Chapter 6 Energy & Mechanism

Enthalpy ΔH

$\Delta H = q$ | q = heat

* Bond breaking requires energy

Homolytic	$X-Y \rightarrow X\cdot + Y\cdot$	$\Delta H = +$
Heterolytic	$X-Y \rightarrow X^+ + Y^\ominus$	$\Delta H = +$

ΔH° = + value = endothermic

ΔH° = − value = exothermic

Entropy ΔS

measure of disorder within system

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{environment}$$

$\Delta S_{total} = +$ more disordered ⟹ Spontaneous process

$AB \rightarrow A + B$

1 thing → two or more things

$X-Y$ (Ring) → X~~~~Y (Linear)

Demonstrate $\Delta S_{Total} = +$

Increase in disorder

Gibb's Free Energy ΔG

$$\Delta S_T = \Delta S_{system} + \Delta S_{Environment}$$

$$\Delta S_T = \Delta S_{Env} + \Delta S_{sys}$$

$$\Delta S_{Env} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_T = -\frac{\Delta H_{sys}}{T} + \Delta S_{sys}$$

$$(-T)\left[\Delta S_T = -\frac{\Delta H_{sys}}{T} + \Delta S_{sys}\right]$$

$$\underbrace{-T\Delta S_T}_{} = \Delta H_{sys} - T\Delta S_{sys}$$

$$\Delta G = -T\Delta S_T$$

$$\Delta G = \underbrace{\Delta H_{sys}}_{\sim \Delta S_{Environmen}} - \underbrace{T\Delta S_{sys}}_{\sim \Delta S_{system}}$$

For Spontaneity ΔS_{Total} = + value

$\therefore$ $-T\Delta S_{Total} = \Delta G = -$ for Spontaneity

(ΔS_{Total} ↑ +)

ΔG = - value Exergonic System

+ value Endergonic System

Equilibrium

$$aA + bB \rightleftharpoons cC + dD$$

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

K_{eq} value is determined by ΔG

$$\Delta G = RT \ln K_{eq} \quad \Big| \quad R = 8.314\ \text{J/mol K}$$

Kinetics

Rate of Reaction

$$\text{Rate} = k[\text{reactants}] = k[A]^x[B]^y$$

most common:

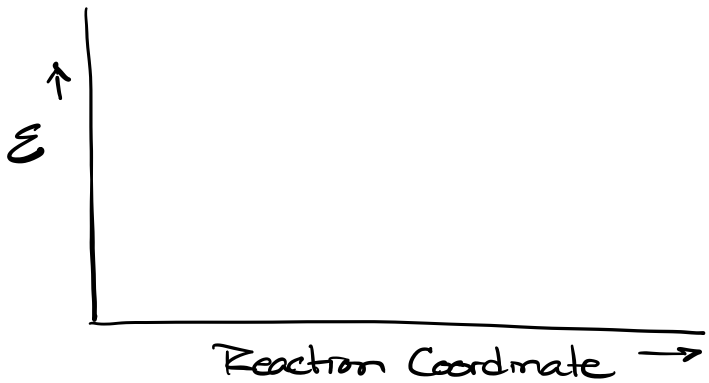
- 1^{st} Order = rate = $k[A]$
- 2^{nd} Order = rate = $k[A]^2$ or $k[A][B]$

3^{rd} Order = rate = $k[A]^2[B]$ or $k[A][B][C]$

Rate constant k is affected by E_A (activation energy), T (temp), Sterics.

