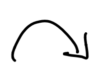
Lecture 17: Kinetics (continued)

Announcements:
- Seminar: Prof. Nate Szymczak (University of Michigan)
  Catalytic Hydrogen Transfer Reactions Enabled by Ligand Design
  Wed, 4pm, 219 BRL
- Problem Set 4 due Thurs, 11/3

Today:
- Arrow-pushing for radical reactions
- Catalysis (in general terms) } Homogeneous Catalysis
- Kinetics of Catalytic Reactions

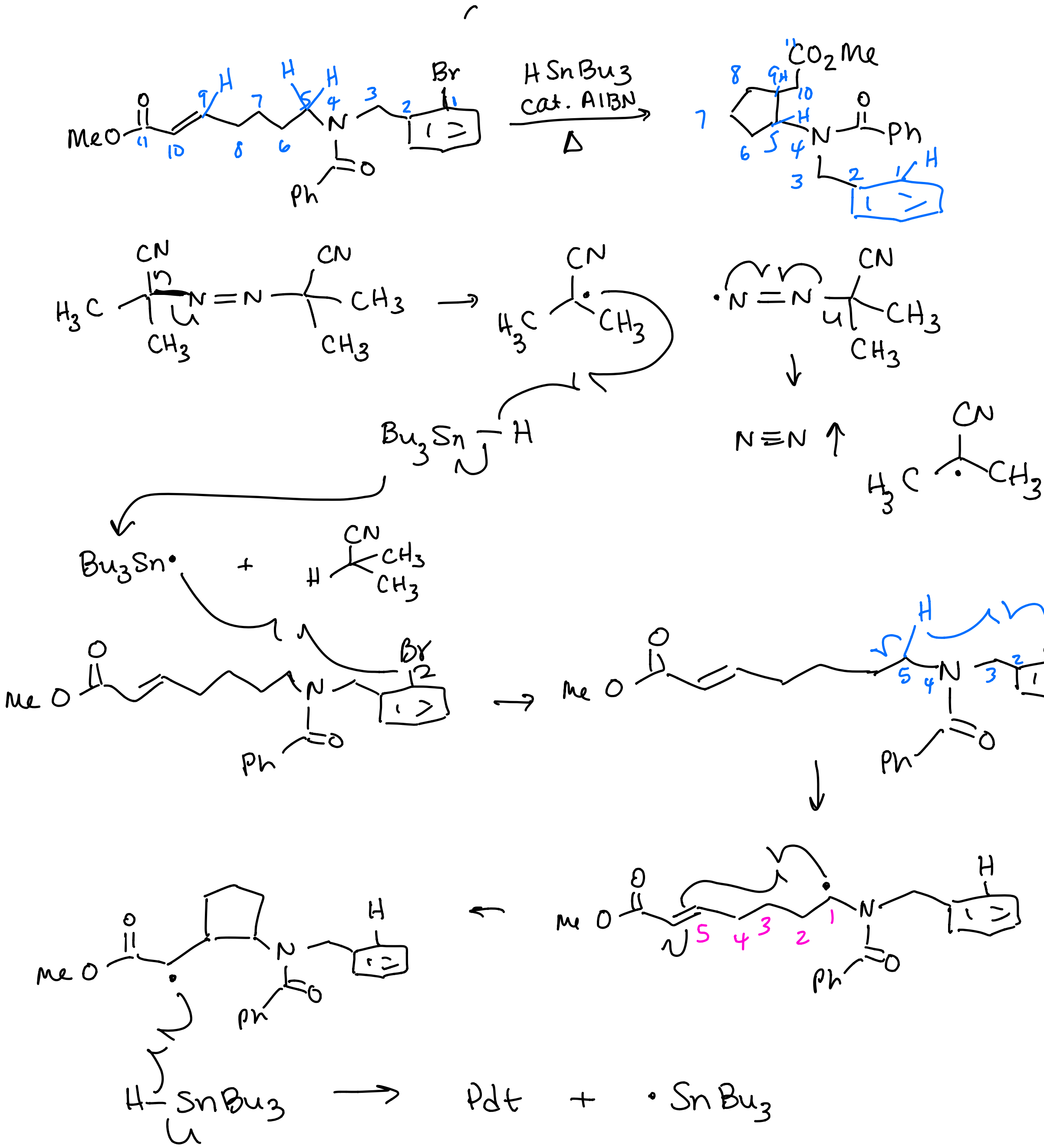
Practice Problem: Mechanism?

