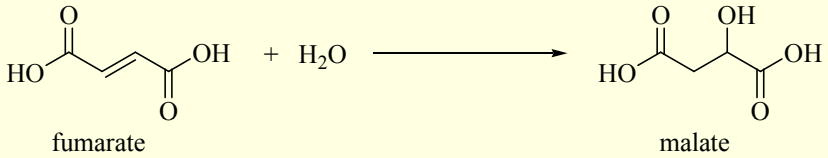
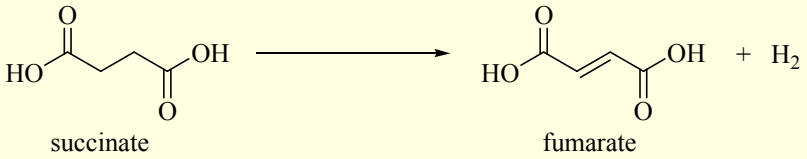
Types of Organic Reactions

1. Addition Reactions: A + B → C

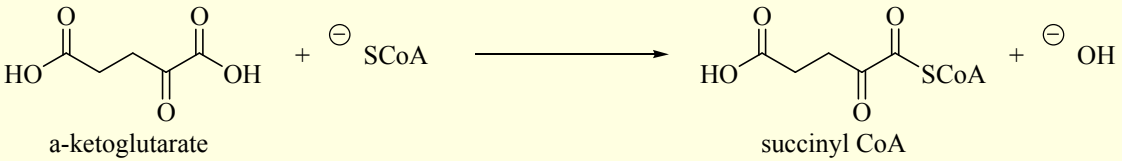


fumarate malate

2. Elimination Reactions: D → E + F

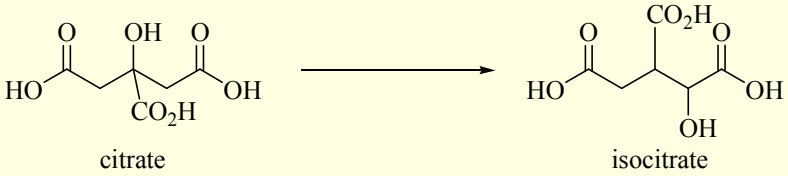


3. Substitution Reactions: G-H + $I^{\ominus}$ → G-I + $H^{\ominus}$



Types of Organic Reactions

4. Rearrangements: J → K



citrate isocitrate

How do these reactions occur?
Why do these reactions occur?

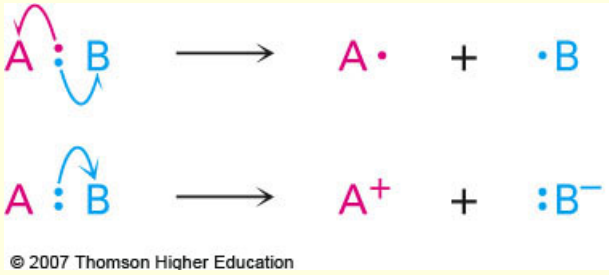
We must explain how electrons are exchanged during the formation of new bonds and breaking of old bonds.

How Reactions Occur

Symmetrical Bond Making/Breaking (homolytic process)

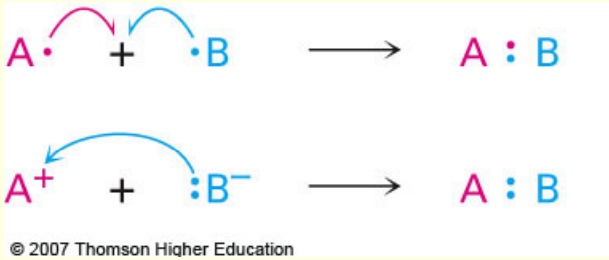
vs

Unsymmetrical Bond Making/Breaking (heterolytic process) - POLAR Reactions



Symmetrical bond-breaking (radical):
one bonding electron stays with each product.

Unsymmetrical bond-breaking (polar):
two bonding electrons stay with one product.

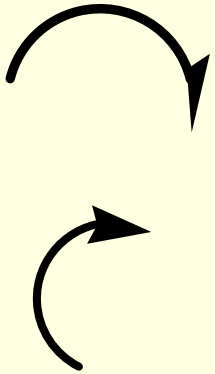


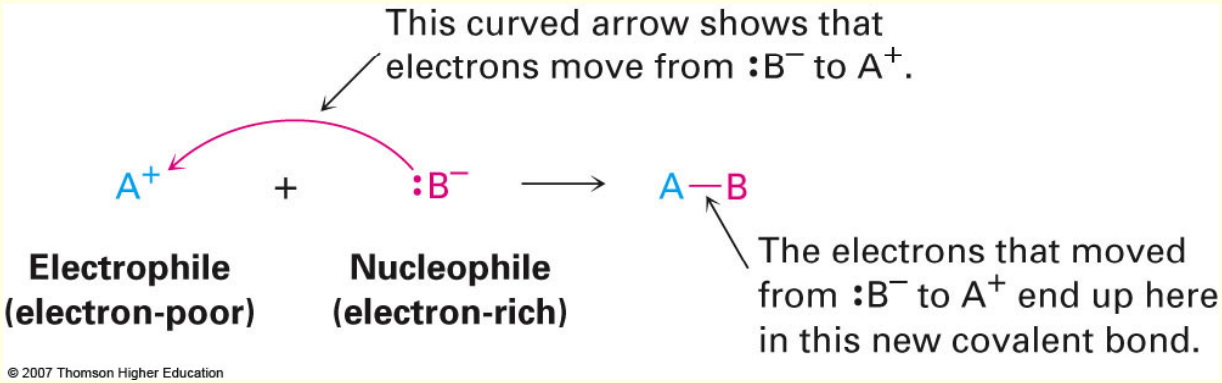
Symmetrical bond-making (radical):
one bonding electron is donated by each reactant.

