Organic Chemistry CHM 3140 Dr. Laurie S. Starkey, Cal Poly Pomona

Study of Chemical Reactions & Mechanisms - Chapter 6 (Klein)

I) Thermodynamics (6.1, 6.2, 6.3, 6.4) (K_{eq}, ΔG, ΔH, ΔS)
    A) E vs. POR diagrams (6.6)
    B) Estimating ΔH using bond dissociation energies
II) Kinetics and reaction rate variables (6.5)
III) Two-step mechanisms and intermediates (6.6)
    A) carbocation stability (6.8)
    B) carbocation rearrangements (6.11)
IV) Mechanisms and arrow-pushing patterns (6.8, 6.9, 6.10)

Read on your own:
6.12 Reversible & Irreversible Arrows

Moved to Ch. 7:
6.7 Nucleophiles & Electrophiles
(& SkillBuilder 6.2)

I. Thermodynamics (6.1 - 6.4)

- compare Energy (stability) of reactants or starting materials (SM) and products
- predict direction of equilibrium (e.g., forward or reverse)

Equilibrium constant (6.4)

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

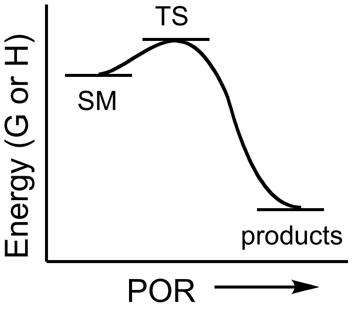
If $K_{eq} > 1$, then forward / reverse reaction is favored
If $K_{eq} < 1$, then forward / reverse reaction is favored

$$\boxed{\begin{array}{l}\Delta G = -RT\ln K_{eq} \\ \Delta G = \Delta H - T\Delta S\end{array}}$$

ΔG = Gibbs free energy (is reaction spontaneous?) (6.3)
ΔH = change in enthalpy (strength of bonds formed and broken) (6.1)
ΔS = change in entropy (usually small for organic reactions) (6.2)
FYI $\Delta S > 0$ if one reactant molecule generates two product molecules

A) Energy vs. Progress of Reaction Diagrams (6.6)

Favorable 1-Step Reaction



Products are lower Energy, more stable.
Products are favored (K_{eq} 1)

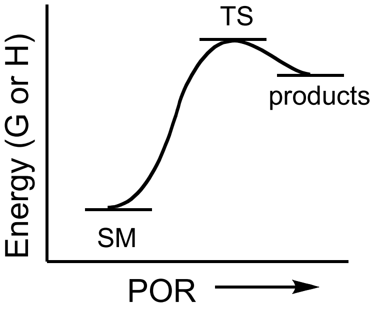
Energy is ________________________

ΔH 0 (________________________)

ΔG 0 (________________________)

forward / reverse reaction is spontaneous

Unfavorable 1-Step Reaction



Reactants/Starting materials (SM) are lower
Energy, more stable. SM are favored (K_{eq} 1)

Energy is ________________________

ΔH 0 (________________________)

ΔG 0 (________________________)

forward / reverse reaction is spontaneous

TS = Transition State has partial bonds, partial charges, E_a = Energy of Activation ($\Delta G^{\ddagger}$)

B) Estimating Δ using bond dissociation energies (6.1)

Bond breaking - releases / consumes energy (ΔH 0, ____________THERMIC

Bond formation - releases / consumes energy (ΔH 0, ____________THERMIC

Use bond dissociation energy (BDE) to estimate ΔH_{rxn}

Homolytic cleavage of a covalent bond: $H{-}H \longrightarrow H^{\bullet} + H^{\bullet}$ $\Delta H^{\circ} = 104$ kcal/mol

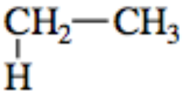
ΔH° for Single Bonds (kcal/mol)

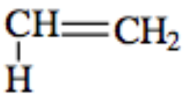
	H	C	N	O	F	Cl	Br	I	Si
H	104	99	93	111	135	103	87	71	76
C		83	73	86	116	81	68	52	72
N			39	53	65	46			
O				47	45	52	48	56	108
F					37				135
Cl						58			91
Br							46		74
I								36	56
Si									53

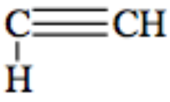
DH° for Multiple Bonds (kcal/mol)

C=C	C=N	O=O	C=O	C=O	C=O	C≡C	C≡N
146	147	119	176 aldehydes	179 ketones	192 CO_2	200	213

Bond strength/length as a function of hybridization:


$\underset{\displaystyle H}{\overset{|}{CH_2}}{-}CH_3$

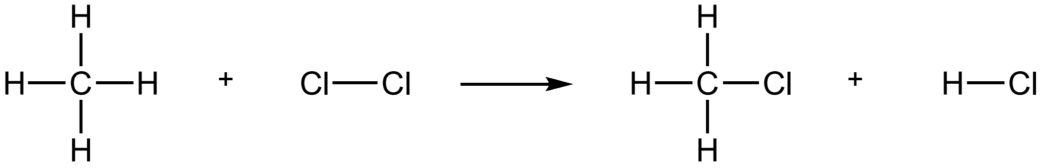

$\underset{\displaystyle H}{\overset{|}{CH}}{=}CH_2$


$\underset{\displaystyle H}{\overset{|}{C}}{\equiv}CH$

hybridization of carbon	sp^3	sp^2	sp
C–H bond length (Å)	1.10	1.08	1.06
C–H bond strength (kcal/mol)	98	108	125
% s character of C–H bond	25%	33%	50%

greater "s character" gives shorter, stronger bonds

Use bond dissociation energy (BDE) to estimate ΔH_{rxn}

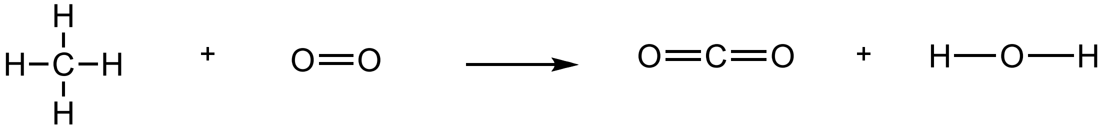


Bonds
broken:
(kcal/mol)

Bonds
formed:
(kcal/mol)

approximate ΔH =

Group work: Estimate ΔH_{rxn} for the following reaction. Is it exothermic or endothermic?



see SkillBuilder 6.1

II) Kinetics (6.5)

Consider the rate/speed of a given reaction: $A + B \longrightarrow C + D$

rate = $k[A]^a[B]^b$

rate expression is determined experimentally
(k = rate constant at a given temperature)

Example: $CH_3Cl + HO^{\ominus} \longrightarrow CH_3OH + Cl^{\ominus}$

Observation in kinetic study:

if $[HO^-]$ is doubled, then rate doubles (reaction is twice as fast)

if $[CH_3Cl]$ is doubled, then the rate doubles

Rate expression:

The reaction is "first-order" with respect to each reactant (exponent = 1)

The reaction is "second-order" overal (sum of exponents).

Group work: what happens to the rate of the above reaction of the amount of solvent is doubled?

a) it is 4x faster
b) it is twice as fast
c) no rate change
d) it is half the rate
e) it is 1/4 the rate

Reaction rate variables: how can we speed up or slow down a reaction?

Note: to achieve transition state (TS), a collision is needed with sufficient Energy ($>E_a$)

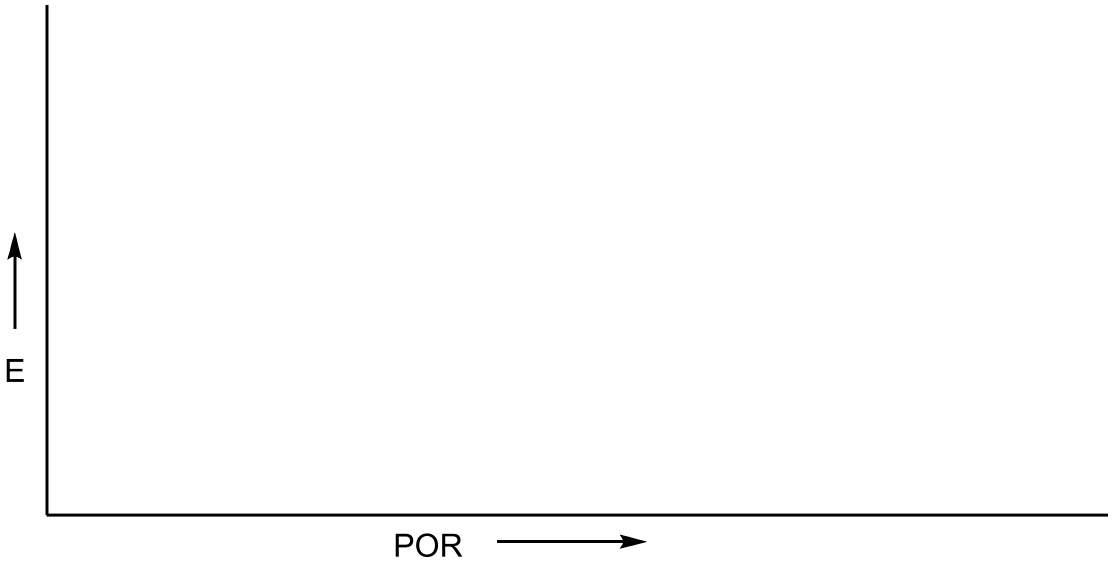
1) increase temperature, increase rate

2) increase concentration, increase rate

3) lower Energy of Activation (E_a), increase rate

III) E vs. POR diagram for a 2-step mechanism (6.6)

Starting Material(s) $\rightleftharpoons$ Intermediate(s) $\rightleftharpoons$ Product(s)
(SM)



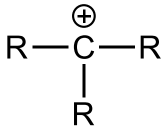
Reactive Intermediates are high-energy species

- produced and then consumed in reaction (doesn't appear in net reaction: SM → Product
- different from Transition State (intermediates have full bonds, full charges)
- examples include carbocations (6.8) and radicals (Chapter 10)

Rate-Determining Step: the reaction step with the highest E_a (highest TS energy) is slowest

A) Carbocations and carbocation stability (6.8)

consider a carbocation:



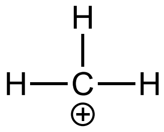
$R-\overset{\oplus}{\underset{R}{C}}-R$

hybridization?

geometry?

