

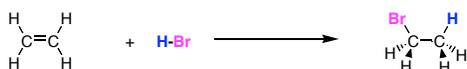
## Chapter 5: An Overview of Organic Reactions

Reactions are organized by:

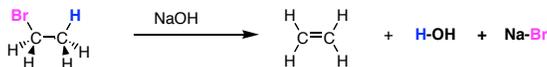
- what kind of reaction occurs (change from reactants to product)
- how the reaction occurs (mechanism)

Kinds of reactions:

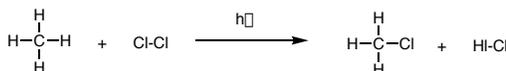
A. Addition reactions: two reactants add to form a product.  
no (or few) atoms are left over



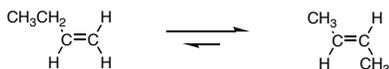
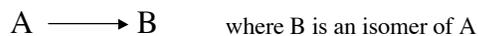
B. Elimination reaction: a single reactant is split into two (or more) products. Opposite of an addition reaction



C. Substitution Reactions: two reactants exchange parts to give new products



D. Rearrangement Reactions: a single reactant undergoes bond reorganization to give a product which is an isomer of the reactant



## Curved Arrow Convention

1. Curved arrows show the movement (flow) of electron during bond breaking and/or bond making processes. The foot of the arrow indicates where the electron or electron pair originates, the head of the arrow shows where the electron or electron pair ends up.
  - A. The movement of a single electron is denoted by a curved single headed arrow (fishhook or hook).  

  - B. The movement of an electron pair is denoted by a curved double headed arrow.
2. If an electron pair moves in on a new atom, another electron pair must leave so that the atom does not exceed a full valance of eight electrons. There are two common exceptions:
  - A. When an atom already has an incomplete valance ( $R_3C^+$ ).
  - B. With second row (or below) elements the octet rule may be violated.
3. The arrows completely dictate the Lewis structure of the product.

## Curved Arrow Convention

### Other Suggestions for Proper Arrow Pushing:

4. The natural polarization of double bonds between unlike atoms is in the direction of the more electronegative atom and this will be the important direction of electron movement.
5. In drawing a mechanism, the formal charges of atoms in the reactants may change in the product. Use your knowledge of Lewis structures and formal charge to determine this.
6. The first step in writing a mechanism is to identify the nucleophile (Lewis base) and the electrophile (Lewis acid). The first arrow is always from the nucleophile to the electrophile.

#### Bond Breaking

1. Homolytic: symmetrical bond breaking process
2. Heterolytic: unsymmetrical bond breaking processes

#### Bond Forming

1. Homogenic: one electron is donated to a bond from two reactants. (radical reactions, odd number of valence electrons)
2. Heterogenic: two electrons of the bond is donated by one reactant. (polar reactions, even number of valence electrons)
3. Pericyclic (Chapter 30)

#### 5.3: Radical Reactions and how they occur

Radicals:

1. Contain an odd number of valence electrons (usually 7)
2. Highly reactive
3. Usually neutral, however radical cations and radical anion are not uncommon