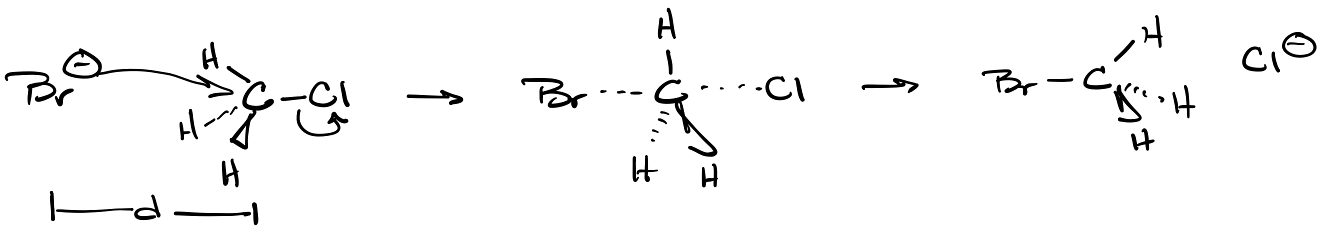
Energy Diagrams

More emphasis on energy diagrams in organic

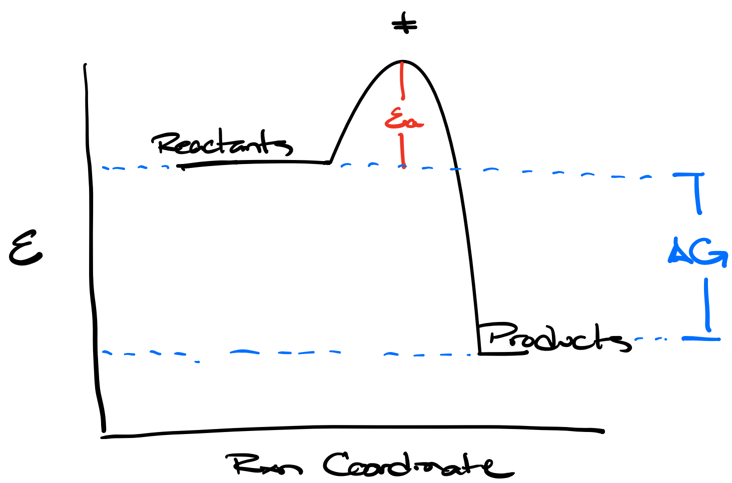


Reaction Coordinate is **not** time

Reaction Coordinate is usually a bond length



measure of Br – C distance can be rxn coordinate



‡ = Transition State

E_a = activation energy

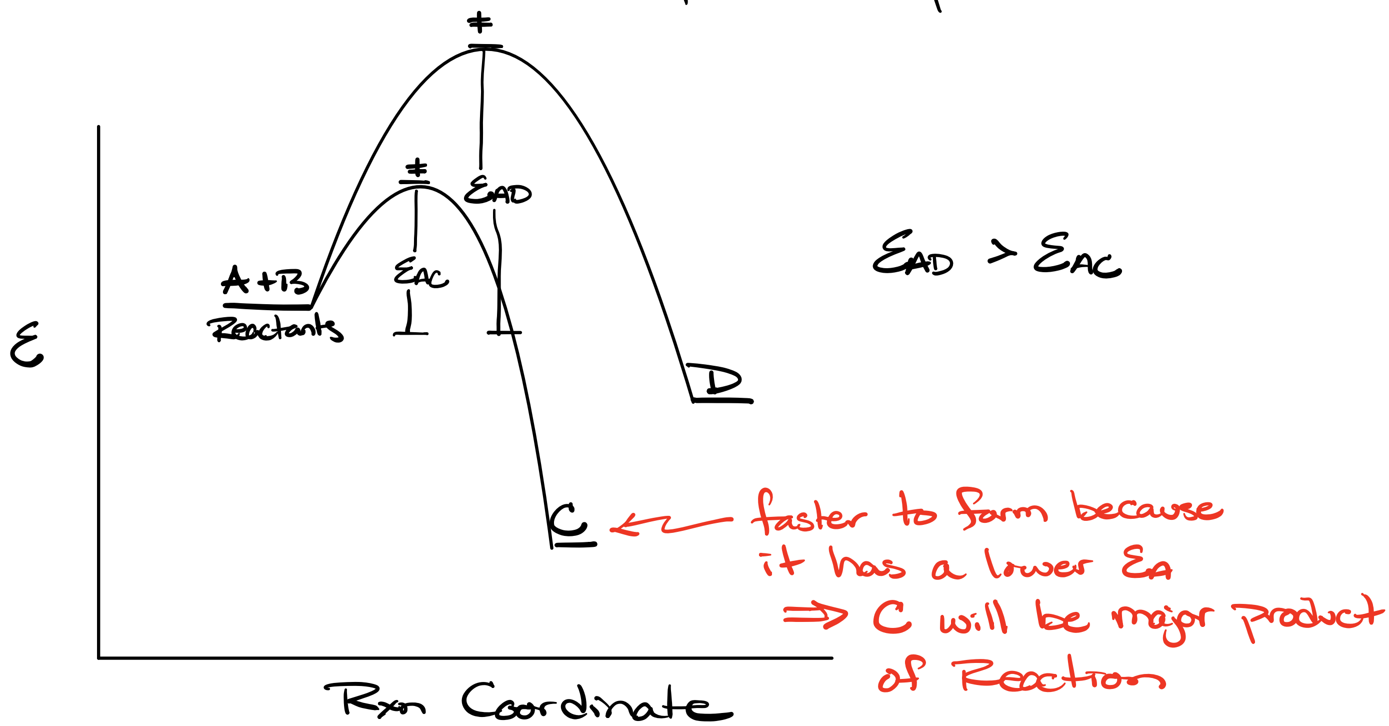
$E_a \propto$ Rate (kinetics)