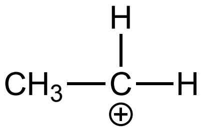
what is in the p orbital?

Carbocations are electron-deficient so they will be stabilized by electron withdrawal / donation



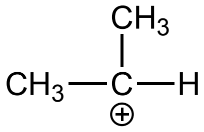
$H-\overset{H}{\underset{\oplus}{C}}-H$

methyl carbocation



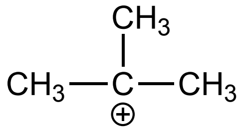
$CH_3-\overset{H}{\underset{\oplus}{C}}-H$

1° carbocation



$CH_3-\overset{CH_3}{\underset{\oplus}{C}}-H$

2° carbocation

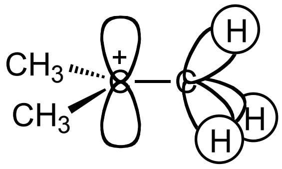


$CH_3-\overset{CH_3}{\underset{\oplus}{C}}-CH_3$

3° carbocation

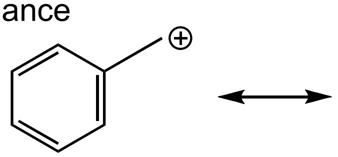
- alkyl groups are polarizable (their electron density can be drawn toward + charge
- alkyl groups are inductively electron withdrawing / donating (called hyperconjugation*)
- this is a stabilizing feature for the positive charge
- if INCREASE # of alkyl substituents, then _______________ stability

*Hyperconjugation in the *tert*-butyl carbocation (a tertiary carbocation) occurs with all 3 methyl groups. This stabilizes the positive charge.



Carbocations can also be stabilized by resonance

allylic carbocation



benzylic carbocation

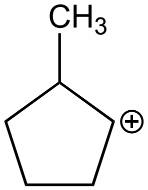
Overall carbocation stability:

benzylic
allylic > 3° > 2° >> 1° > methyl

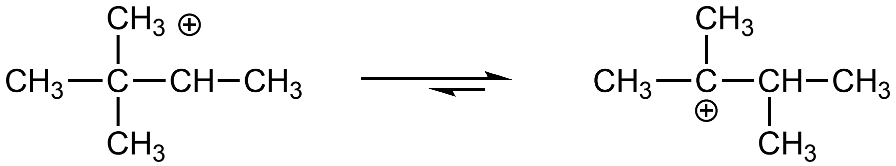
B) Carbocation rearrangements (6.11)

It is possible for neighboring groups to "shift" over to the positively charged carbon, if the relocated positive charge ends up in a more favorable position.

Hydride shift:



Methyl shift:



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\overset{\oplus}{C}H-CH_3 \rightleftharpoons CH_3-\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_3$$

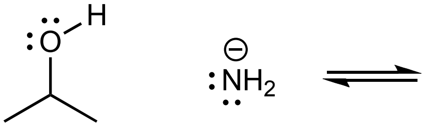
see SkillBuilder 6.6

IV) Mechanisms and arrow-pushing patterns (6.8, 6.9, 6.10)

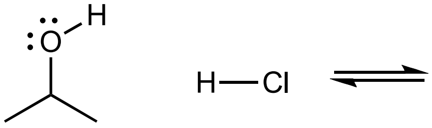
In addition to **carbocation rearrangements**, the following patterns of arrow-pushing will also be encountered in mechanisms found throughout organic chemistry:

Proton Transfer (Ch. 3) Draw curved arrows to show the mechanism and draw the organic product:

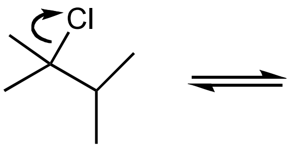
Deprotonation of a substrate

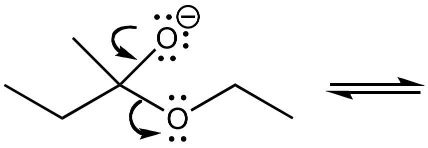


Protonation of a substrate

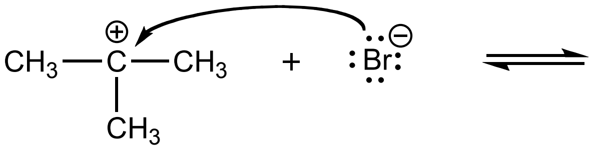


Loss of a Leaving Group (Ch. 7) Provide the products that result from the following curved arrows:





Nucleophilic Attack (Ch. 7) Provide the product that results from the following curved arrow:



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\oplus}{C}}-CH_3 + :\ddot{Br}:^{\ominus} \rightleftharpoons$$

see SkillBuilders 6.3, 6.4, 6.5