#### Reactivity:

1. Atom abstraction (substitution)
2. Addition (to double bonds)

## Chlorination of methane

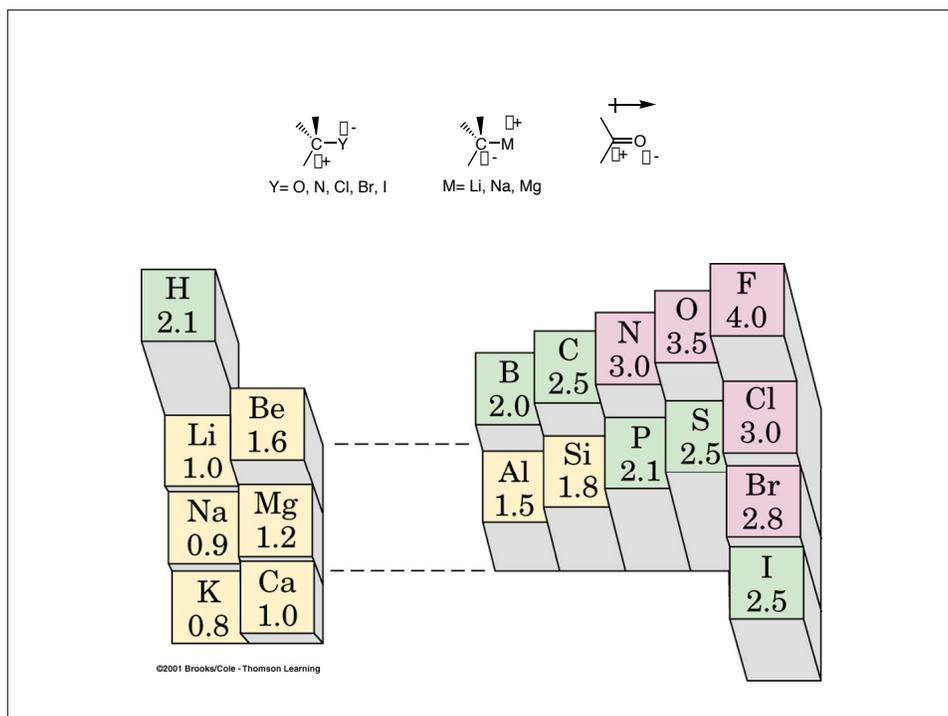
Mechanism of free radical chlorination

- three distinct steps
  1. Initiation
  2. Propagation
  3. Termination

Alkane chlorination is generally not a useful synthetic reaction  
Radical chain mechanism is a very important processes and  
will be discussed in more detail in Chapter 10

## Polar Reactions and How They Occur

- result from attractive forces between positive (or partial positive,  $\delta^+$ ) and negative (or partial negative,  $\delta^-$ ) charges on molecules
- most organic molecules are charge neutral and most polar reactions are a result of bond polarity caused by unsymmetrical sharing of electrons by atoms due to electronegativity differences
- Polarizability: change in electron distribution around atoms due to an external influence
  - large atoms with loosely held valence electrons are more polarizable than small atoms with tightly held valence electrons. I is more polarizable than F



Electron rich ( $\ominus$ ) sites in a functional group of one molecule react with an electron-poor ( $\oplus$ ) site of a functional group

If the sites are in different molecules: biomolecular or intermolecular  
 If the sites are in the same molecule: unimolecular or intramolecular

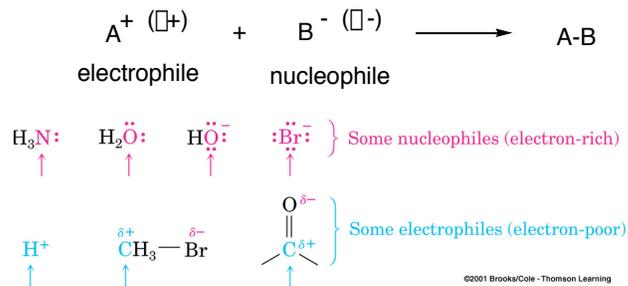
Electrophile: electron poor

Nucleophile: electron rich

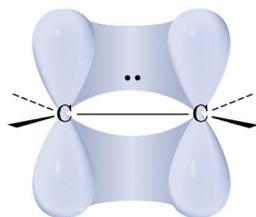
note: similarity to Lewis acid-base definition

Lewis acid: electron pair acceptor (electrophile)

Lewis base: electron pair donor (nucleophile)



## 5.5 Addition of HBr to Ethylene

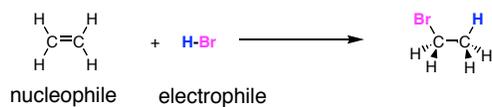


**Carbon-carbon  $\pi$  bond:**  
weaker: more accessible electrons

C-C  $\sigma$ -bond:  $\Delta H^\circ = 376$  KJ/mol  
C-C  $\pi$ -bond:  $\Delta H^\circ = 235$  KJ/mol

$\pi$ -bond of an alkene can  
act as a nucleophile!!

