

PART 2

Addition, Stereochemistry, and Delocalization



Chapter 3. Alkenes

4. Reactions of alkenes
5. Stereochemistry
6. Alkynes
7. Electron delocalization

Chapter 3

Alkenes



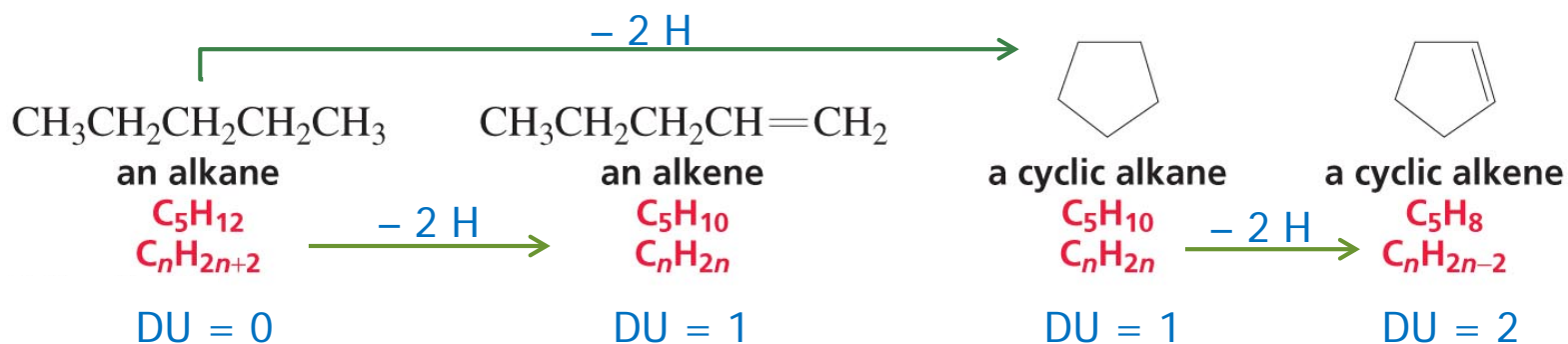
Structure and nomenclature

Reactivity

Thermodynamics and kinetics

Alkenes

- HC containing a C=C (double bond)
 - common name ~ olefin [oil-forming]
 - alkane ~ paraffin [little affinity]
 - unsaturated, C_nH_{2n}
 - alkane ~ saturated, C_nH_{2n+2}
- degree of unsaturation [DU]



- 1 DU per 1 π bond or 1 ring ($-2H$)
 - $DU = (\text{max \# of H} - \text{\# of H})/2$

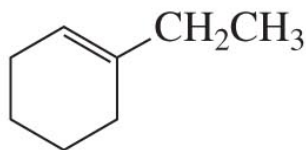
□ isomers of C_8H_{14}

■ $DU = (18 - 14)/2 = 2$

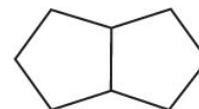
several compounds with molecular formula C_8H_{14} :



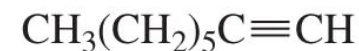
A



B



C



D

© 2011 Pearson Education, Inc.

- Do Prob 3c p122.
- Having fun? Draw all the constitutional isomers of C_5H_8 .

Nomenclature of alkenes

Ch 3 #5

- similar to alkanes
- **common** and **systematic**

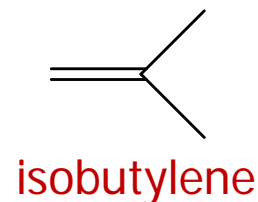
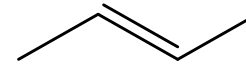
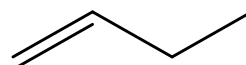
$\text{H}_2\text{C}=\text{CH}_2$
systematic name: ethene
common name: ethylene

© 2011 Pearson Education, Inc.

$\text{CH}_3\text{CH}=\text{CH}_2$
propene
propylene



- butylene, pentylene, ---?



- vinyl and allyl group

$\text{CH}_2=\text{CH}-$
ethenyl
vinyl

$\text{CH}_2=\text{CHCH}_2-$
propenyl
allyl

allyl carbon

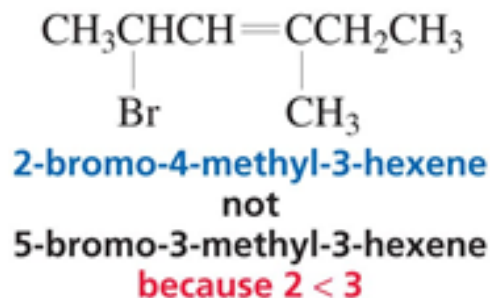
$\text{CH}_2=\text{CHCl}$
chloroethene
vinyl chloride

$\text{CH}_2=\text{CHCH}_2\text{Br}$
3-bromopropene
allyl bromide

allyl from allene
 $\text{CH}_2=\text{C}=\text{CH}_2$
hybridization?
orbital structure?

4. Alphabetize subs

5. (Lowest # for =, then) lowest # for subs.



