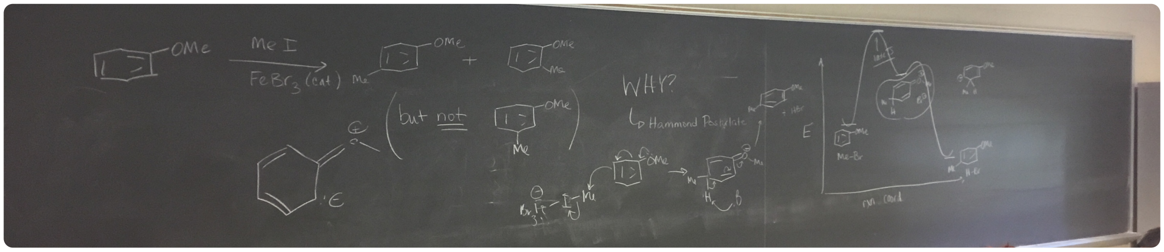
Lecture 14: Kinetics

Announcements:

- Problem Set 3 due Thursday, 10/20
- Office Hours: Wed 2:30, 208 LDL (MPW)
  Thurs, 10-11, 220 BRL (SS)
- Seminar Friday, 4pm, 219 BRL: Prof Antonio Echavarren
  "Total Synthesis with a Golden Touch"
- Thurs in lecture: Midterm 1 (be prepared to go to the board!)

Today:

- Hammond Postulate (continued)
- Composition of Transition States from Kinetics (rate equations)
- Midterm 1: statistics, brief comments, and returning the exam



Electrophilic Aromatic Substitution as an Example for the Hammond Postulate

↳ Based on Hammond postulate, we should make arguments based on intermediate.

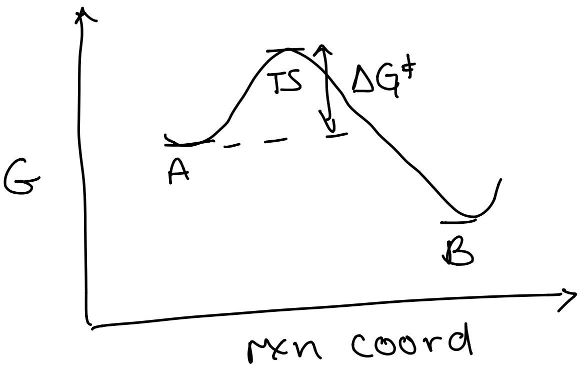
For electrophilic aromatic substitution, we get the same answer whether we consider starting material or intermediate. Hammond Postulate matters more when the answer would be different between these 2.

Last time: energies of TS's.

Now: composition of TS's

Recall: 1-step rxn

$A \longrightarrow B$



$$\text{rate} = \frac{-d[A]}{dt} = \frac{d[B]}{dt} = \underset{\uparrow\ \Delta G^\ddagger}{k}\,[A]$$

Multi-component Reactions

- Elementary steps that occur before or during the rate-determining step can be detected.
- In practice: Propose >1 mechanism & use kinetics to rule one (or more) out.
- Experimentally determine rate law.

$$A + B + C \longrightarrow P$$

rate = $k[A]^m[B]^n[C]^p$

m, n, p → composition <u>relative</u> to ground state.

# of A's, B's, & C's in rate-determining step.

rate = $k[A]^1$ } Same # of A in GS & TS.