### Electrophilic addition reaction



## 5.6: Curved Arrows in Polar Reaction Mechanisms

- Electrons move from a nucleophilic source to an electrophilic source
- The nucleophile can be either negatively charged or neutral, but must have an available non-bonding pair of electrons
- The electrophile can be either positively charged or neutral
- All reactants, intermediates and products ***MUST*** be proper Lewis structures

### 5.7: Describing a Reaction: Equilibria, Rates & Energy Changes

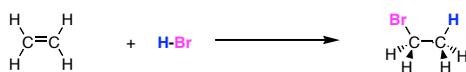


$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$K_{eq}$  tells us which side of the equilibrium arrows is energetically more favorable.

if:  $K_{eq} > 1$ , then [products] is greater than [reactants] and products are favored

$K_{eq} < 1$ , then [reactants] is greater than [products] and reactants are favored



$$K_{eq} = \frac{[\text{CH}_3\text{CH}_2\text{Br}]}{[\text{H}_2\text{C}=\text{CH}_2] [\text{HBr}]} = 7.5 \times 10^7$$

99.999997 % towards products

$K_{eq} > 10^3$ , “complete reaction”

In order for  $K_{eq}$  to favor products, the total energy of the products must be lower than the total energy of the reactants

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

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

Standard Gibbs Free Energy ( $\Delta G^\circ = \Delta G^\circ_{\text{products}} - \Delta G^\circ_{\text{reactants}}$ )

$\Delta G^\circ < 0$  exergonic (spontaneous), equilibrium favors products

$\Delta G^\circ > 0$  endergonic (non-spontaneous), equilibrium favors reactant



$$K_{eq} = \frac{[\text{CH}_3\text{CH}_2\text{Br}]}{[\text{H}_2\text{C}=\text{CH}_2] [\text{HBr}]} = 7.5 \times 10^7$$

$$\Delta G^\circ = -(8.314 \times 10^{-3}) (298) \ln (7.5 \times 10^7) = -45 \text{ KJ/mol}$$

Enthalpy ( $\Delta H^\circ$ ): heat of reaction.

Change in total bond energies during a reaction

$\Delta H^\circ < 0$ : bond energies of the products are stronger (more stable) than those of the reactants. The reaction is favored, heat is released, exothermic.

$\Delta H^\circ > 0$ : bond energies of the products are weaker (less stable) than those of the reactants. The reaction is disfavored, heat is absorbed, endothermic.

Entropy ( $\Delta S^\circ$ ): Entropy change: measure of molecular disorder

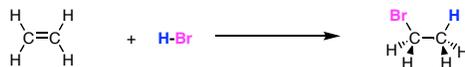
$\Delta S^\circ < 0$ : disorder is decreased (more order), disfavored