6. No need to number = in cyclic alkene (always 1=2).
Number subs to give lowest #.



even though
 $1+6 > 2+3$



7. If the same # for =, number subs to give lowest #.

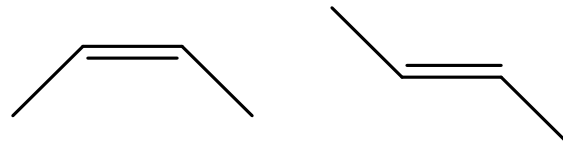
cis and trans isomers of alkenes

Ch 3 #8

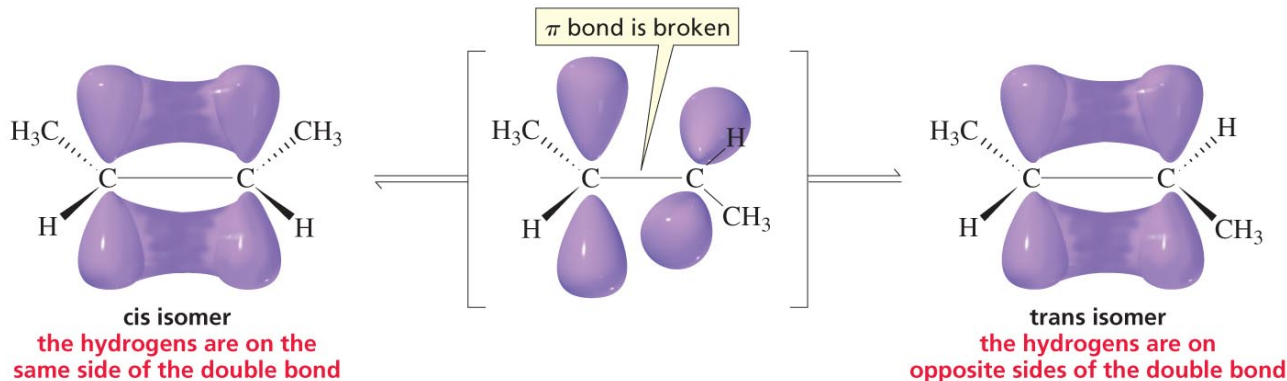
□ isomers

- constitutional isomers ~ different connectivity Chapter 2
- stereoisomers ~ different spatial arrangement
 - geometric isomers ~ cis-trans or Z-E ~ around = or ring
 - enantiomers [optical isomers] ~ around chiral carbon Chapter 5

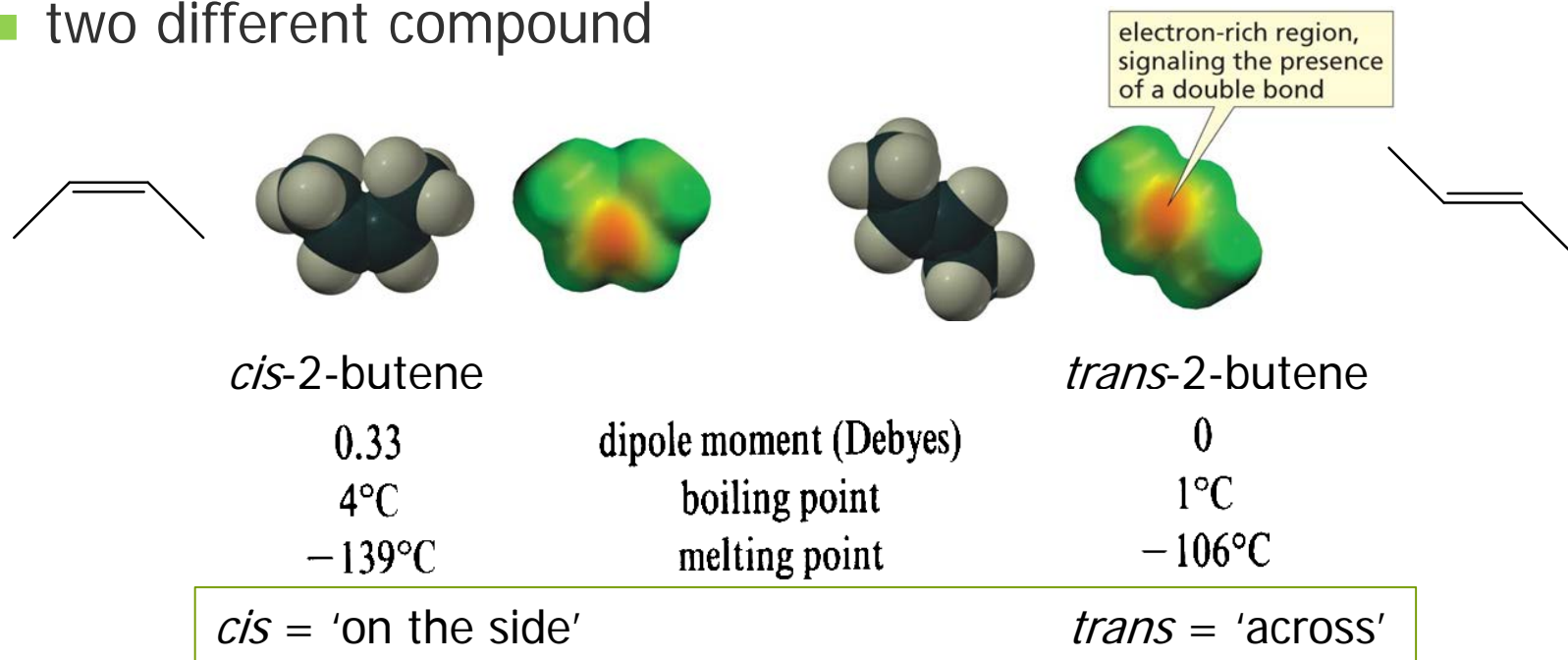
□ *cis*- and *trans*-2-butene



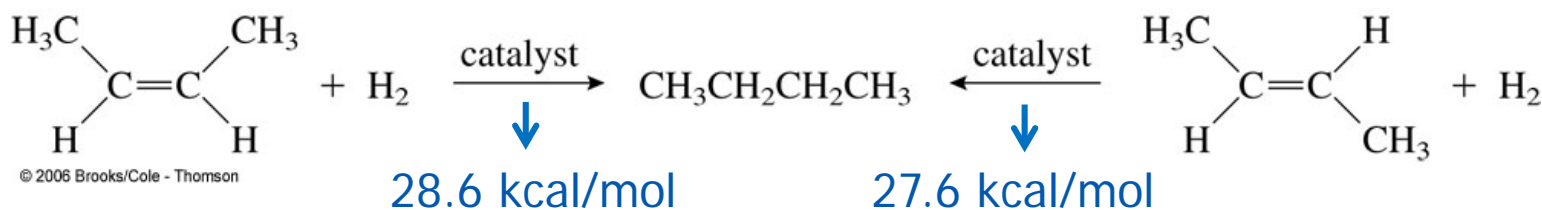
□ different conformation? configuration?



