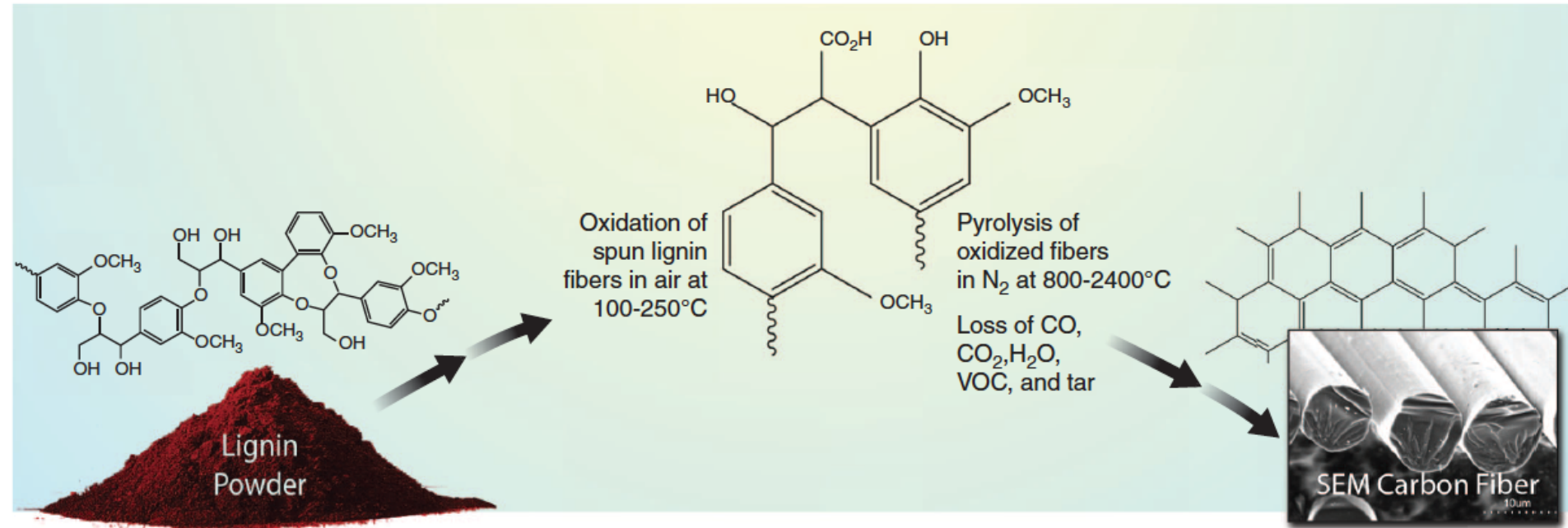http://www.flashevap.com/bigthings.htm

Lignin: a potential chemical replacement for petroleum-based materials

- 300 billion tons available annually/worldwide, largely from pulp & paper industry
- 2nd most abundant biopolymer on Earth (1st is cellulose)
- Largest barrier to entry is cost-effective "depolymerization" chemistry
- Structurally similar to polystyrene.
- Applications include fuels, composites, plastics, chemicals

http://www.ipst.gatech.edu/faculty/ragauskas_art/technical_reviews/lignin%20applications2.pdf
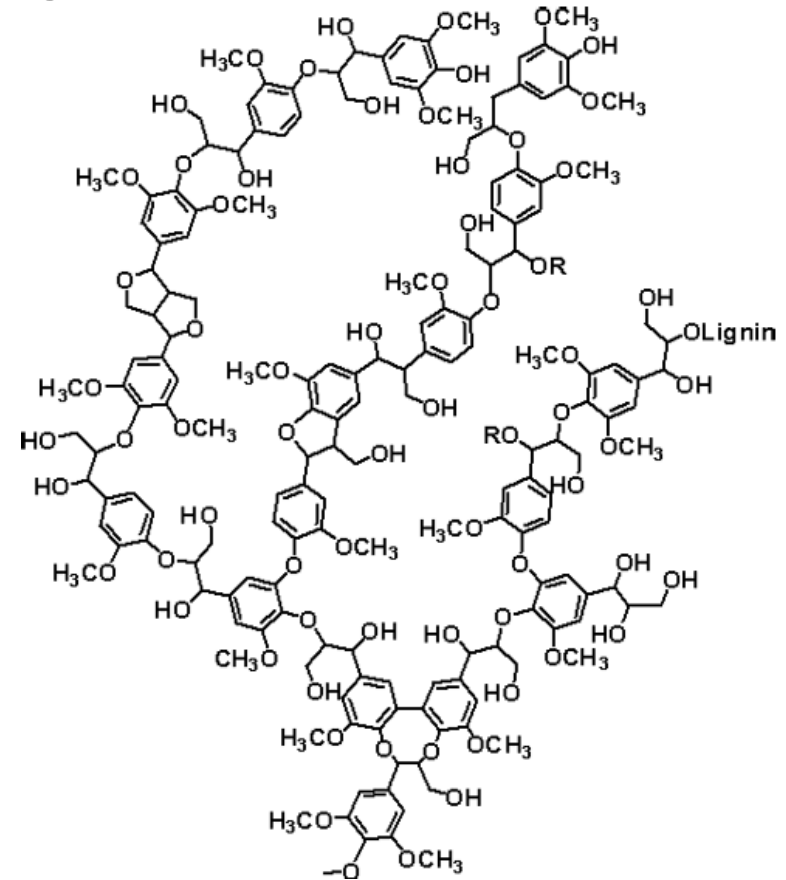
Carbon Fiber from Lignin

- Strong and lightweight

- Approximately 10 x added-value

- Lignin ~ $100/ton
  Carbon fiber ~ $1000/ton

- Native lignin works best

Raguaskas and Wyman *Science*, 344, **2014**

Chapter 6 Homework

- In chapter: 1, 2, 3, 4, 6, 7, 8, 10, 11, 12, 13
- End of chapter: 20, 22, 26, 28, 29, 33, 38, 40

HW Problems

Chapter 7:

In Chapter: 1, 2, 3, 4, 6, 9, 10, 11, 13, 14, 15

End of Chapter: 26, 30, 35, 36, 37, 38, 39