Unsymmetrical bond-making (polar):
two bonding electrons are donated by one reactant.

Indicating Electron Movement in Reaction Mechanisms

- Curved arrows indicate breaking and forming of bonds
- Arrowheads with a “half” head (“fish-hook”) indicate homolytic and homogenic steps (called ‘radical processes’)
- Arrowheads with a complete head indicate heterolytic and heterogenic steps (called ‘polar processes’)

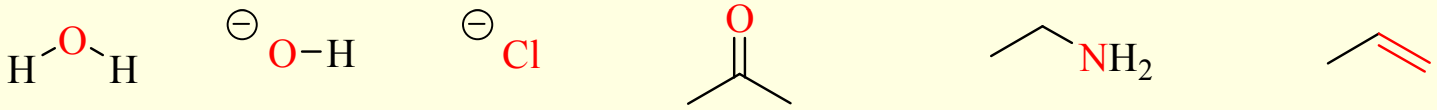




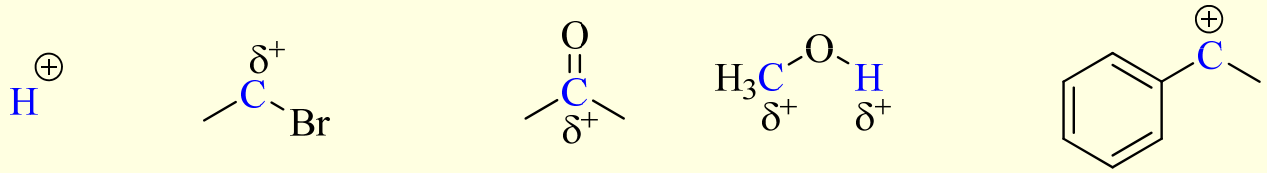
Polar Reactions

Opposite charges attract

- Nucleophiles (electron rich sites, seek nucleus) - have lone pair of electrons or C=C bond

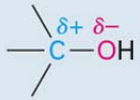
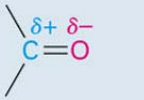
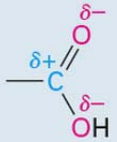
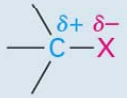
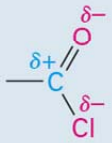
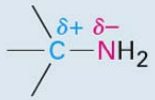
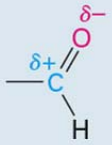


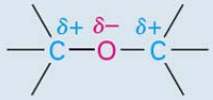
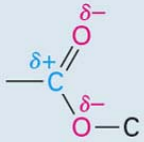
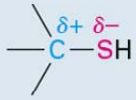
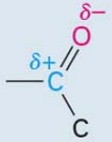
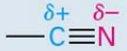
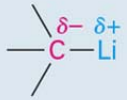
- Electrophiles (electron poor sites, seek electrons) - have formal positive charge or partial positive charge via bond dipole



Nucleophiles are synonymous with Lewis Bases, Electrophiles are synonymous with Lewis Acids, Polar reactions are Lewis Acid-Base reactions.

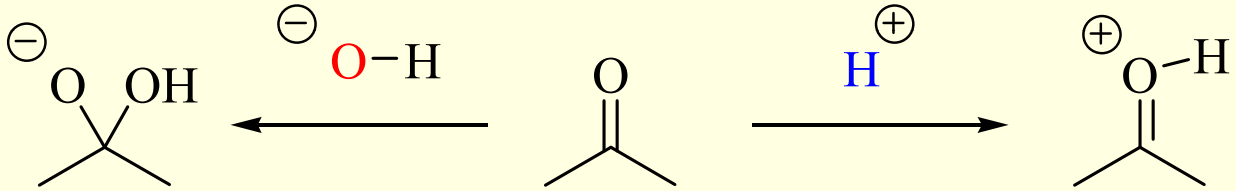
Table 5.1 Polarity Patterns in Some Common Functional Groups

Alcohol		Carbonyl	
Alkene		Carboxylic acid	
	Symmetrical, nonpolar		
Alkyl halide		Carboxylic acid chloride	
Amine		Aldehyde	

Ether		Ester	
Thiol		Ketone	
Nitrile			
Grignard reagent			
Alkyllithium			

Nucleophiles and Electrophiles

Note that compounds can be nucleophilic and electrophilic. You must look at specific atoms and what the compound is reacting with to determine how it will react:



Judging relative 'strengths' of Nuc and E+

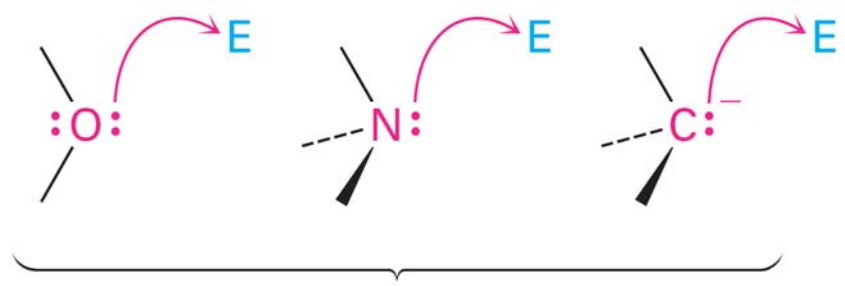
Strong Nuc
less stable anion
more stable anion
lone pair less EN atom
lone pair more EN atom
C=C
Weak Nuc