- *cis*- and *trans*-2-butene
 - two different compound



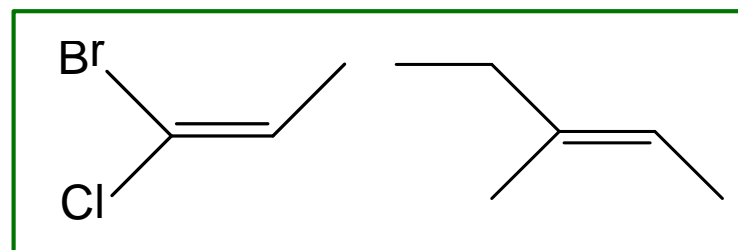
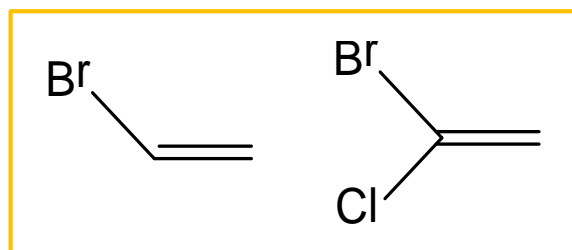
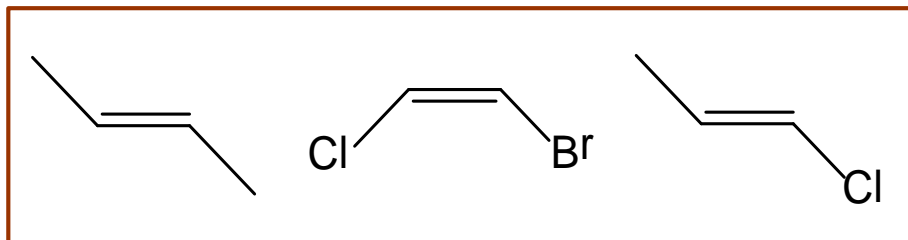
- *cis*-isomer is of higher energy ← steric strain



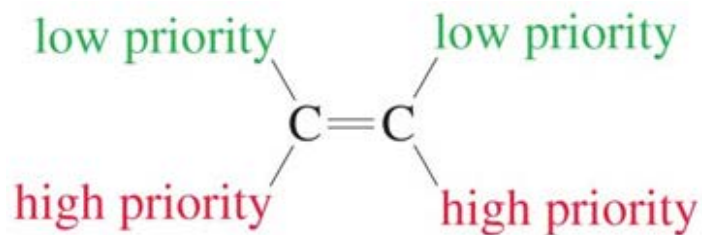
Z-E designation

Ch 3 #10

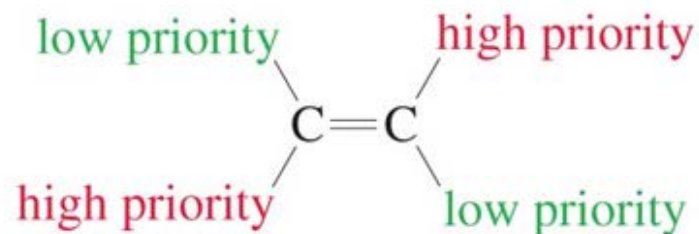
- *cis-trans* designation for 1,2-disubstituted alkenes only



- for tri- or tetrasubstituted ~ *Z-E* designation



Z isomer
zusammen ['together']



E isomer
entgegen ['opposite']

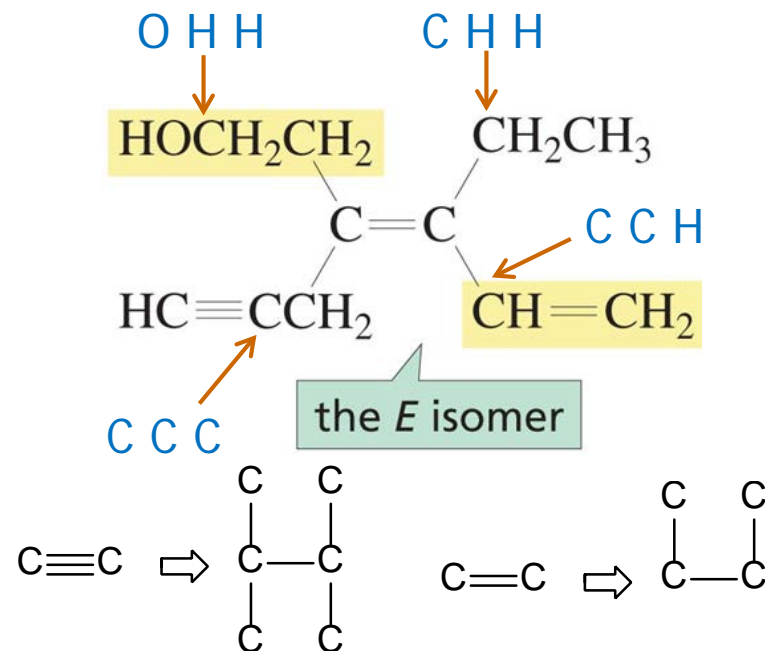
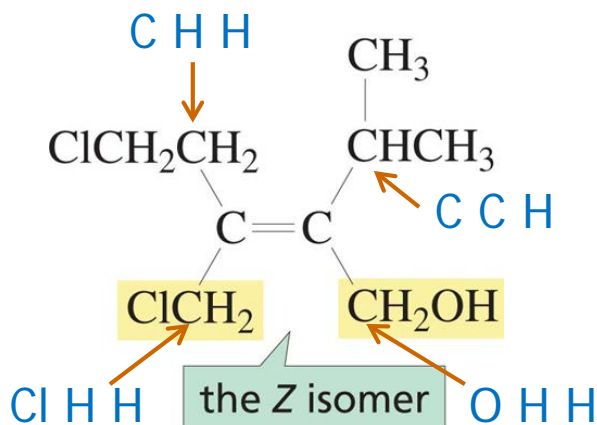
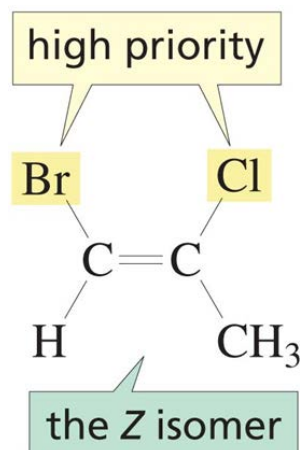
□ rules for priority

■ Cahn-Ingold-Prelog sequence rule

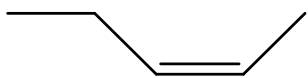
Rule 1. higher priority for higher **atomic number**

Rule 2. higher atomic number **at the first point of difference**

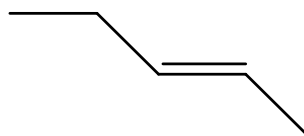
Rule 3. Divide-duplicate **multiple bond**



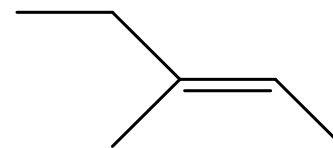
- Prob 12(a) Draw E, Z isomers of $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$