ΔG = Change in Gibb's

$\Delta G \propto K_{eq}$ (Thermodynamics)

Consider a reaction with multiple products

$$A + B \longrightarrow \underbrace{C + D}_{\text{Two different products}}$$



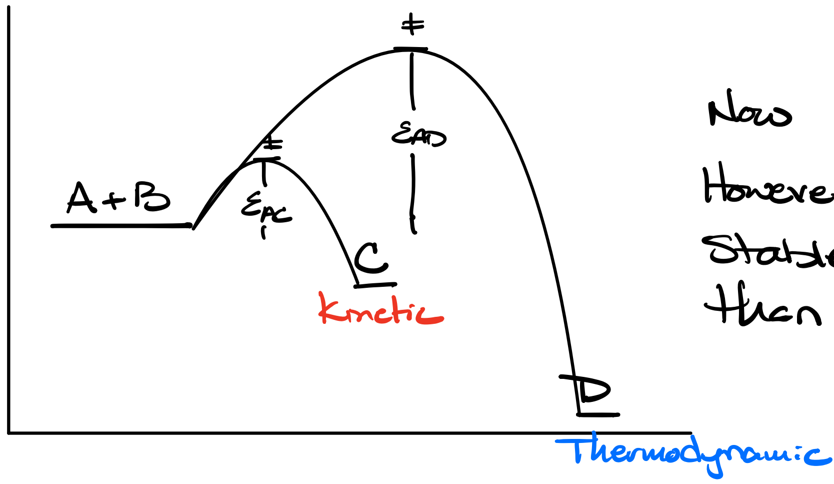
$E_{AD} > E_{AC}$

When a product is fast to form (Lower E_A) we call it the kinetic product

C is the kinetic product

When a product is favored by energy, lower ΔG, the product is called the Thermodynamic product

C is also the Thermodynamic product



Now $\mathcal{E}_{AD} > \mathcal{E}_{AC}$

However D is more stable thermodynamically than C

Kinetic product ⇒ 1st product to form ⇒ lowest $\mathcal{E}_A$

⇒ C is first to form

D is slow to form, but when D is formed it is <u>much</u> less reversible.

D is the thermodynamic product

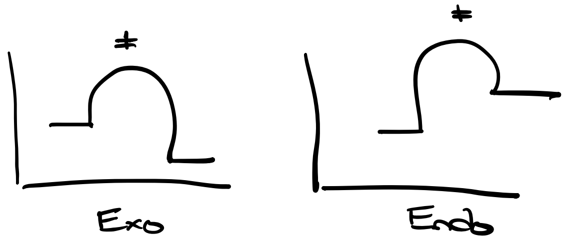
Kinetic Product favored by Colder temps, Short Rxn time