Strong E+
less stable cation
more stable cation
neutral atom incomplete octet
large partial positive atom
small partial positive atom
Weak E+

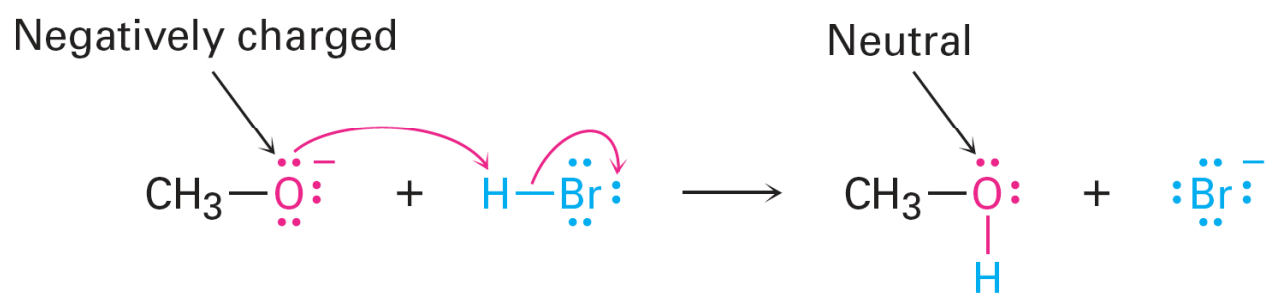
Drawing Reaction Mechanisms

Use of curved arrows to show electron movement in bond making and bond breaking process. For polar reactions, electrons move as a pair. Note that charges must also balance.

- The arrow goes from the nucleophilic reaction site to the electrophilic reaction site

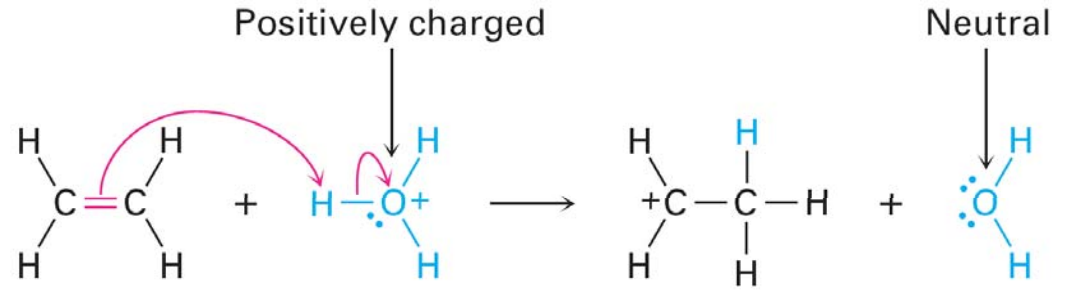


- The nucleophilic site can be neutral or negatively charged

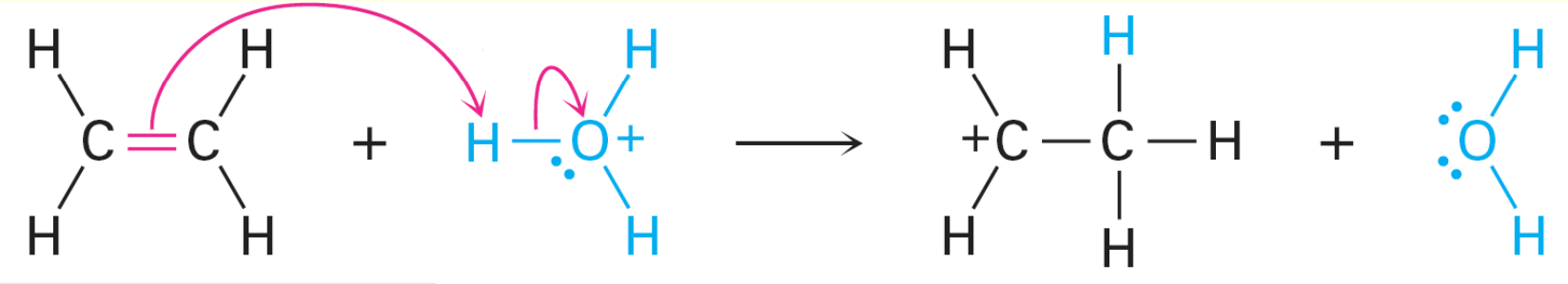


Drawing Reaction Mechanisms

- The electrophilic site can be neutral or positively charged

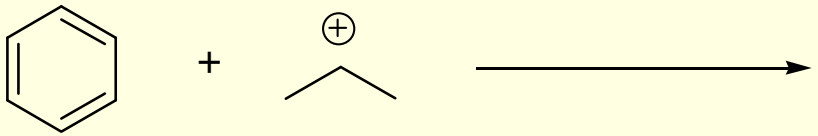


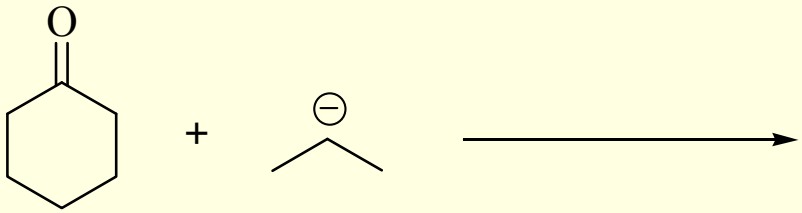
- The octet rule must be followed

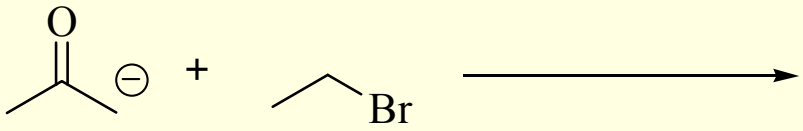


- (never have +2 or -2 charge on a single atom)