(*Z*)-2-pentene
cis-2-pentene

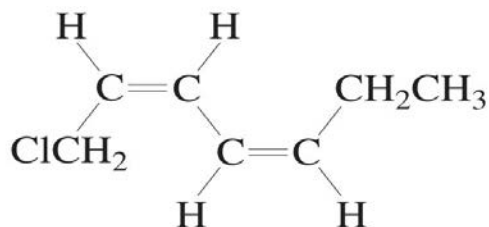


(*E*)-pent-2-ene
trans-2-pentene

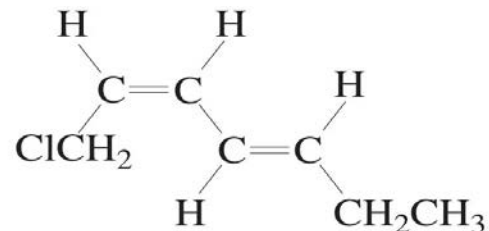


(*E*)-3-methylpent-2-ene
trans-3-methylpent-2-ene

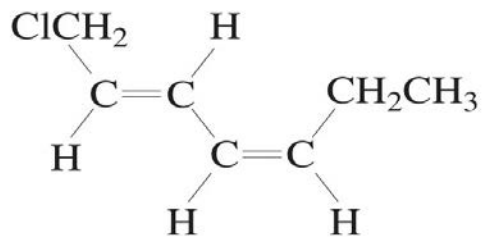
- Box p132 isomers of $\text{ClCH}_2\text{CH}=\text{CHCH}=\text{CHCH}_2\text{CH}_3$



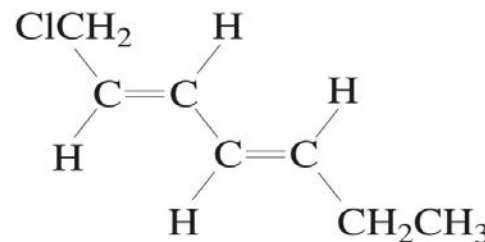
(*2Z,4Z*)-1-chloro-2,4-heptadiene



(*2Z,4E*)-1-chloro-2,4-heptadiene



(*2E,4Z*)-1-chloro-2,4-heptadiene



(*2E,4E*)-1-chloro-2,4-heptadiene

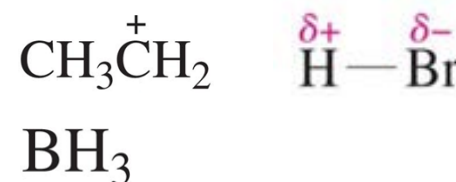
Reaction mechanism

Ch 3 #13

- mechanism ~ how the reaction proceeds
- Organic reactions are **interaction betw e-deficient and e-rich** atoms or molecules.
- functional group ~ where the reaction takes place; either

- **electrophile ~ e-deficient ft'nal grp**

- looks for electron (pair)
- with (partial or full) positive charge, or
- with incomplete octet [empty orbital]



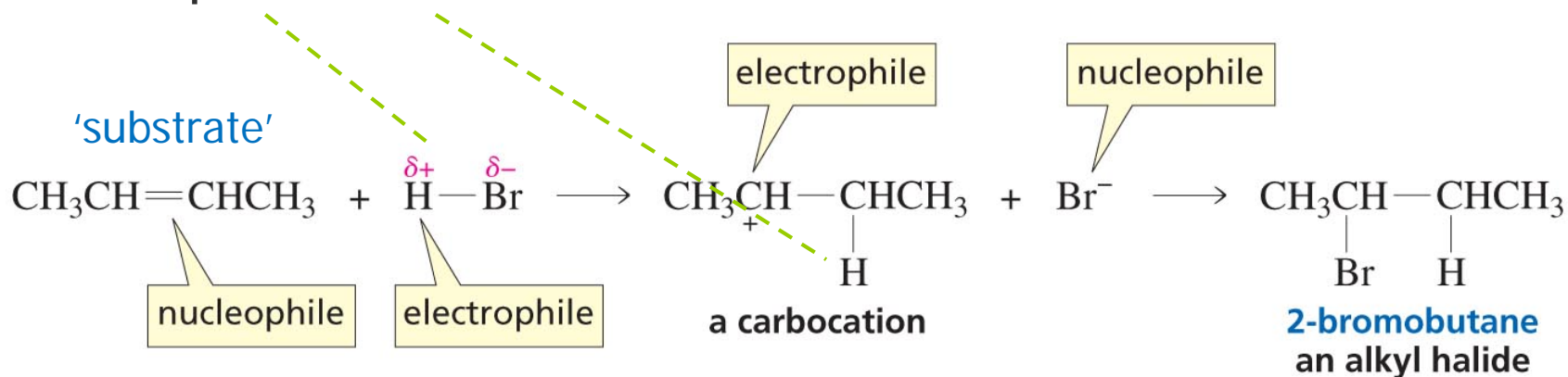
- **nucleophile ~ e-rich ft'nal grp**

- looks for electrophile
- with e pair (to share with electrophile), or
- with π electrons



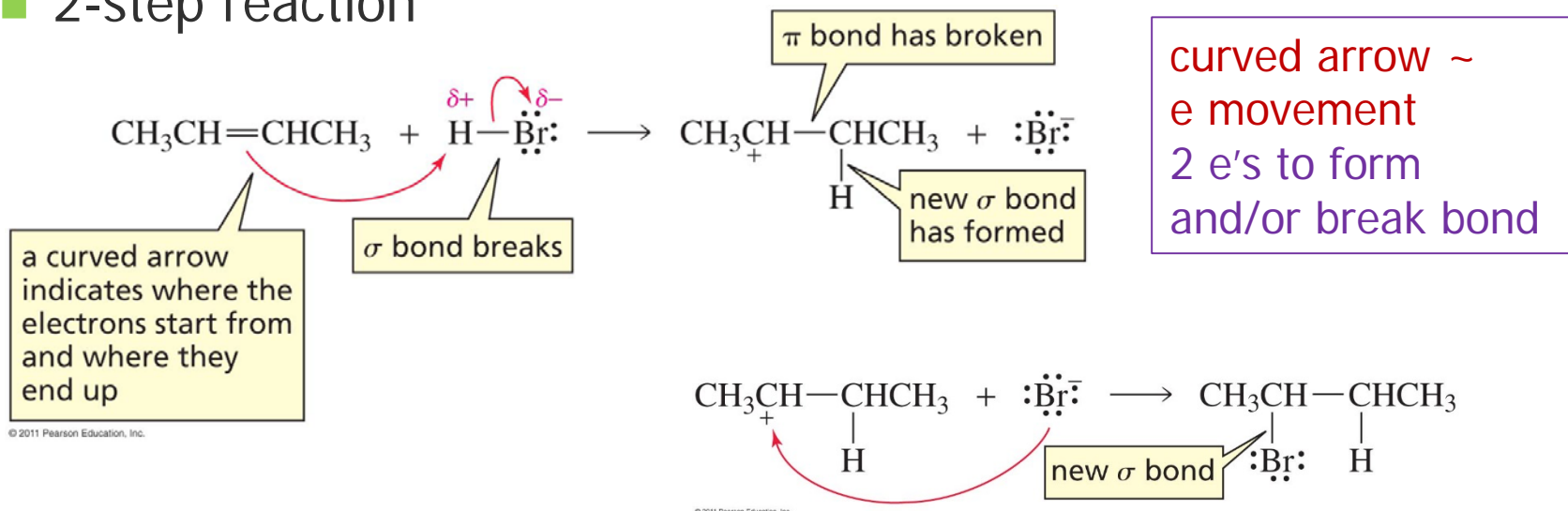
➤ org rxn ~ 'A Nucleophile reacts with an electrophile.'