Thermodynamic Product favored by higher Temp, Long Rxn time

Thermodynamic vs. kinetic Control

Reaction Mechanisms

$A \rightarrow B$ Single step

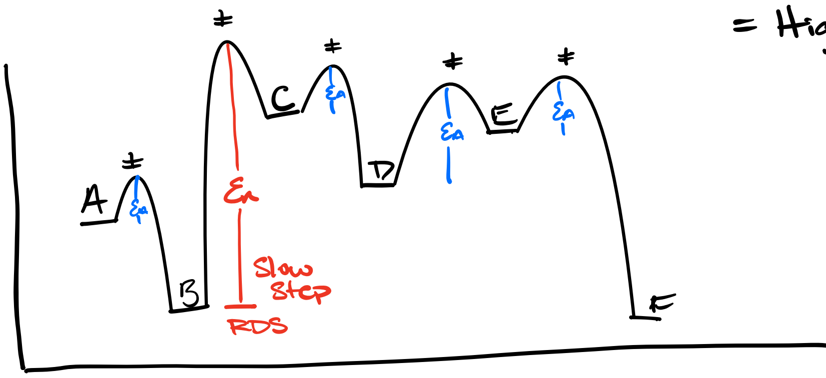


RDS

$A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow F$ many step

Intermediates

Rate Determining Step = RDS
= Highest E_A Step

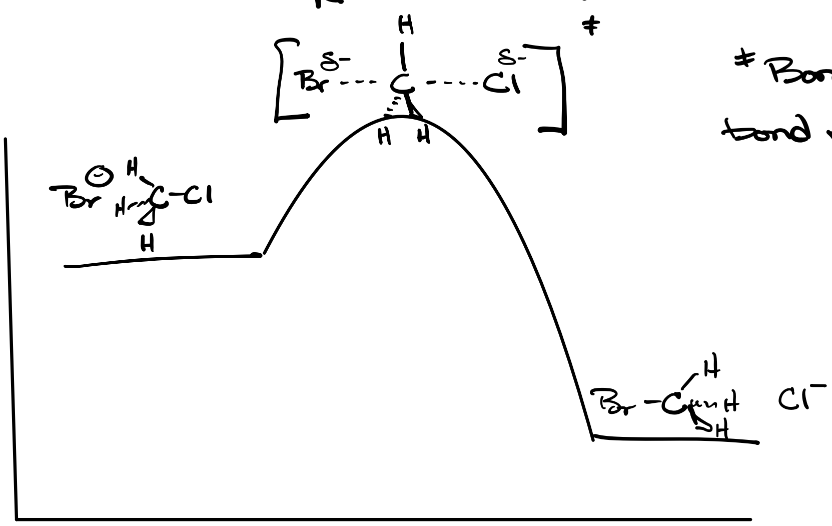


Transition States

$Br^- + CH_3Cl \longrightarrow CH_3Br + Cl^-$

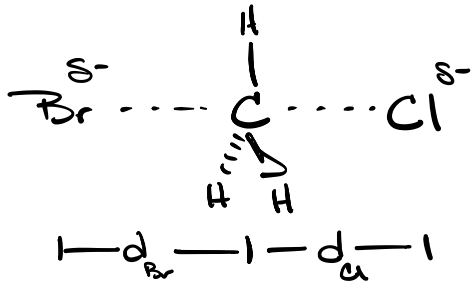
Substitution Nucleophilic 2nd order

S_N2 Reaction



‡ Bond breaking & bond making simultaneously

If Bond breaking & making simultaneous, are the equal?



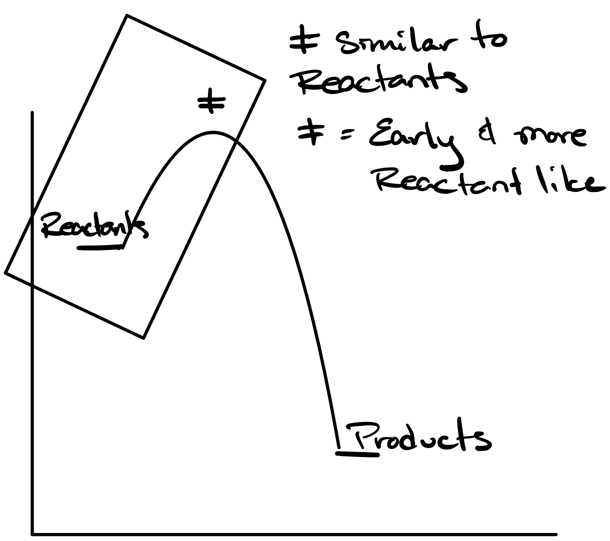
$d_{Br} = d_{Cl}$?