Tips for Radical Mechanisms

1) Count 5 (especially helpful for H-abstractions)
2) Anything that stabilizes a cation <u>or</u> anion stabilizes a radical.
3) Use  (<u>Not</u> )

↑ pushing 1 e- (need 2 of these to make a bond)

↑ pushing 2 e-s.



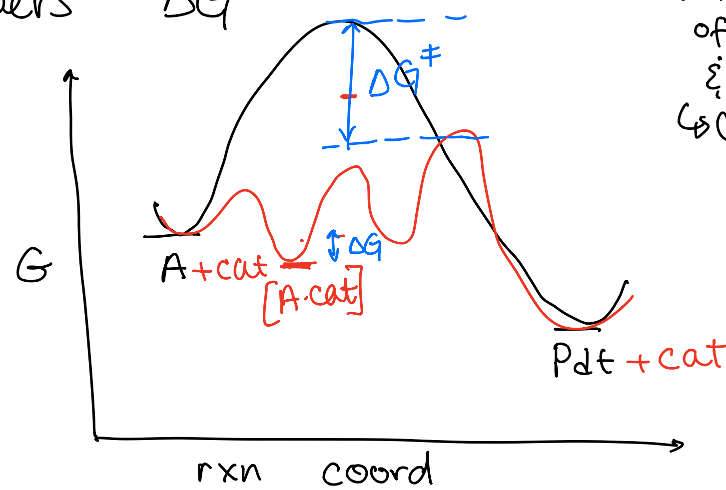
HSnBu3
cat. AIBN
Δ
CO2Me
Ph
Br
MeO
CN
H3C
CH3
N=N
N≡N
Bu3Sn–H
Bu3Sn•
H–SnBu3
Pdt + •SnBu3

Catalysis

Important in
- pharmaceuticals
- biological systems (enzymes)
- energy research

what is it?

Lowers $\Delta G^{\ddagger}$



Linus Pauling:
Differential binding of catalyst to substrate & transition state.
↳ Catalyst binds TS more strongly.

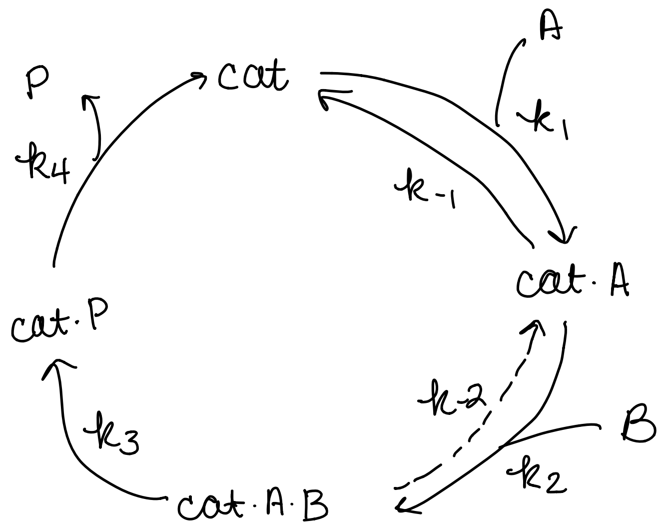
$$K_{cat} = \frac{[sub \cdot cat]}{[sub][cat]}$$