□ electrophilic addition reaction of alkenes



© 2011 Pearson Education, Inc.

■ 2-step reaction



© 2011 Pearson Education, Inc.

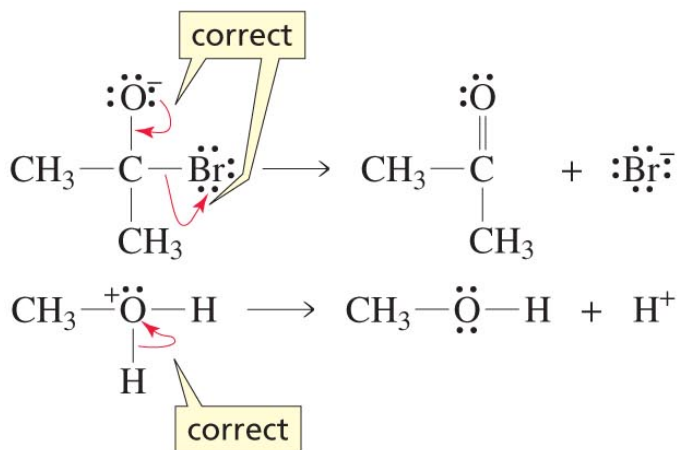
© 2011 Pearson Education, Inc.

Drawing curved arrows

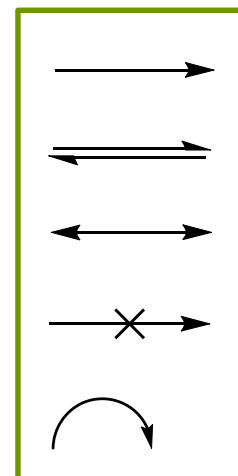
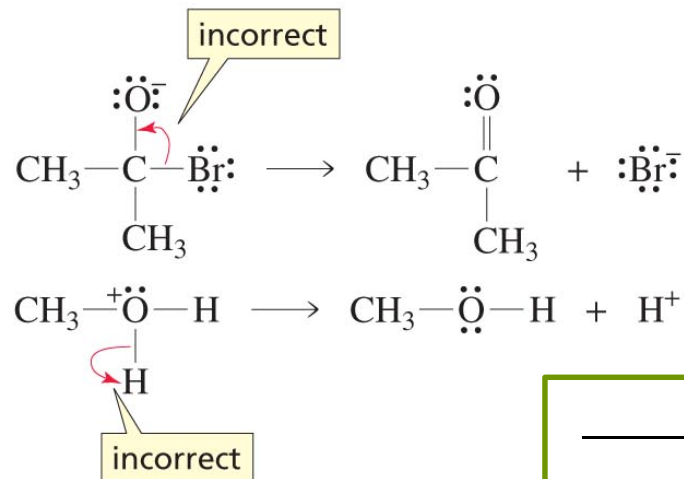
Box p136

Ch 3 #15

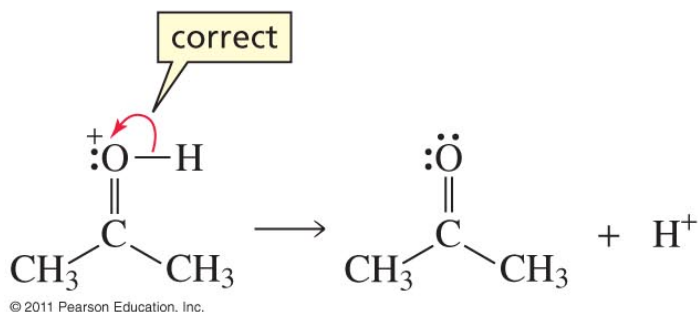
- arrows follow e flow (from - to +)



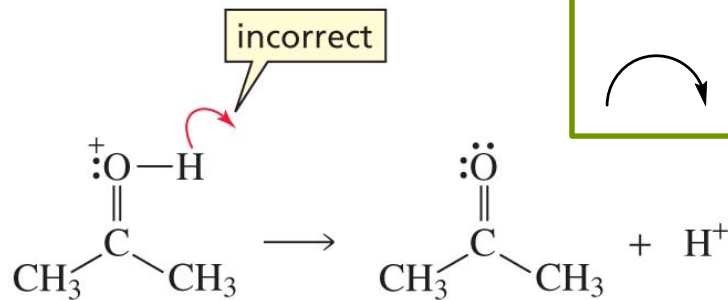
© 2011 Pearson Education, Inc.