$d_{Br} > d_{Cl}$ or $d_{Br} < d_{Cl}$?

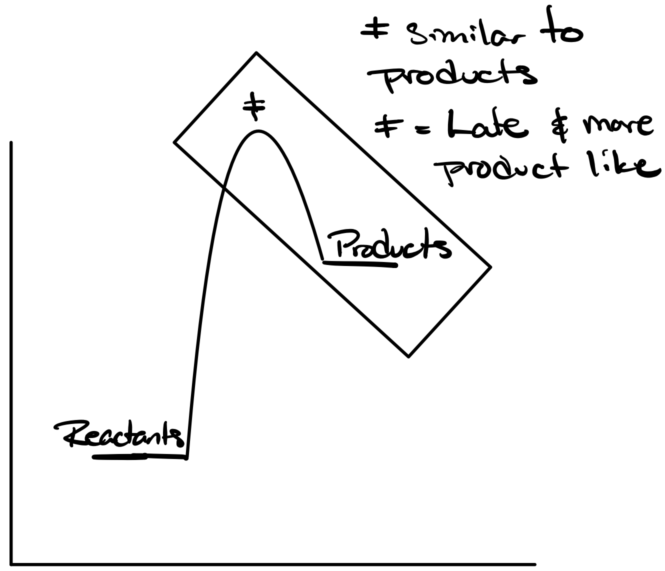
Hammond Postulate

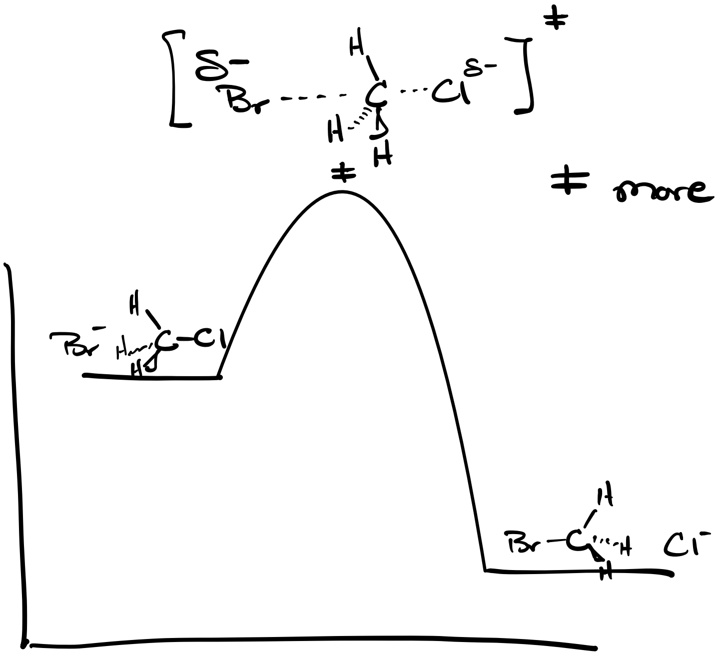
George S. Hammond

If two states are similar in energy, then they are similar in structure.