$\Delta S^\circ > 0$ : disorder is increased (less order), favored

Table 5.3 (page 173) Bond dissociation energies

TABLE 5.3 Some Bond Dissociation Energies					
Bond	$D$ (kJ/mol)	Bond	$D$ (kJ/mol)	Bond	$D$ (kJ/mol)
H-H	436	(CH <sub>3</sub> ) <sub>3</sub> C-Br	263	CH <sub>3</sub> -CH <sub>3</sub>	376
H-F	570	(CH <sub>3</sub> ) <sub>3</sub> C-I	209	C <sub>2</sub> H <sub>5</sub> -CH <sub>3</sub>	355
H-Cl	432	H <sub>2</sub> C=CH-H	444	(CH <sub>3</sub> ) <sub>2</sub> CH-CH <sub>3</sub>	351
H-Br	366	H <sub>2</sub> C=CH-Cl	368	(CH <sub>3</sub> ) <sub>2</sub> C-CH <sub>3</sub>	339
H-I	298	H <sub>2</sub> C=CHCH <sub>2</sub> -H	361	H <sub>2</sub> C=CH-CH <sub>3</sub>	406
Cl-Cl	243	H <sub>2</sub> C=CHCH <sub>2</sub> -Cl	289	H <sub>2</sub> C=CHCH <sub>2</sub> -CH <sub>3</sub>	310
Br-Br	193	 -H	464	H <sub>2</sub> C=CH <sub>2</sub>	611
I-I	151	 -Cl	405	 -CH <sub>3</sub>	427
CH <sub>3</sub> -H	438	 -H	368	 -CH <sub>2</sub> -CH <sub>3</sub>	332
CH <sub>3</sub> -Cl	351	 -Cl	293		368
CH <sub>3</sub> -Br	293	 -Br	337	CH <sub>3</sub> -H	408
CH <sub>3</sub> -I	234	 -OH	469	HO-H	498
CH <sub>3</sub> -OH	380	H <sub>2</sub> C=C-H	552	HO-OH	213
CH <sub>3</sub> -NH <sub>2</sub>	335			CH <sub>3</sub> O-H	437
C <sub>2</sub> H <sub>5</sub> -H	420			CH <sub>3</sub> S-H	371
C <sub>2</sub> H <sub>5</sub> -Cl	338			C <sub>2</sub> H <sub>5</sub> O-H	436
C <sub>2</sub> H <sub>5</sub> -Br	285				322
C <sub>2</sub> H <sub>5</sub> -I	222			CH <sub>3</sub> CH <sub>2</sub> O-CH <sub>3</sub>	339
C <sub>2</sub> H <sub>5</sub> -OH	380			NH <sub>2</sub> -H	449
(CH <sub>3</sub> ) <sub>2</sub> CH-H	401			H-CN	518
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl	339				
(CH <sub>3</sub> ) <sub>2</sub> CH-Br	274				
(CH <sub>3</sub> ) <sub>2</sub> C-H	390				
(CH <sub>3</sub> ) <sub>3</sub> C-Cl	330				

From Table 5.3 (page 172)



Bonds broken

C=C  $\sigma$ -bond 235 KJ/mol  
H-Br 366 KJ/mol

Bonds formed

H<sub>3</sub>C-H<sub>2</sub>C-H -420 KJ/mol  
H<sub>3</sub>C-H<sub>2</sub>C-Br -285 KJ/mol

calc.  $\Delta H^\circ = -104$  KJ/mol

expt.  $\Delta H = -84$  KJ/mol (~ 30 % error)

Table values of  $\Delta H^\circ$  are measured in the gas phase for homolytic bond breaking. Solvation and the actual mechanism of the reaction can play a very large role in the measured heat of reaction.



H<sub>3</sub>C-H  $\Delta H^\circ = 438$  KJ/mol

H<sub>3</sub>CCH<sub>2</sub>-H 420

(H<sub>3</sub>C)<sub>2</sub>CH-H 401

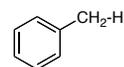
(H<sub>3</sub>C)<sub>3</sub>C-H 390

H<sub>2</sub>C=CH-H 444

H<sub>2</sub>C=CH-CH<sub>2</sub>-H 361



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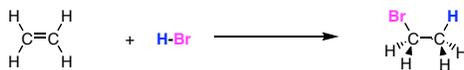


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Substitution is an important consideration in  $\Delta H^\circ$ . The bond energies reflect the stability of the radical product

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

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



$$K_{eq} = \frac{[\text{CH}_3\text{CH}_2\text{Br}]}{[\text{H}_2\text{C}=\text{CH}_2][\text{HBr}]} = 7.5 \times 10^7$$

$$\Delta G^\circ = (8.314 \times 10^{-3}) (298) \ln (7.5 \times 10^7) = -45 \text{ KJ/mol}$$

$$\Delta H^\circ = -84 \text{ KJ/mol}$$

$$\Delta S^\circ = -0.132 \text{ KJ/mol} \quad \Delta S < 0, \text{ less disorder, unfavorable}$$