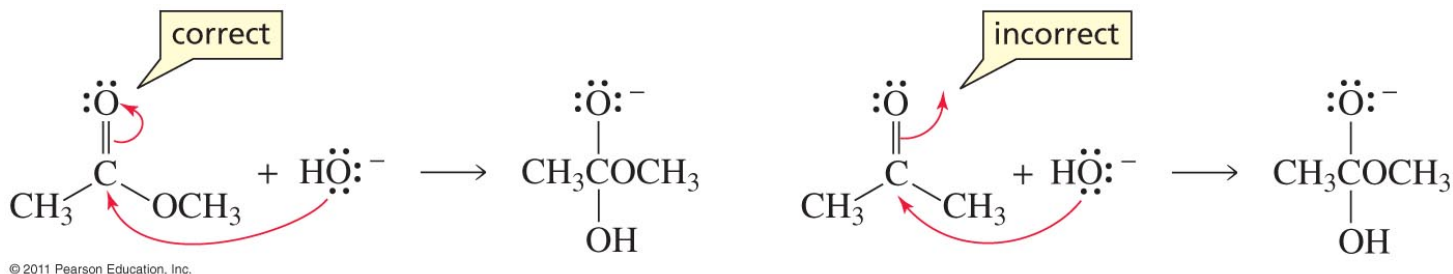
- arrows not for atom movement



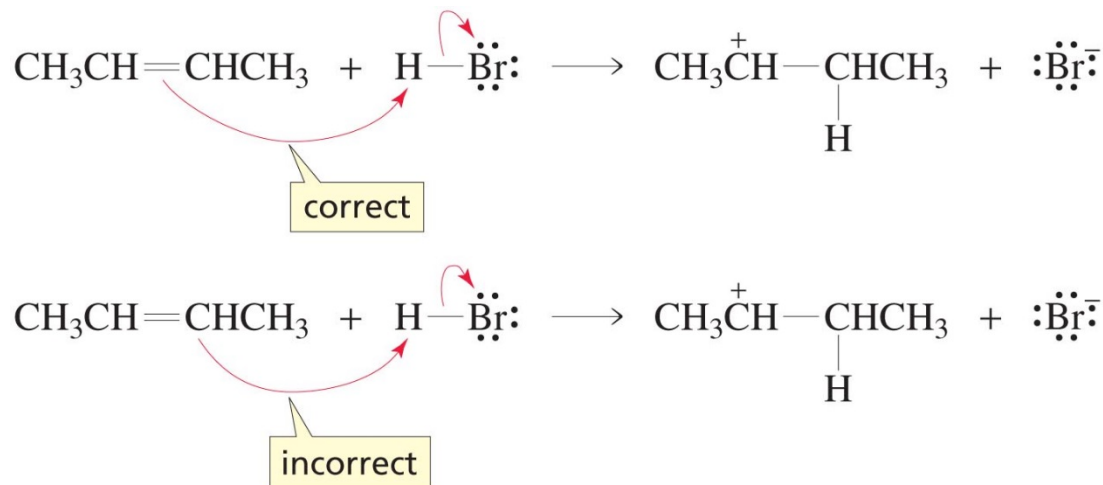
© 2011 Pearson Education, Inc.



- arrows point to atom or bond (not to space)

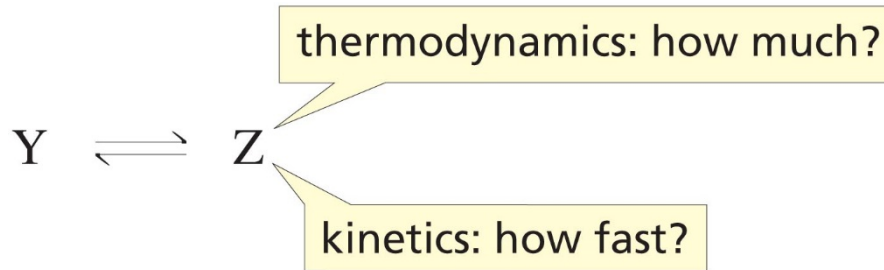


- arrows start at e source (e pair not atom)

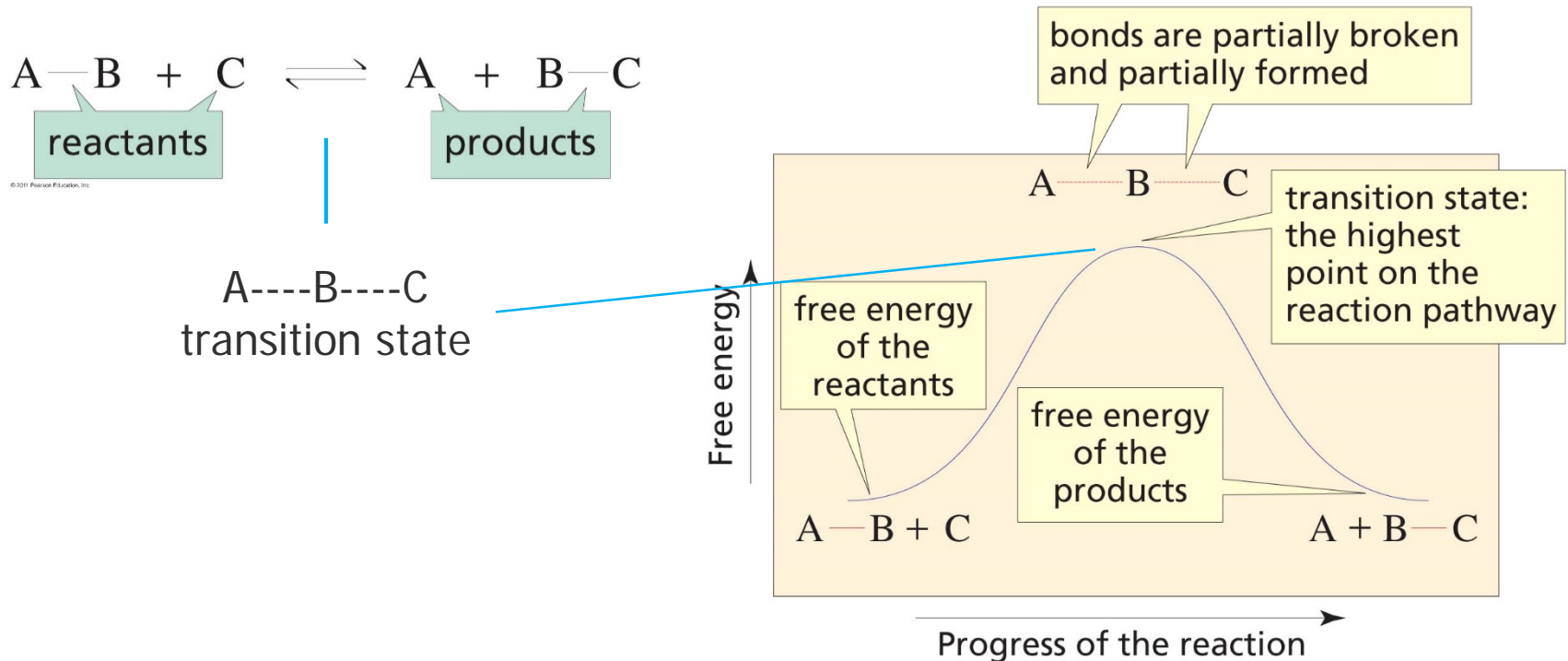


- For more, [Study guide pp103-115](#)