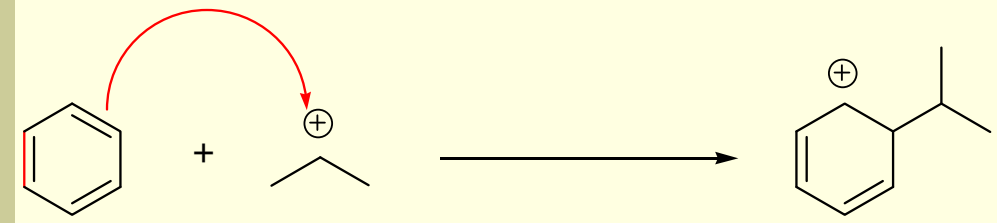
Drawing Reaction Mechanisms

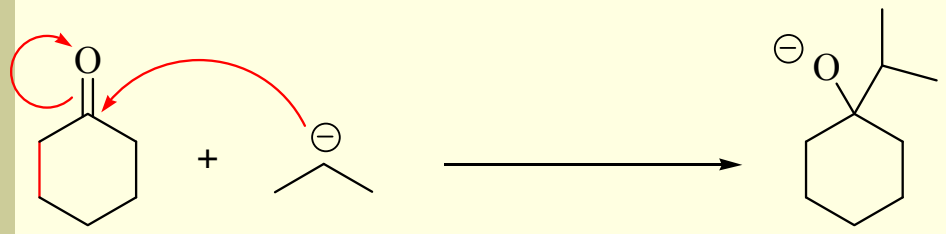


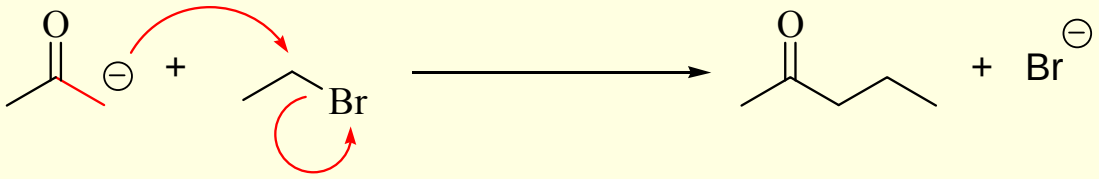




Drawing Reaction Mechanisms

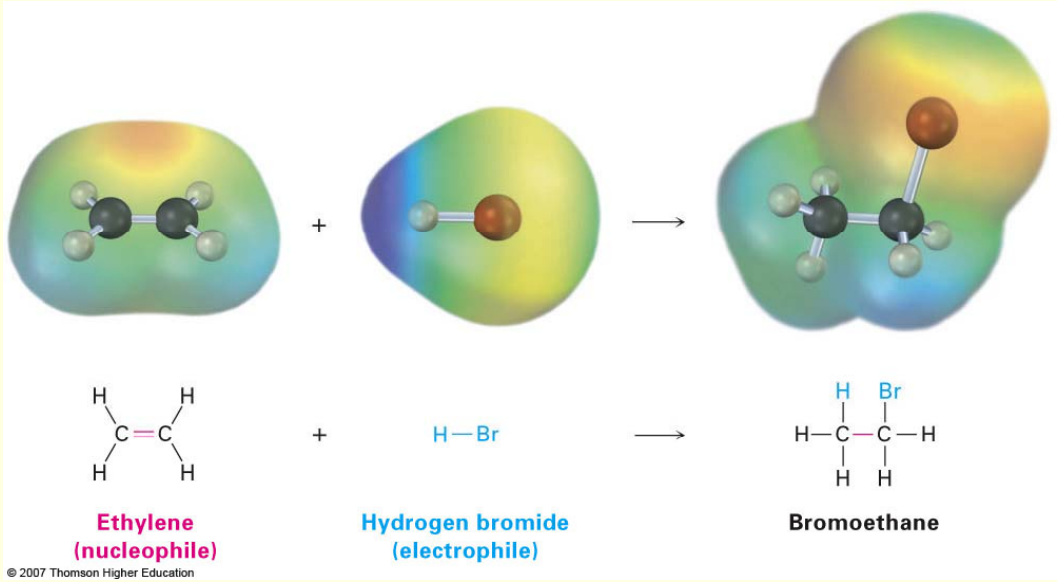




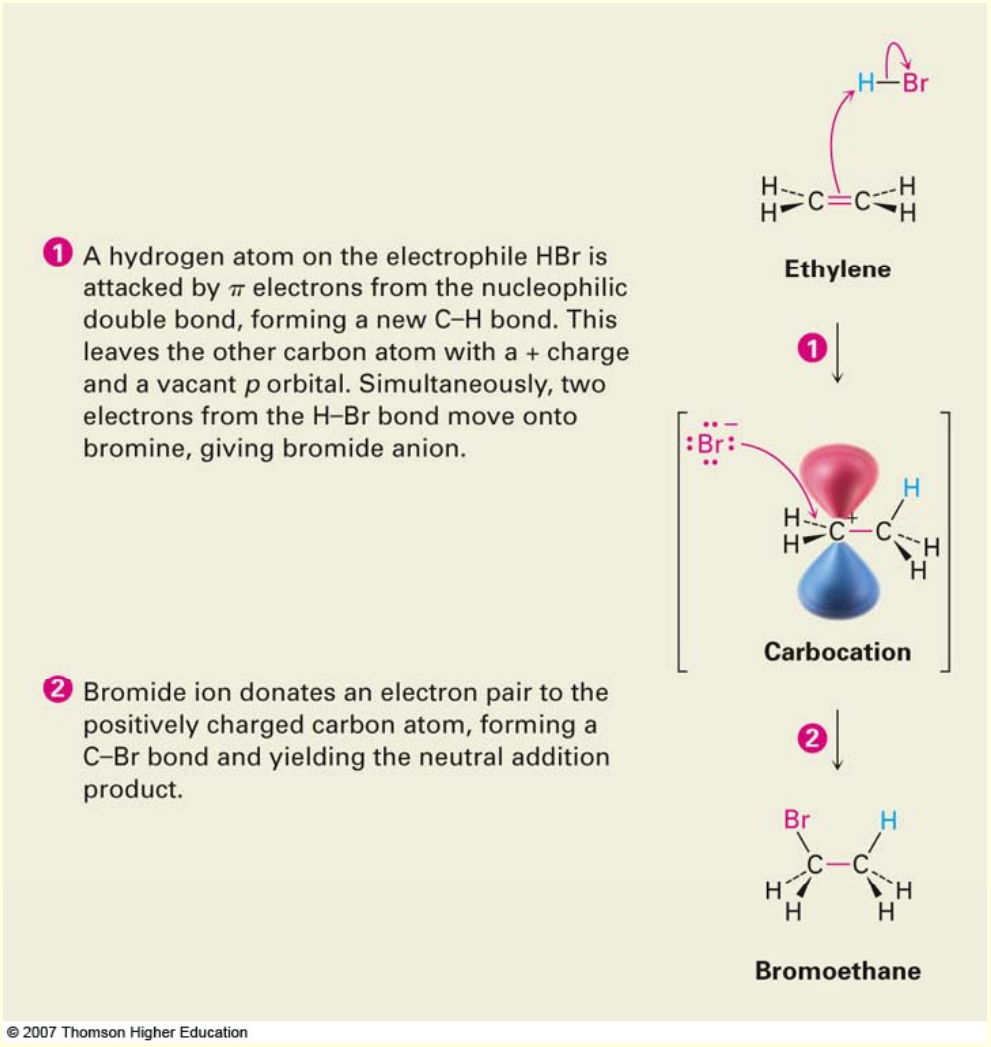


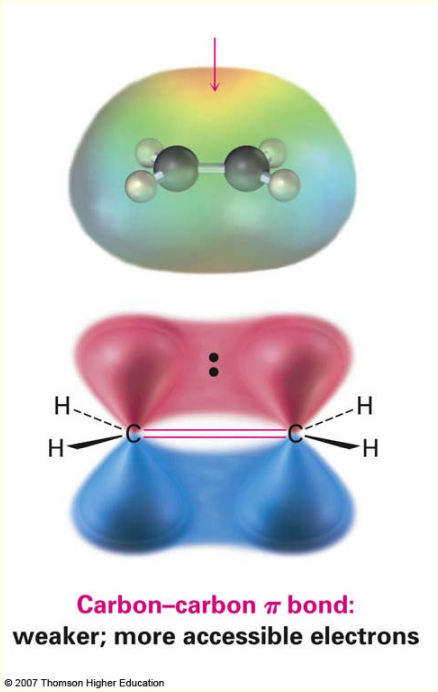
An Example of a Polar Reaction: Addition of HBr to Ethylene

- HBr adds to the π part of C-C double bond
- The π bond is electron-rich, allowing it to function as a nucleophile
- H-Br is electron deficient at the H since Br is much more electronegative, making HBr an electrophile



Mechanism of Addition of HBr to Ethylene