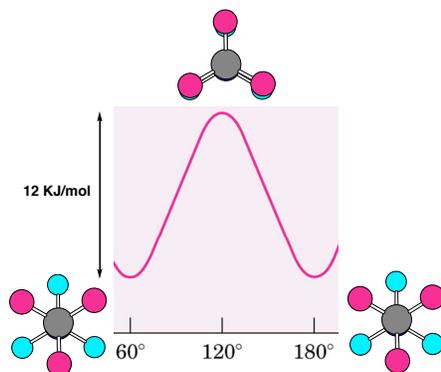
two molecule going to one is more ordered

Solvation can also play a significant role of  $\Delta S^\circ$ , particularly for polar reaction.

Thermodynamics (equilibrium, Gibbs Free Energy) can only tell us position of an equilibrium ( $K_{eq}$ ) or if a reaction is theoretically possible. It does not tell us how fast a reaction occur. There is no formal relationship between thermodynamics and kinetics

Rate = how fast (or slow) a reaction will occur

The rate of a reaction depends on the activation energy ( $\Delta G^\ddagger$ )



Transition state: structure corresponding to the highest energy level (maxima) on an energy diagram.

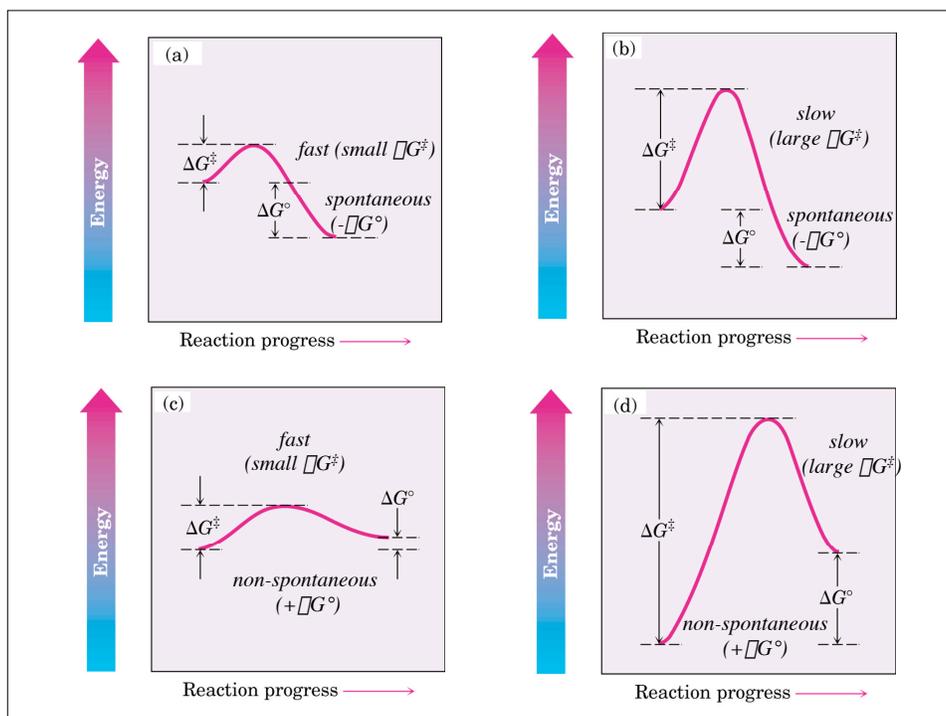
Transition states can not be isolated or “trapped.” Intermediates in principle, can be isolated or “trapped.” Intermediates are “local minima” on reaction energy diagrams

Activation Energy ( $\Delta G^\ddagger$ ): Energy difference between reactants and the transition state.  $\Delta G^\ddagger$  determines how fast a reaction will occur (rate).