Thermodynamics and kinetics



□ reaction coordinate diagram



Thermodynamics

Ch 3 #18

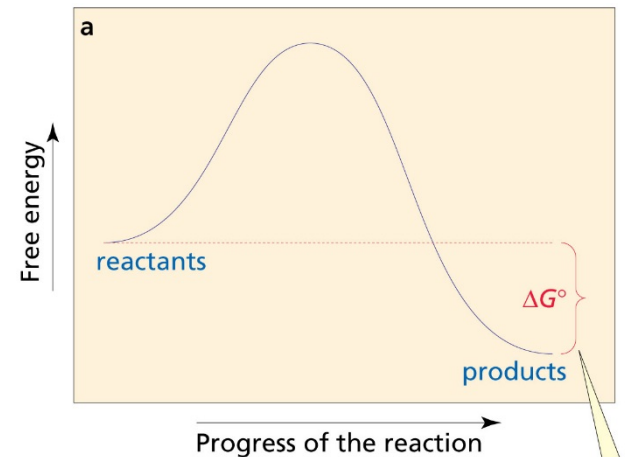


$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[\text{C}]^s [\text{D}]^t}{[\text{A}]^m [\text{B}]^n}$$

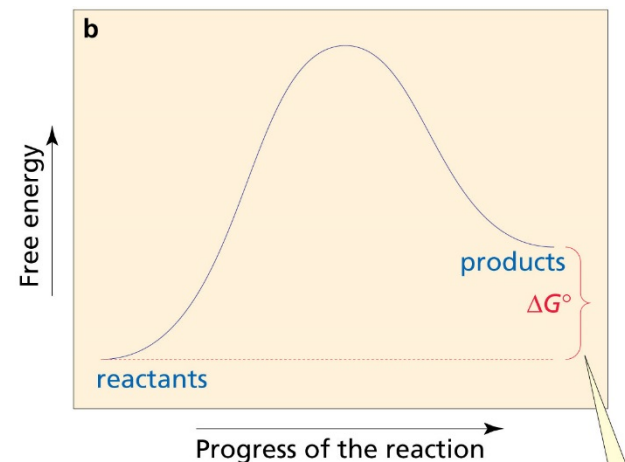
© 2011 Pearson Education, Inc.

- $\Delta G^\circ = -RT \ln K$
 - $\Delta G^\circ = G^\circ(\text{products}) - G^\circ(\text{reactants})$
 - $\Delta G^\circ < 0$ ~ exergonic
 - $K > 1$ ~ products favored
 - $\Delta G^\circ > 0$ ~ endergonic
 - $K < 1$ ~ reactants favored

Table 3.1 p139 for ΔG° , K , and %product

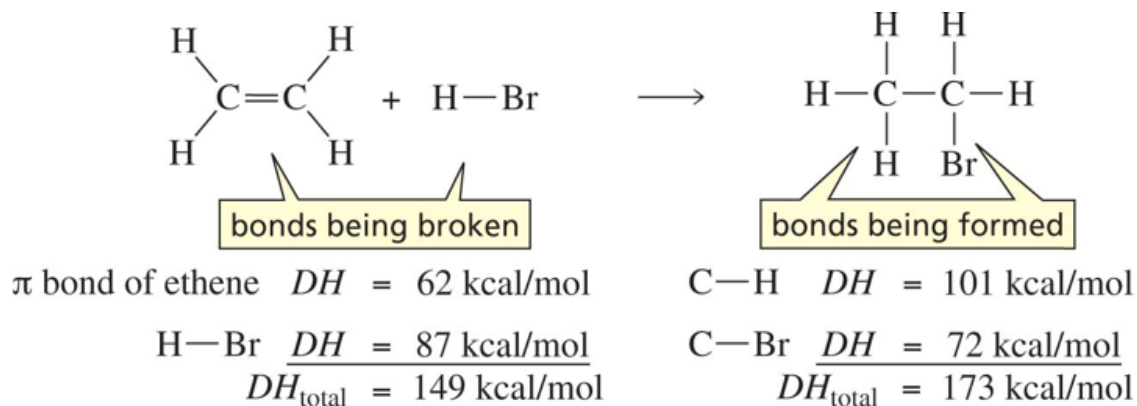


© 2011 Pearson Education, Inc.



© 2011 Pearson Education, Inc.

- $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$
 - $\Delta S^\circ \sim$ change in degree freedom
 - change in volume, # of molecules, ---
 - $\Delta H^\circ \sim$ change in heat
 - heat IN – heat OUT
 - \sum bond dissociation energy – \sum bond formation energy



- $\Delta H^\circ < 0$, exothermic; $\Delta H^\circ > 0$, endothermic
- determines the direction of reaction when $T\Delta S^\circ$ is not large

Kinetics

□ ΔG^\ddagger determines the rate of reaction.

■ ΔG^\ddagger ~ free energy of activation

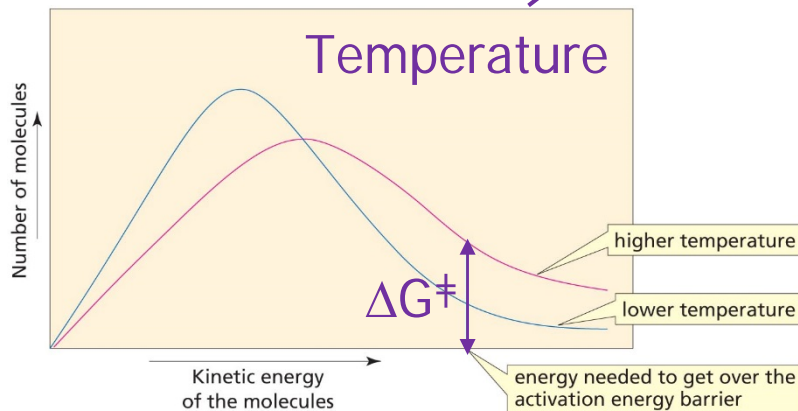
■ ΔG° determines the direction.

$$\text{rate of a reaction} = \left(\text{number of collisions per unit of time} \right) \times \left(\text{fraction with sufficient energy} \right) \times \left(\text{fraction with proper orientation} \right)$$

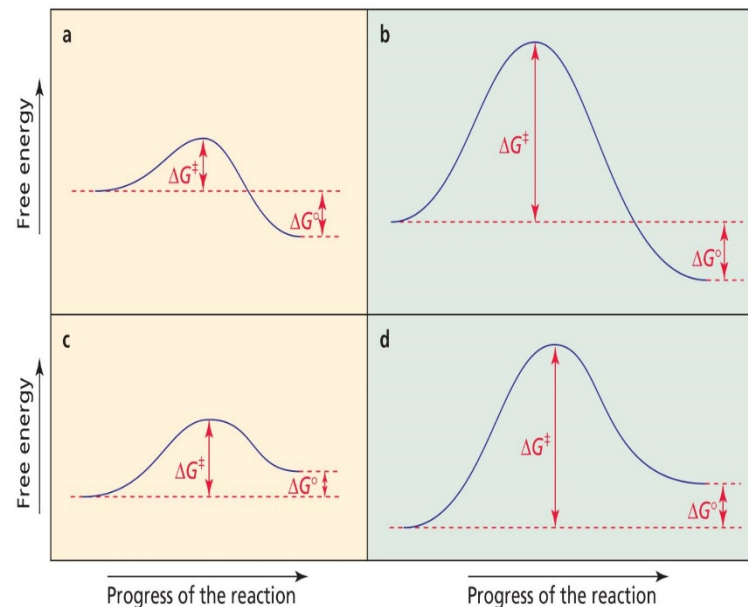
© 2011 Pearson Education, Inc.

conc'n of reactants

catalyst may help



© 2011 Pearson Education, Inc.



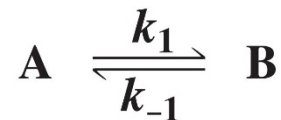
© 2011 Pearson Education, Inc.

□ rate law

- 1st-order reaction ~ rate = k [A]
- 2nd-order reaction ~ rate = k [A][B] or k [A]²
- k ~ rate constant
- $k = A \exp [-E_a/RT]$
 - A ~ (collision) frequency factor
 - E_a ~ activation energy

True activation energy is G^\ddagger
 $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$
 $E_a = \Delta H^\ddagger + RT$
 E_a is an approximate ΔG^\ddagger ,
 and lowered by catalyst.

□ rate and equilibrium



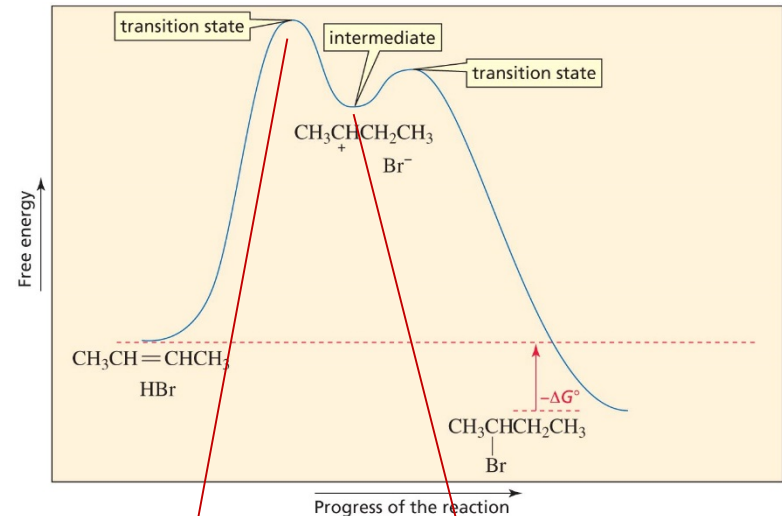
forward rate = reverse rate

$$k_1 [A] = k_{-1} [B] \quad \longrightarrow \quad K_{\text{eq}} = \frac{k_1}{k_{-1}} = \frac{[B]}{[A]}$$

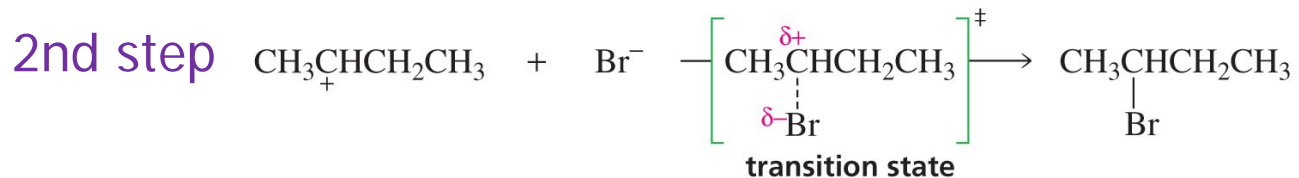
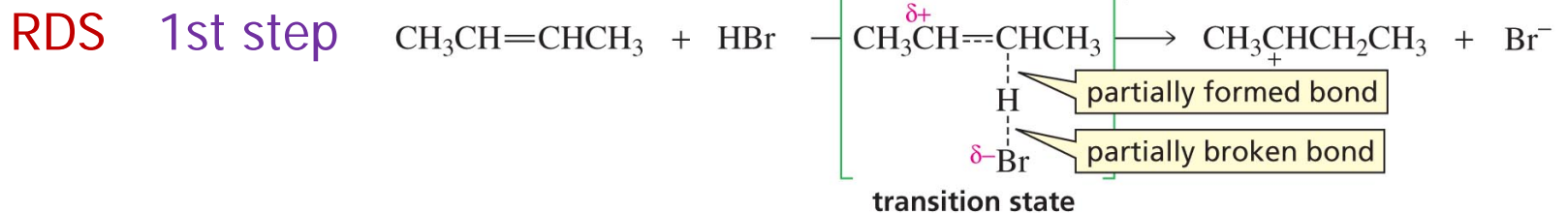
Transition state and intermediate

Ch 3 #22

- transition state ~ [TS]‡
 - bonds partially broken or formed
 - unstable ~ cannot be isolated
- intermediate
 - metastable ~ may be isolated
 - betw steps of multi-step reactions



© 2011 Pearson Education, Inc.



© 2011 Pearson Education, Inc.