Exothermic

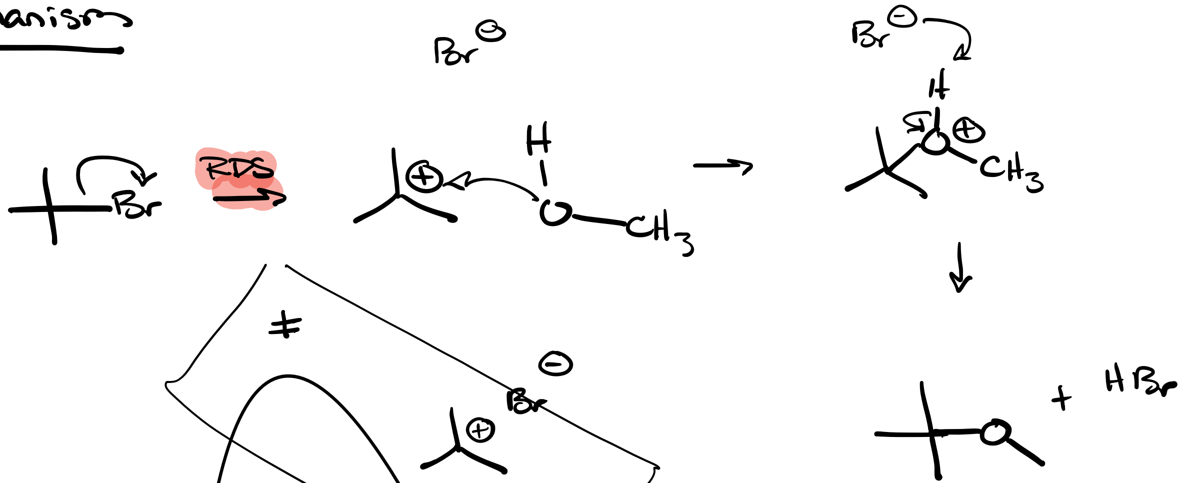


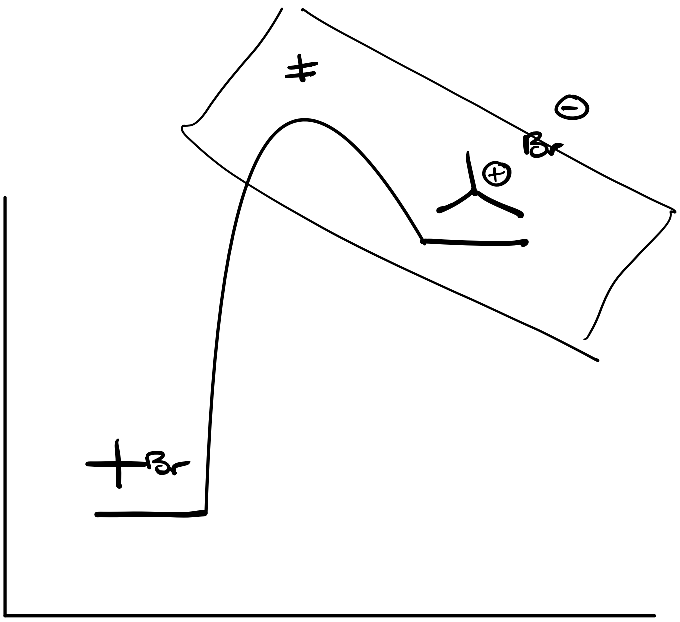


‡ more reactant like

S_N1

<u>Mechanism</u>





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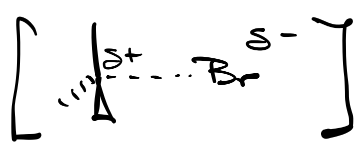
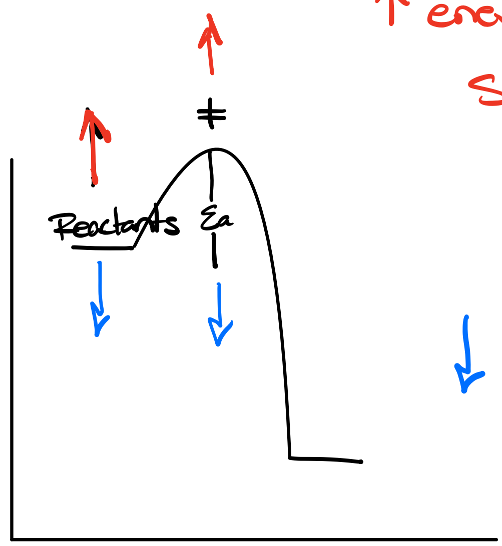


Product like

Power of Hammond



↑ energy of reactants, ↑ ‡, ↑ Ea

Slow Rxn down

- Sterics
- Solvents
- Resonance

↓ energy of reactants, ↓ ‡, ↓ Ea

Speed Rxn up

- Lowering Sterics
- more favorable Solvent
- More resonance

Next week Start digging into Rxn Mechanism Steps.