Why Reactions Occur

All organic reactions we will study will reach equilibrium that favors the more stable side. In most cases, these will be reaction products as written from left to right (note, however, sometimes you must predict which side is favored as in acid-base reactions).

$$\Delta G^{o} = - RT \ln K_{eq} = \Delta H - T\Delta S$$

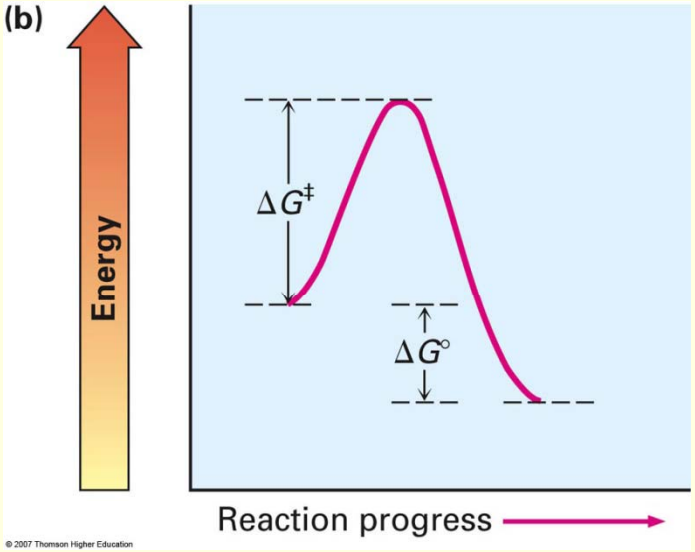
If *K*eq > 1, energy is released to the surroundings
(**exergonic** reaction, negative value of ΔG^{o}, reaction favored)

If *K*eq < 1, energy is absorbed from the surroundings
(**endergonic** reaction, positive value of ΔG^{o}, reaction not favored)

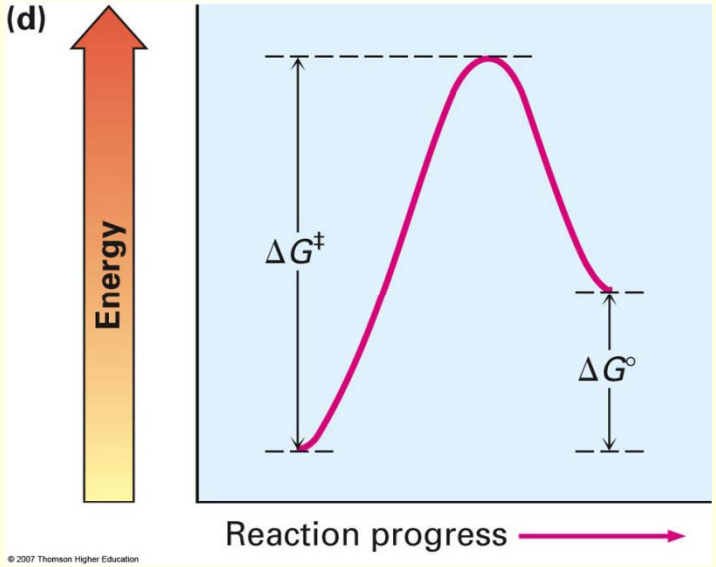
Energy changes in a reaction are illustrated by Energy Diagrams

Reaction Energy Diagrams

One Step Reactions:



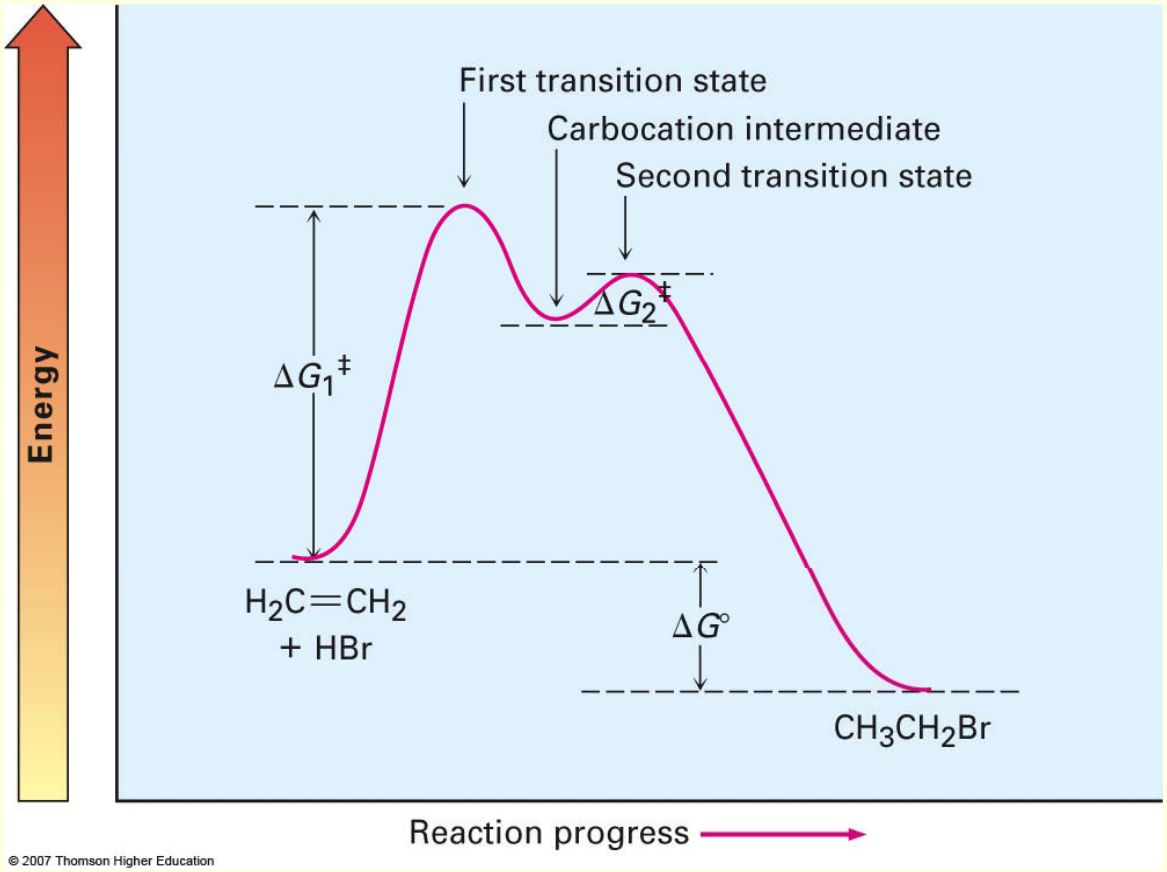
Exergonic (- ΔG)
(thermo favored)



Endergonic (+ ΔG)
(thermo not favored)

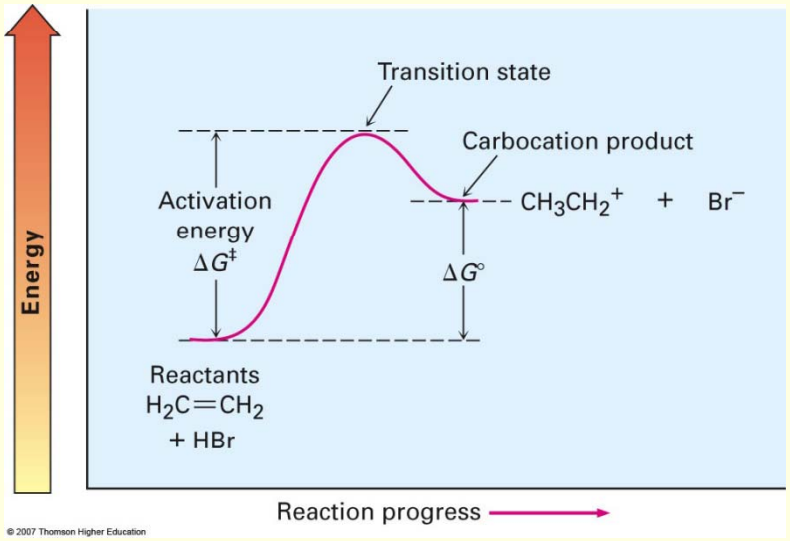
Reaction Energy Diagrams

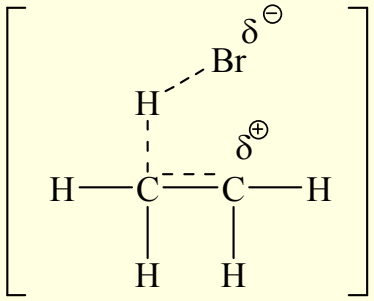
Multiple Step Reactions:

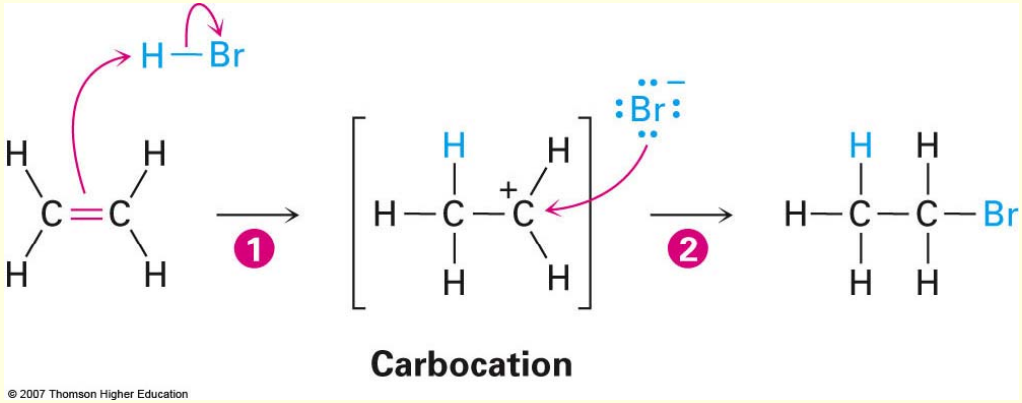


Reaction Energy Diagrams

- The highest energy point in a reaction step is called the **transition state**
- The energy needed to go from reactant to transition state is the **activation energy (ΔG‡)**

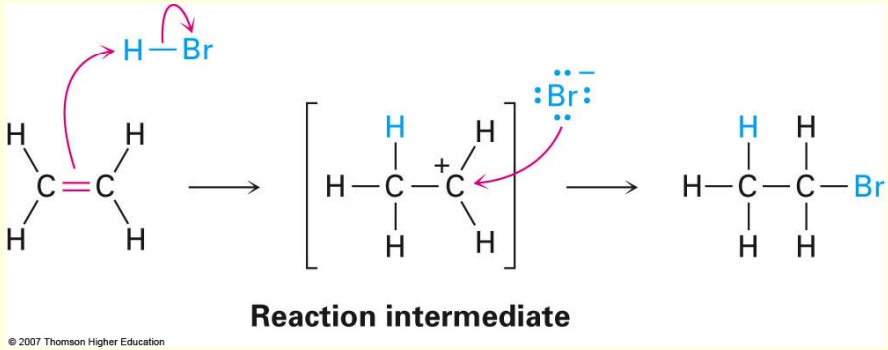


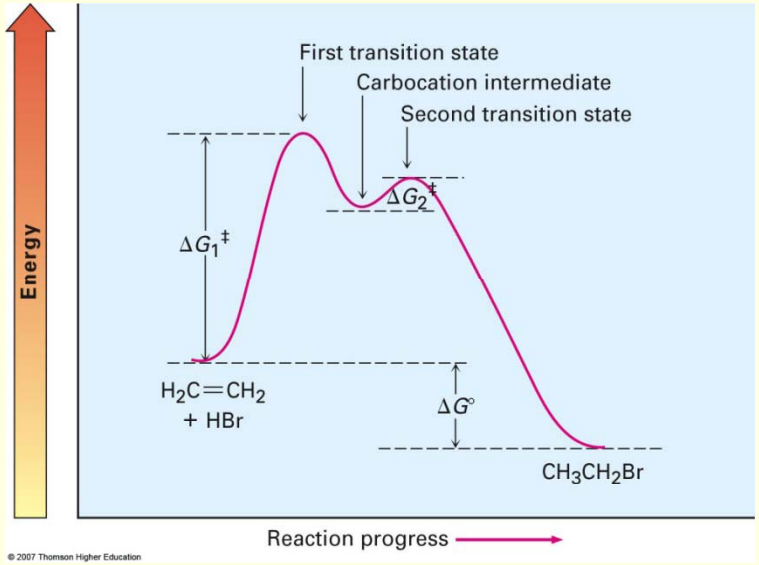




Reaction Energy Diagrams

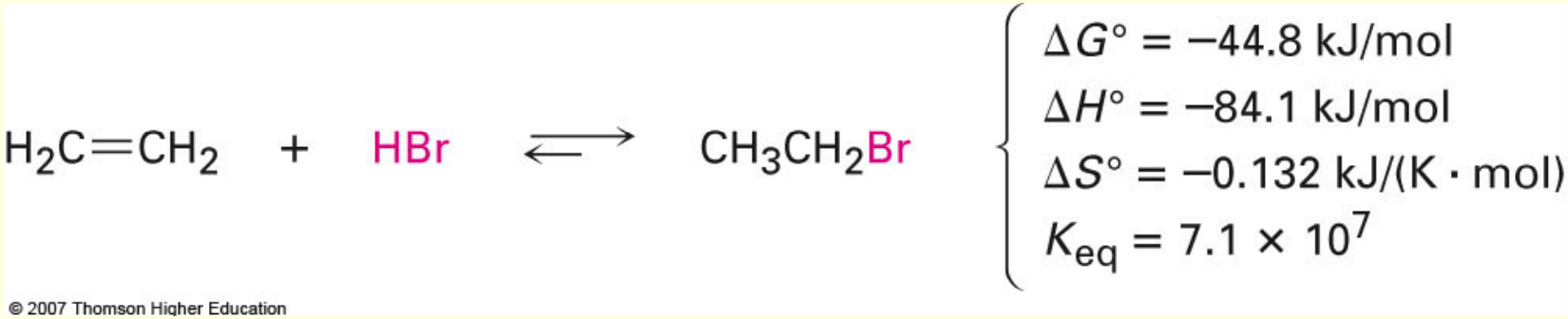
- If a reaction occurs in more than one step, it must involve species that are neither the reactant nor the final product
- These are called **reaction intermediates** or simply "intermediates"
- Each step has its own free energy of activation
- The complete diagram for the reaction shows the free energy changes associated with an intermediate





Estimating ΔG from ΔH

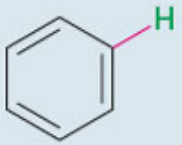
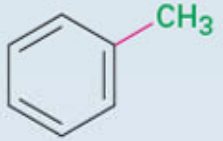
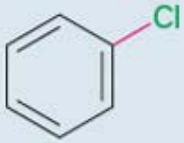
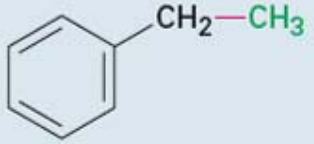
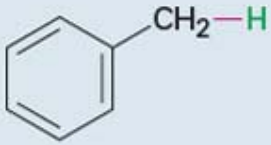
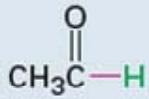
ΔH = (energy needed to break bonds) - (energy released when bonds form)



Bonds Breaking	Bonds Forming
C=C = 611 kJ/mol	C-C = 355 kJ/mol
H-Br = 366 kJ/mol	C-Br = 285 kJ/mol
	C-H = 420 kJ/mol

ΔH = (977 kJ/mol) - (1060 kJ/mol) = - 83 kJ/mol (exothermic)

Table 5.3 Some Bond Dissociation Energies, *D*

Bond	*D* (kJ/mol)	Bond	*D* (kJ/mol)	Bond	*D* (kJ/mol)
H—H	436	$(CH_3)_3C$—I	209	C_2H_5—CH_3	355
H—F	570	H_2C=CH—H	444	$(CH_3)_2CH$—CH_3	351
H—Cl	432	H_2C=CH—Cl	368	$(CH_3)_3C$—CH_3	339
H—Br	366	H_2C=$CHCH_2$—H	361	H_2C=CH—CH_3	406
H—I	298	H_2C=$CHCH_2$—Cl	289	H_2C=$CHCH_2$—CH_3	310
Cl—Cl	243		464	H_2C=CH_2	611
Br—Br	193				427
I—I	151				
CH_3—H	438		405		
CH_3—Cl	351				332
CH_3—Br	293				
CH_3—I	234		368		
CH_3—OH	380				368
CH_3—NH_2	335				

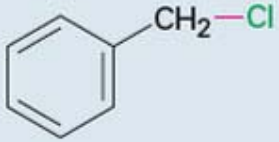
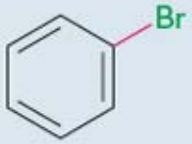
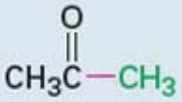
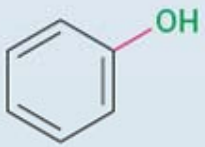
C_2H_5—H	420		293	HO—H	498
C_2H_5—Cl	338			HO—OH	213
C_2H_5—Br	285			CH_3O—H	437
C_2H_5—I	222		337	CH_3S—H	371
C_2H_5—OH	380			C_2H_5O—H	436
$(CH_3)_2CH$—H	401				322
$(CH_3)_2CH$—Cl	339		469		
$(CH_3)_2CH$—Br	274			CH_3CH_2O—CH_3	339
$(CH_3)_3C$—H	390				
$(CH_3)_3C$—Cl	330	HC≡C—H	552	NH_2—H	449
$(CH_3)_3C$—Br	263	CH_3—CH_3	376	H—CN	518

Table 5.2 | Explanation of Thermodynamic Quantities: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Term	Name	Explanation
ΔG°	Gibbs free-energy change	The energy difference between reactants and products. When ΔG° is negative, the reaction is **exergonic**, has a favorable equilibrium constant, and can occur spontaneously. When ΔG° is positive, the reaction is **endergonic**, has an unfavorable equilibrium constant, and cannot occur spontaneously.
ΔH°	Enthalpy change	The heat of reaction, or difference in strength between the bonds broken in a reaction and the bonds formed. When ΔH° is negative, the reaction releases heat and is **exothermic**. When ΔH° is positive, the reaction absorbs heat and is **endothermic**.
ΔS°	Entropy change	The change in molecular randomness during a reaction. When ΔS° is negative, randomness decreases; when ΔS° is positive, randomness increases.

Are the following reactions thermodynamically favored?