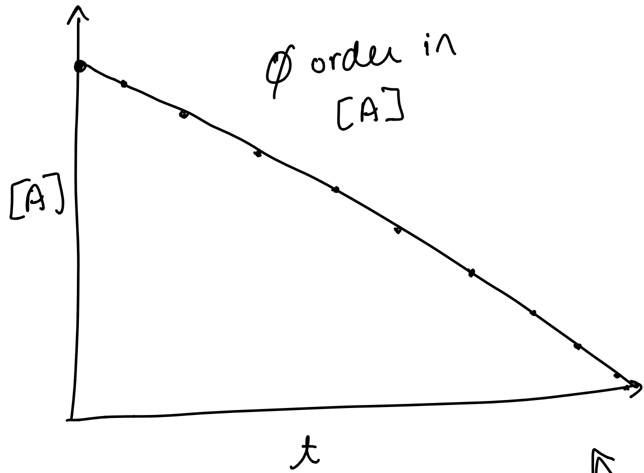
GS	TS
1 A	1 A
2 A	2 A
10 A	10 A

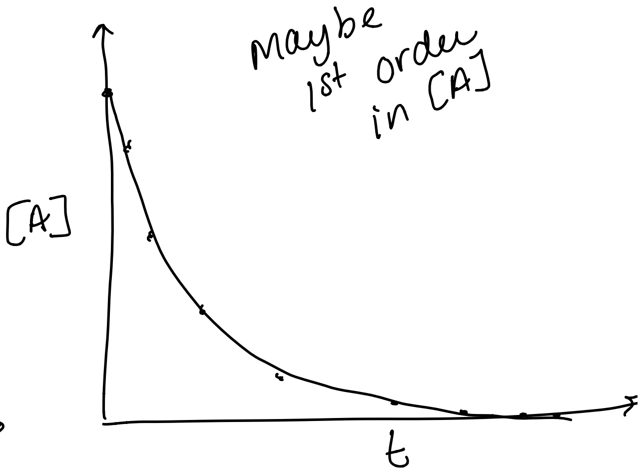
rate = $k[A]^2$ } Twice as many A's in TS as GS.

rate = $k[A]^{1/2}$ } Half as many " " " " "

What do different kinetic orders "look like"?

$$A \xrightarrow{k} P$$

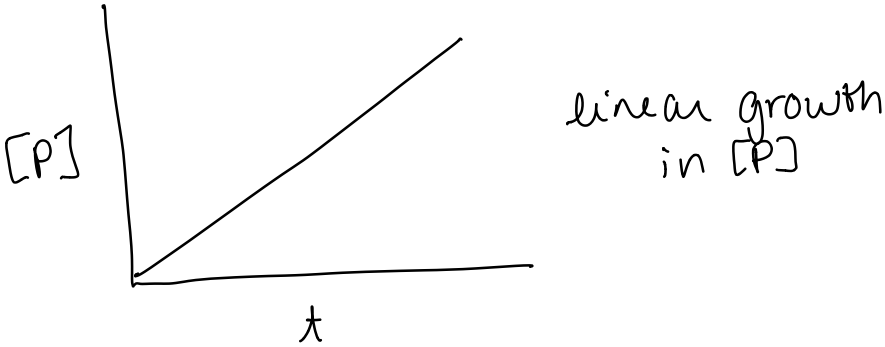




Zero-Order Kinetics

$A \xrightarrow{k} P$ (probably not 1 step)

$$\text{rate} = \frac{-d[A]}{dt} = \frac{d[P]}{dt} = k[A]^0 = k$$

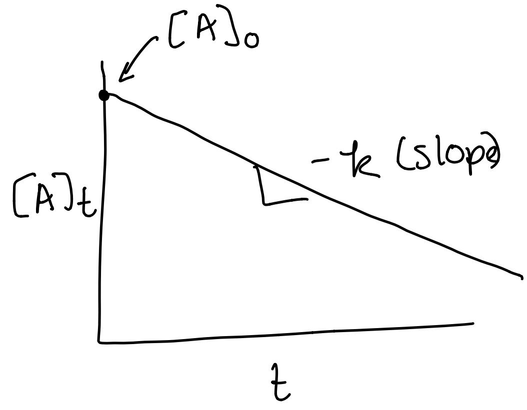


Integrated Rate Law: (Old school, but linear)

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

$$\int_0^t d[A] = \int_0^t -k\,dt$$

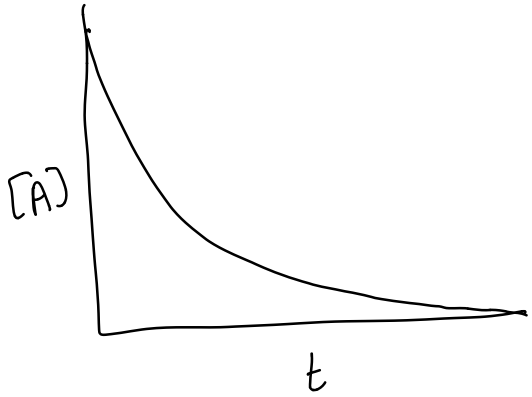
$$[A]_t - [A]_0 = -kt$$

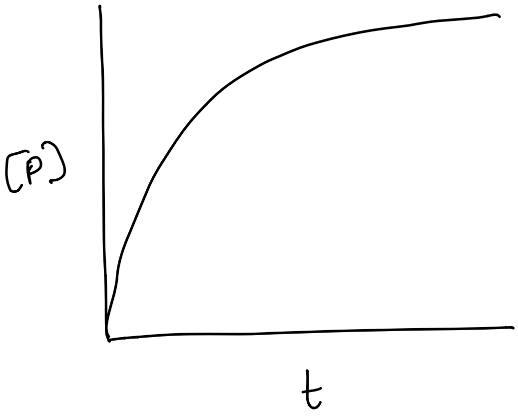


First Order Kinetics

$A \xrightarrow{k} P$ w/ 1st order dependence on [A]

$$\text{rate} = -\frac{d[A]}{dt} = \frac{d[P]}{dt} = k[A]$$





- not linear
- reaction slows down at the end.

Integrated Rate Law:

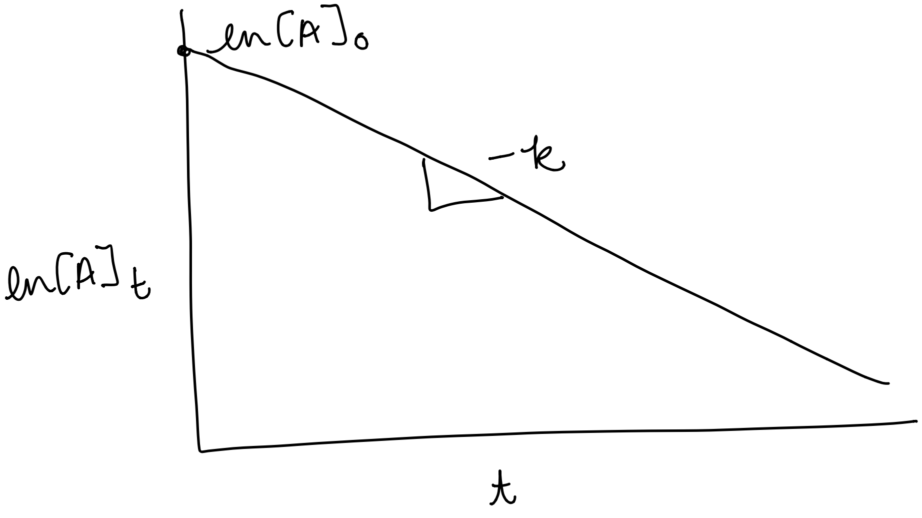
$$-\frac{d[A]}{dt} = k[A]$$

$$\int_0^t \frac{d[A]}{[A]} = \int_0^t -k \, dt$$

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

measurable & known

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



Practical Considerations:

- ln x tend to look linear.
  - ↳ Measure [A] over 3-5 half-life.
- How many data points? As many as possible.
  - ≥ 10 - 20
  - Spread over entire range

vs.

better

How long to 50% SM & 50% P?

$$[A]_t = \frac{1}{2}[A]_0$$

$$[A]_0 = 2[A]_t$$

$$\ln[A]_t - \ln \underbrace{2[A]_t}_{[A]_0} = -kt$$

$$\ln \frac{\cancel{[A]}_t}{2\cancel{[A]}_t} = -kt$$

$$\ln \tfrac{1}{2} = -kt$$

$$\underbrace{\ln 1}_{=0} - \ln 2 = -kt$$

$$\ln 2 = kt$$

$$t_{1/2} = \frac{\ln 2}{k}$$ } Does <u>not</u> depend on $[A]$ or $[A]_0$

"half-life"

Why this matters to <u>you</u>...

$t_{1/2}$	time (h)	% yield
1	2	50
2	4	75
3	6	87.5
4	8	93.75
5	10	96.875