Large  $\Delta G^\ddagger$  - slow reaction rate

Small  $\Delta G^\ddagger$  - fast reaction rate

Reactions with  $\Delta G^\ddagger < 80 \text{ KJ/mol}$  will readily take place at room temperature ( $298^\circ\text{C}$ )



Random motion  $\longrightarrow$  molecular collisions

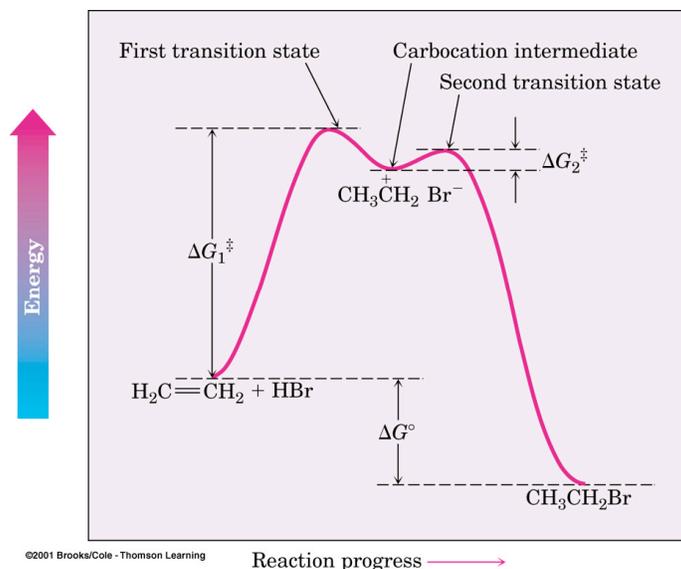
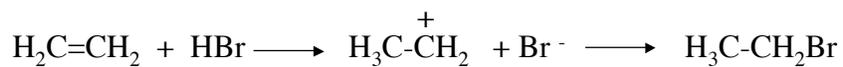
Reactions result from collisions between molecules, however not all collisions result in a reaction. They must be of the right energy and orientation.

Heating a reaction:

increases the frequency of collisions

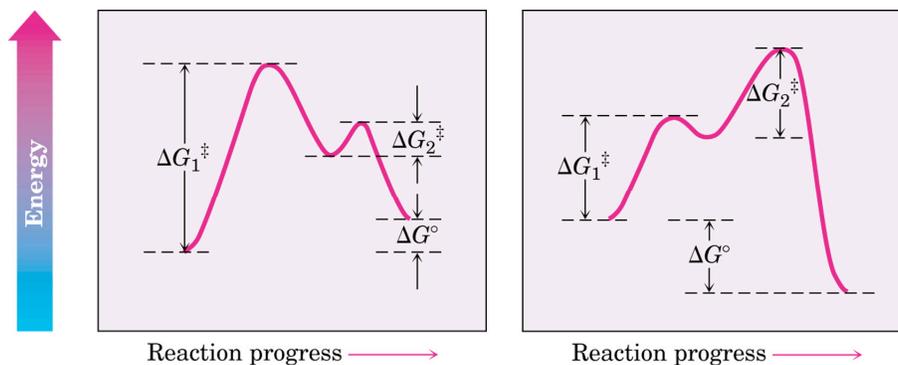
increases the energy of collisions

Once the transition state of a reaction has been reached, the transition structure can revert to reactants or proceed on to products. Both processes are energetically downhill (favorable).



Reaction Intermediate: Compound which is briefly formed during a multistep chemical reaction, They are usually short lived and react further to give a more stable product in a second step.

In a two-step reaction involving an intermediate, both steps have a  $\Delta G^\circ$  and  $\Delta G^\ddagger$ .



A transition state is a structure that a reaction must pass through in order to be converted to products. They have very short lifetimes, on the order of a molecular vibration. They can not be isolated and normally can not be observed.

For the addition of HBr to ethylene, the transition state would look something like:

