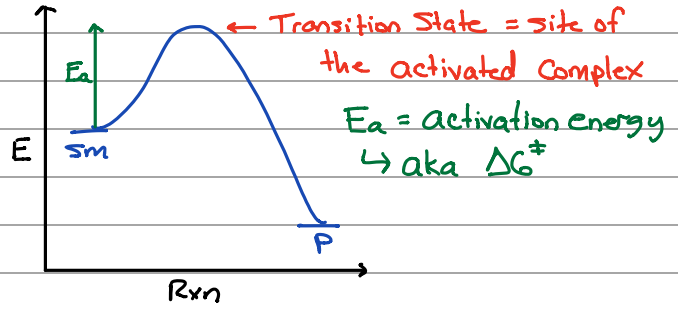
We can never prove a mechanism. We can only definitively rule out a possible mechanism.

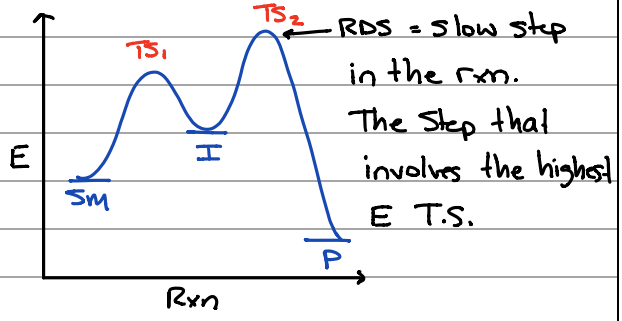
Kinetic Study - experimental measurements on a rxn mixture
- determining how fast product forms as a function of concentrations, temp, etc.

Reaction Coordinate Diagram



← Transition State = site of the activated complex

Ea = activation energy
↳ aka $\Delta G^{\ddagger}$



RDS = slow step in the rxn. The step that involves the highest E T.S.

TS = energy maxima
lifetime of a vibration

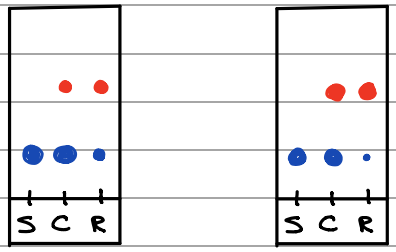
I = intermediate = energy minima
Can in principle be isolated

Rates and Rate Constants

Rate = k[R] ← conc of reactants
↑ rate constant

How fast SM is consumed or how fast product is produced.

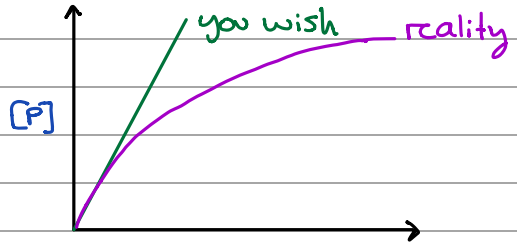
Rate is highest at inception → Slows to zero at the end of the rxn



1 hr
50% complete

2 hr ... done?
NO!

Why? Rxns are not linear



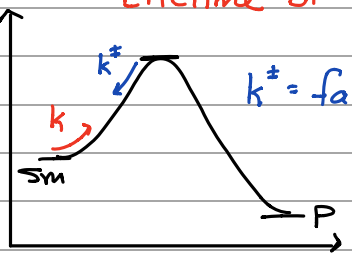
Rate ∝ [Reactants]
As [Reactants] ↓, rate ↓

Transition State Theory

- Assume the SM + TS are in equilibrium
  - if you can measure the [TS] ← In reality you can't

Lifetime of TS = bond vibration $\approx 10^{12}\ s^{-1}$

$$SM \underset{k^{\ddagger}}{\overset{k_1}{\rightleftharpoons}} TS^{\ddagger} \rightleftharpoons P$$



$k^{\ddagger}$ = fast!! = rate of bond vibration

- Activation Parameters: $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$

$$K_{eq} = \frac{k_f}{k_r} = \frac{[P]}{[SM]} \Rightarrow K_{eq}^{\ddagger} = \frac{[TS]^{\ddagger}}{[SM]} = \frac{k}{k^{\ddagger}}$$

$$K_{eq} = e^{-\Delta G/RT} \Rightarrow \frac{k}{k^{\ddagger}} = e^{-\Delta G^{\ddagger}/RT} \Rightarrow k = k^{\ddagger} e^{-\Delta G^{\ddagger}/RT}$$

} Eyring Equation

$$k^{\ddagger} = \frac{\kappa k_B T}{h} \quad (C')$$

κ = transmission coeff ≈ 1

k_B = Boltzmann Constant = 1.380×10^{-23} J/K

h = Plancks Constant = 6.626×10^{-34} J/s

$$k = C' T e^{-\Delta G^{\ddagger}/RT} \Rightarrow k = C' T e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \Rightarrow \frac{k}{C'T} = e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

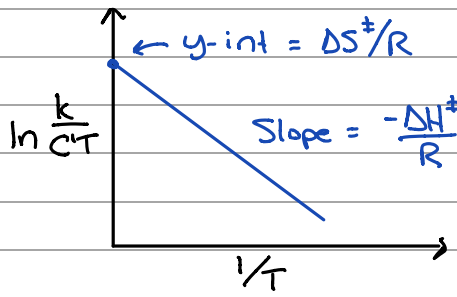
For  $\xrightarrow{\Delta}$ 

⇓ take ln

$$\ln\left(\frac{k}{C'T}\right) = \frac{-\Delta H^{\ddagger}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^{\ddagger}}{R}$$

$y = -22663x + 1.0958$ (See Excel Data) $y = mx + b$

$$\frac{-\Delta H^{\ddagger}}{R} = -22663 \Rightarrow \Delta H^{\ddagger} = 45\ kcal/mol$$



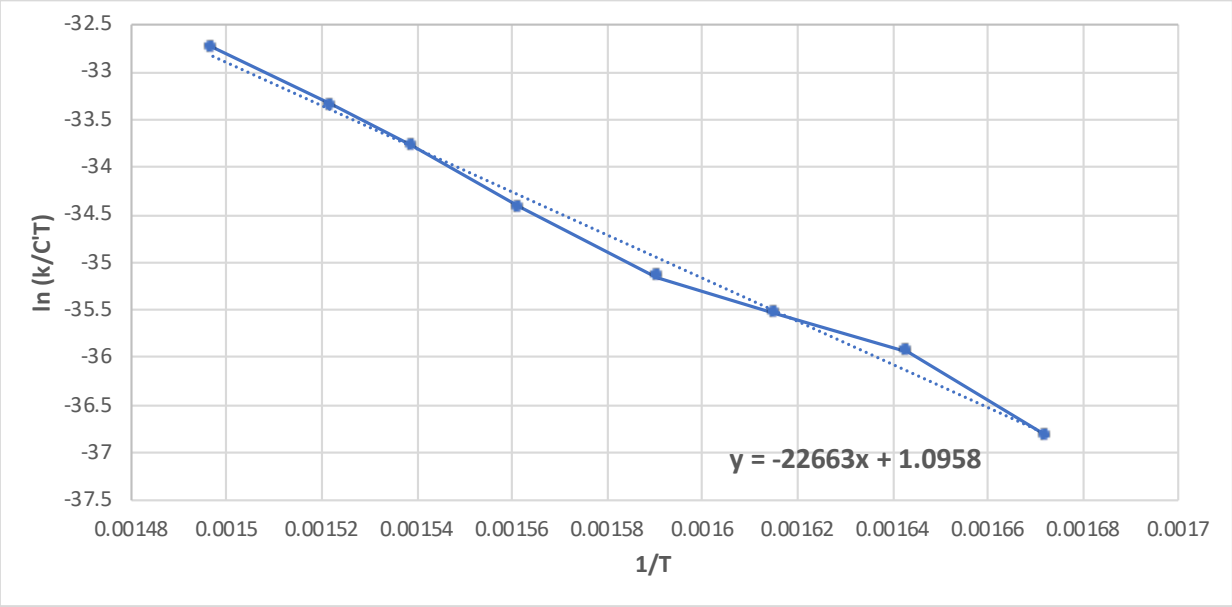
$$E_a = \Delta H^{\ddagger} + RT = 45\ kcal/mol + 0.6 = 45.6\ kcal/mol$$ at 298 K

$$\frac{\Delta S^{\ddagger}}{R} = 1.0958 \Rightarrow \Delta S^{\ddagger} = 2.18\ \frac{cal}{mol \cdot K} = 2.18\ eu$$

Temp (^{o}C)	k x 10^{-3} (s^{-1})	1/T (K)	ln k	ln (k/C'T)
324.8	1.27	0.00167238	-6.6687384	-36.821906
335.4	3.14	0.00164325	-5.7635325	-35.934272
345.9	4.75	0.00161538	-5.3496107	-35.537457
355.6	7.1	0.00159046	-4.9476605	-35.151054
367.2	15	0.00156165	-4.1997051	-34.42138
376.6	29.2	0.00153905	-3.5335866	-33.769834
383.8	44.8	0.00152219	-3.1055471	-33.352815
394.8	84.1	0.00149712	-2.4757487	-32.739622

Experimental Data

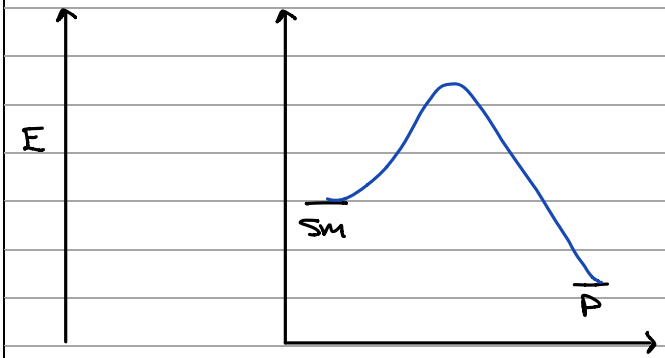
C' 20830000000

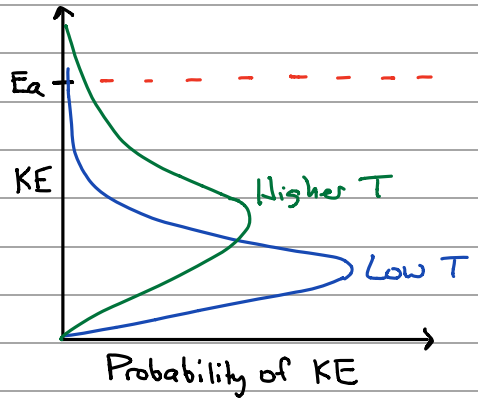


Boltzmann Distribution

k is temp dependent

As T↑, molecules have ↑KE





Activation Parameters

$\Delta H^{\ddagger}$ - bond strengths, solvent effects

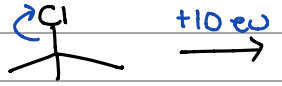
SN2: $Et-S^{\ominus} + H_3C-I \rightarrow$ endothermic $\rightarrow Et-S^{\delta-}\cdots C(H_3)\cdots I^{\delta-}$

Polar aprotic help stabilize TS → lowers $\Delta H^{\ddagger}$

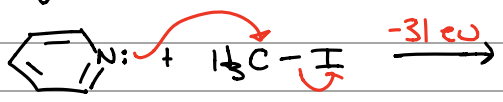
Weak partial bonds

$\Delta S^{\ddagger}$ - order gained or lost going from SM → TS

⊕ → likely a dissociative step



⊖ → likely an associative step



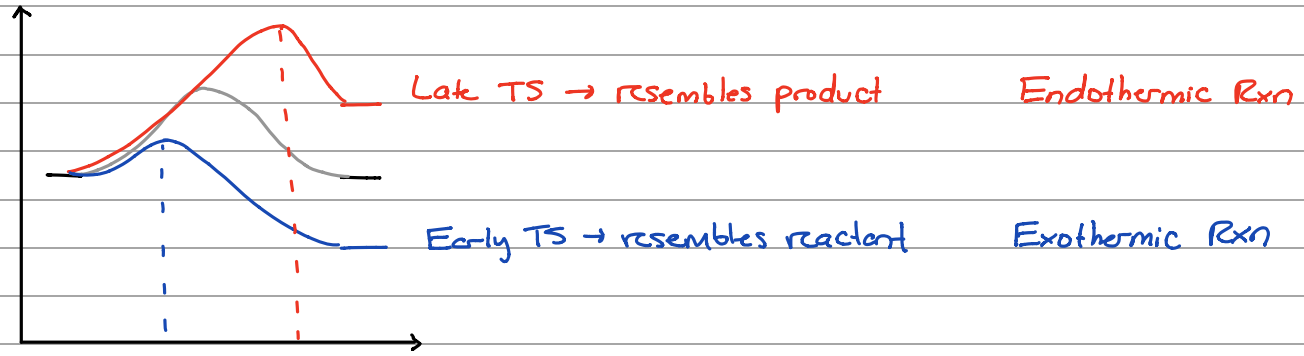
$-31\ eu = \frac{-31\ cal}{mol \cdot K} \times 298\ K \times \frac{1\ kcal}{1000\ cal}$

$= -9.2\ \frac{kcal}{mol}$ } Change in $\Delta G^{\ddagger}$

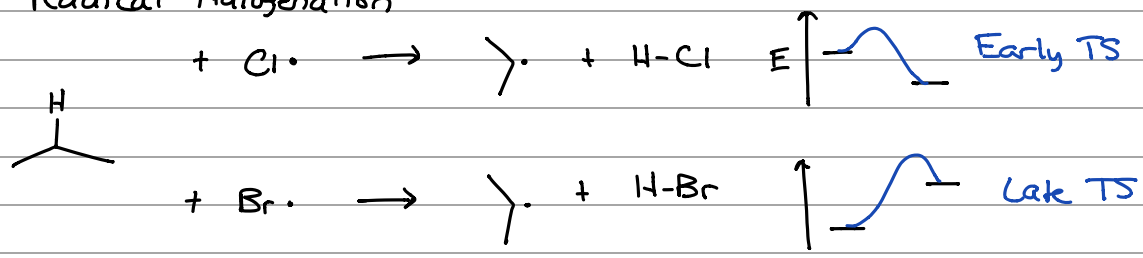
Postulates & Principles Related to Kinetics

1. Hammond Postulate

The transition state structure most resembles the adjacent reactant, intermediate, or product that it is closest in energy to.



Ex: Radical Halogenation



much more selective

2. Reactivity Selectivity Principle

Reactivity: Being higher in energy or
Having a more exothermic rxn (TS more resembles reactant)

Selectivity: In a selective rxn, one product is formed in a higher yield than another.

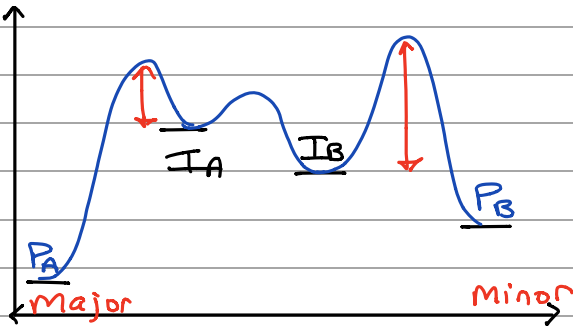
Ex: Radical Halogenation

Cl· is more reactive than Br·

↑ non-selective

↑ Selective rxn

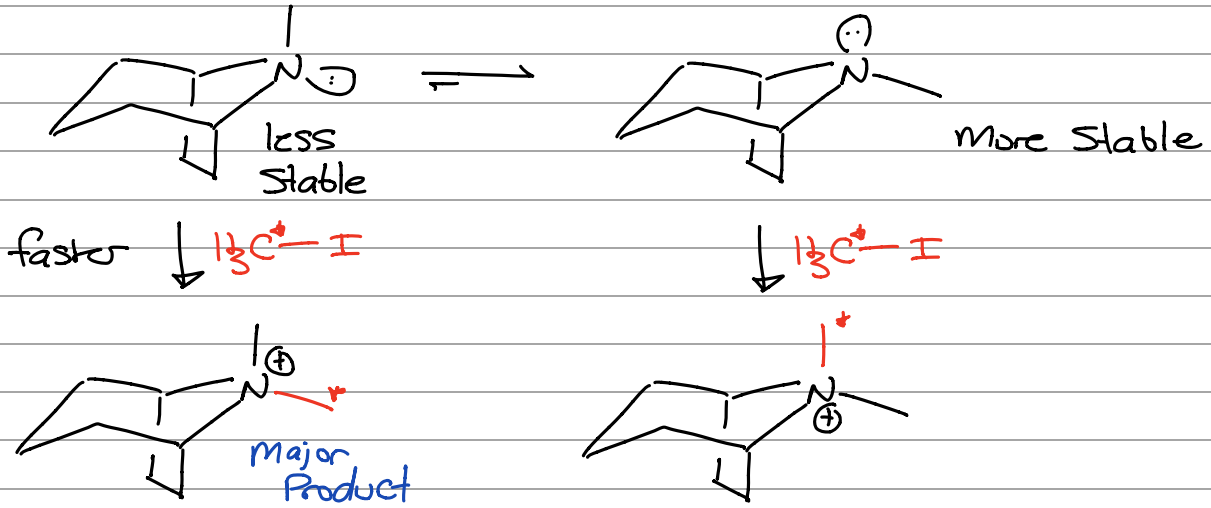
3. The Curtin-Hammett Principle



I_A + I_B are isomers, conformers, or intermediates that interconvert by a low barrier

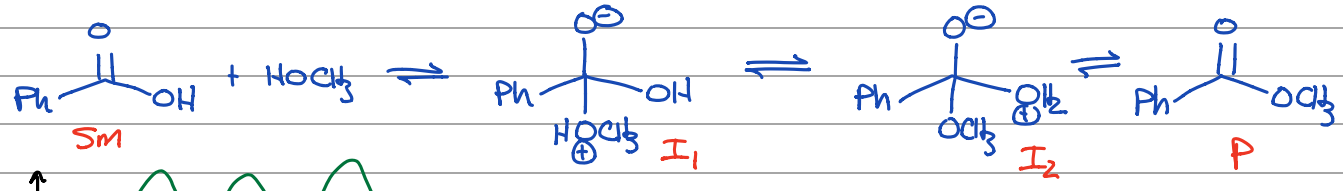
* Only applies to rxns under Kinetic Control

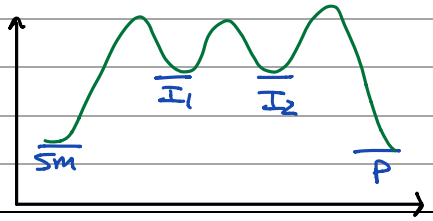
Relative energies of I_A + I_B are meaningless. The product composition is controlled by the $\Delta G^{\ddagger}$ of the transition states.



4. Principle of Microscopic Reversibility

Rxns proceed through identical transition states + intermediates in the forward and reverse.

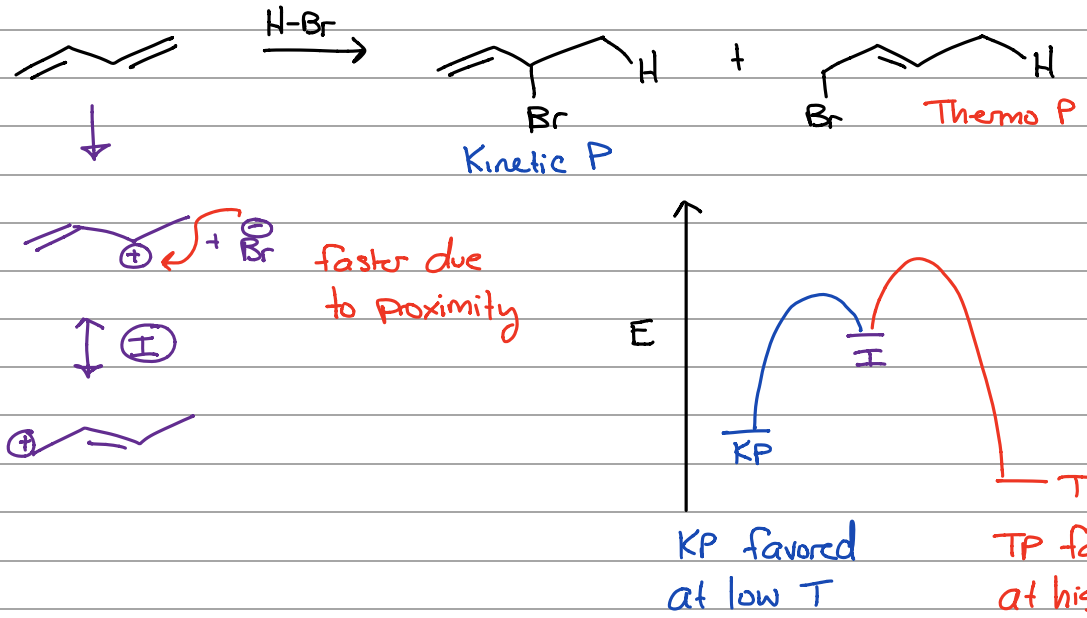




Route from SM → P identical to P → SM

5. Kinetic vs Thermodynamic Control

Kinetic Product → formed faster → lower E TS
Thermo Product → Lowest energy / most stable product



Kinetic Measurements

Kinetic measurements at a single temp provide the rate law
↳ Change in reactant or product conc over time

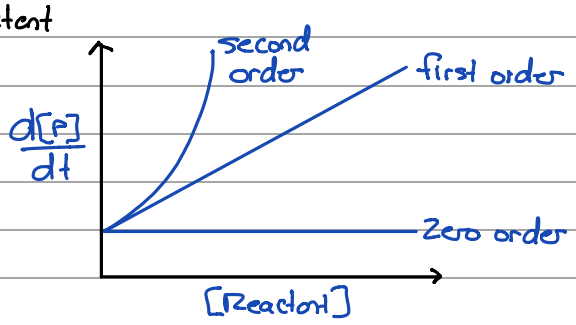
Consider $A + B + C \rightarrow P$

- If rate ↑ x2 with x2 [A] → Rxn is 1st order in A
- If rate ↑ x4 with x2 [B] → Rxn is 2nd order in B
- If changing [C] rate does not change → Rxn is zero order in C

Differential Rate Eqn (i.e. Rate Law): $\frac{d[P]}{dt} = k[A]^a[B]^b[C]^c \Rightarrow \frac{d[P]}{dt} = k[A][B]^2$

Overall Rxn Order = 3rd

1. Take a reactant & study rate at several different concentrations
2. Discover the kinetic order w/ respect to that reactant
3. Repeat w/ each reactant
4. Write the rate law for the rxn



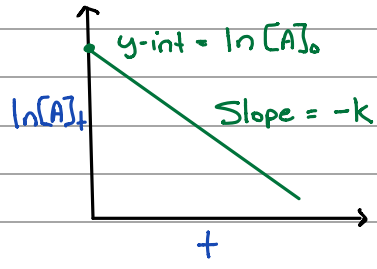
1. First Order

$A \rightarrow P$ $\quad \frac{d[P]}{dt} = -\frac{d[A]}{dt} = k[A]$

⇓ math

$\ln[A] = -kt + \ln[A]_0$

$y = mx + b$

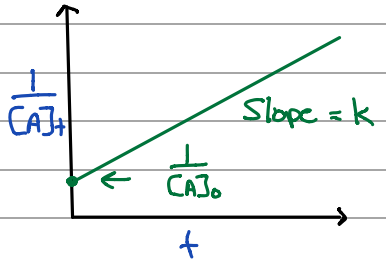


2. Second Order (type 1)

$A + A \rightarrow P$ $\quad \frac{d[P]}{dt} = -\frac{d[A]}{dt} = k[A]^2$

⇓ math

$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

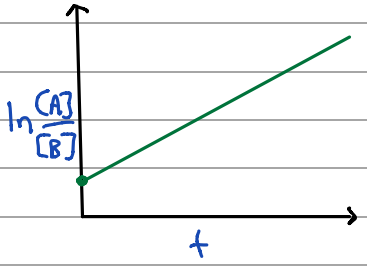


3. Second Order (type II)

$A + B \rightarrow P$ $\qquad \frac{d[P]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$

Int. Rate Law: $\ln\frac{[A]}{[B]} = k([B]_0 - [A]_0)t + \ln\frac{[A]_0}{[B]_0}$

$y = m \quad x + b$



* Difficult to simultaneously monitor A + B

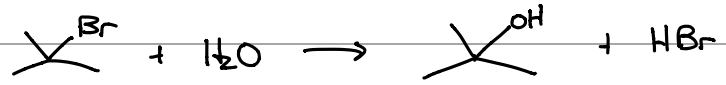
4. Pseudo First Order Conditions

- Use one reactant in large excess $\qquad [B] \approx [B]_0$

$k_{obs} = k' = k[B]_0$

$\frac{d[P]}{dt} = k[A]\underbrace{[B]}_{\text{Constant}} = k'[A]$ $\qquad$ Can divide $k'/[B]_0$ to get k

This can also be used if B = Catalyst

Consider: 

Kinetic Expts find rxn to be 1st order in tBu-Br

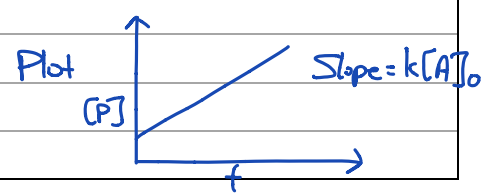
Rate = k []

Since C-Br breaks + C-O forms, we can deduce this rxn must have at least two elementary steps

5. Initial Rate Kinetics

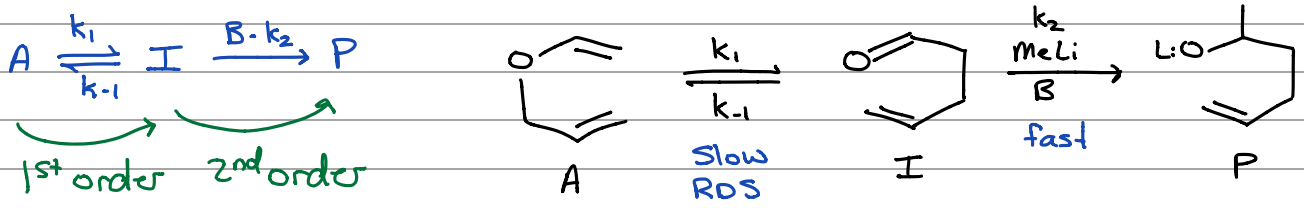
- Study rxn kinetics at the beginning of the rxn (partial conversion)
- Avoids issues associated w/ by-product formation

$\frac{d[P]}{dt} = k[A]$ ← essentially constant at beginning



6. Steady State Approximation - Simplifies a complex rate law

The Concentration of reactive intermediate is Constant during the rxn.



One Scenario

Rate: $\frac{d[P]}{dt} = k_2[I][B]$

$\frac{d[I]}{dt} = k_1[A] - k_{-1}[I] - k_2[I][B] = 0$ ← by SSA

⇓

Solve for [I]

$k_1[A] = k_{-1}[I] + k_2[I][B]$

$k_1[A] = [I](k_{-1} + k_2[B])$

$[I] = \frac{k_1[A]}{k_{-1} + k_2[B]}$

$\text{Rate} = \frac{k_2 k_1 [A][B]}{k_{-1} + k_2[B]}$

If $k_2 \gg k_{-1}$

⇓

Rate = k[A] to a good approximation

Rule of thumb for single [I]

$\text{Rate} = \frac{\text{rate constants} \cdot \text{conc of forward steps}}{\text{Sum rate constants and ways I can branch}}$

I is never involved in rate

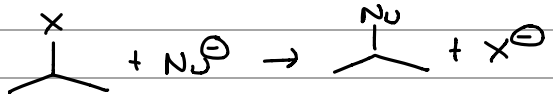
7. Pre-Equilibrium?

May want to cover next year

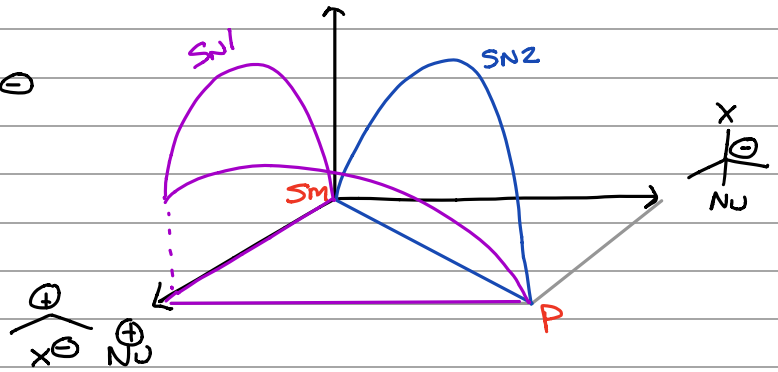
Multiple Rxn Coordinates

When a rxn has two or more possible pathways, this can't be represented on a single rxn coordinate

Consider Nu Substitution

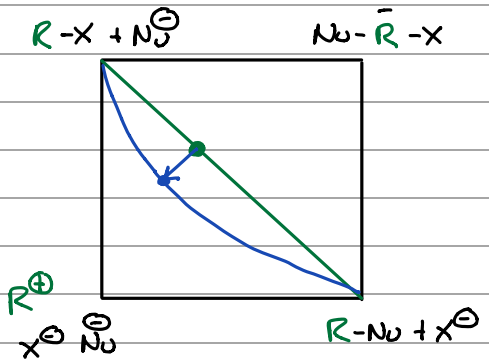


SN1 + SN2



More O'Ferrall - Jencks Plots

Viewing the the 3D energy surface from the top down w/o respect to E.



R = CH_3 → Pure SN2

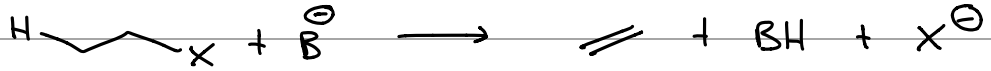
R = iPr → Has SN1 Character

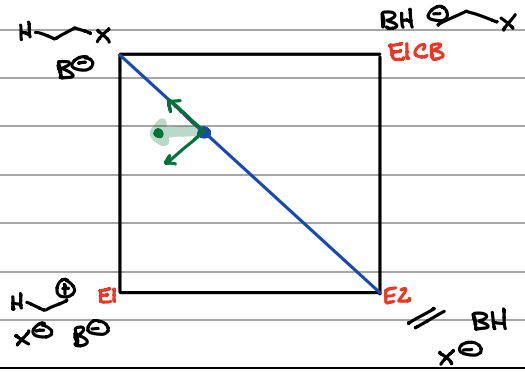
↓

More Stable $R^{\oplus}$

- Perpendicular Movement to more stable Corner = anti-Hammond Effect

Example:





- make $X^{\ominus}$ more Stable
  - Hammond Effect → P more Stable than reactants. Parallel movement of TS
  - Anti-Hammond Effect → more Stable $A^{\ominus}$ in E1 Corner