$$1 < \frac{k_{cat}}{k_{uncat}} = \frac{K^{\ddagger}_{cat}}{K_{cat}}$$

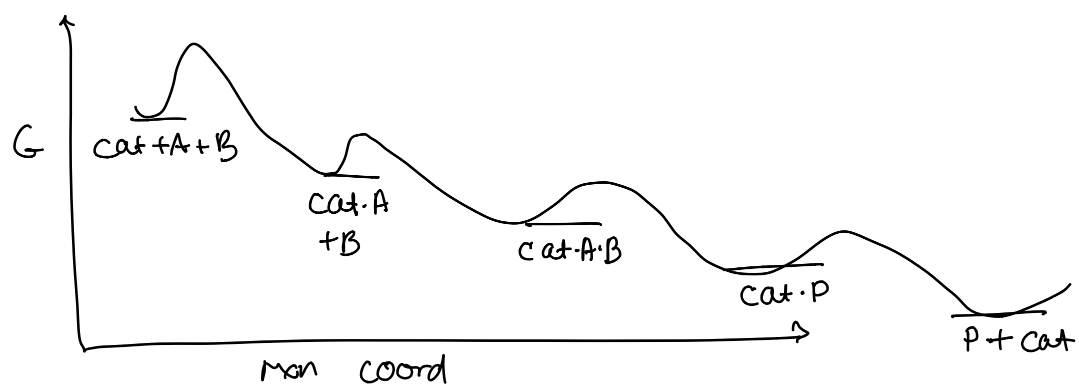
Turnover of catalyst: catalyst can & does repeat catalytic cycle.
↳ Practical outcome: Substoichiometric amounts of catalyst used.
↳ catalyst doesn't change

Kinetics of Catalytic Cycle

rate = k_{obs} [cat]



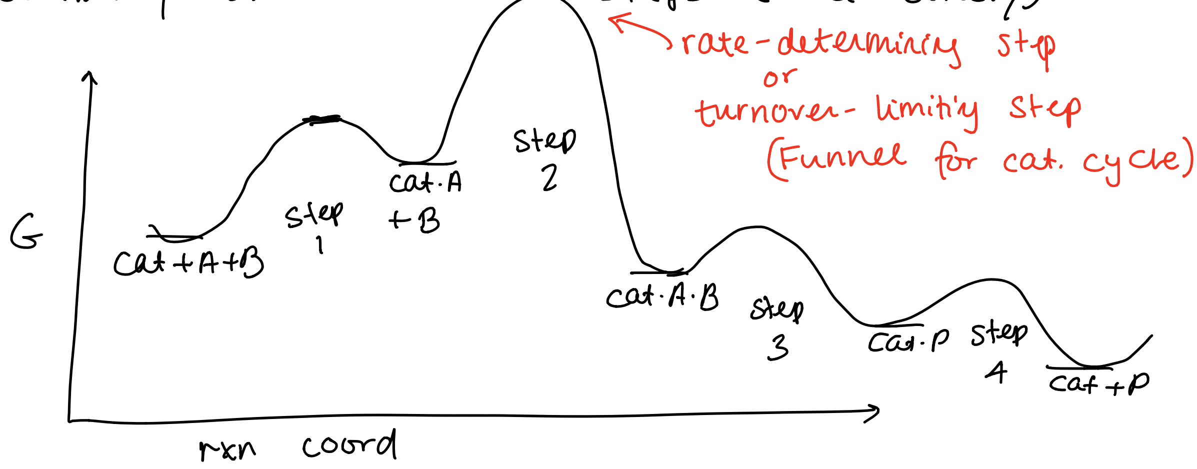
Possibility #1 : All steps = irreversible



rate = k_{obs} [cat][A][B]

atypical

Possibility #2: Reversible steps (more likely)



rate = k_2[cat·A][B]

Equilibrium Approx: $K_1 = \frac{k_1}{k_{-1}} = \frac{[cat \cdot A]}{[cat][A]}$

$$[cat \cdot A] = \frac{k_1 [cat][A]}{k_{-1}}$$

$$rate = \frac{k_1 k_2 [cat][A][B]}{k_{-1}}$$

Steady State: $rate = \frac{k_1 k_2 [cat][A][B]}{k_{-1} + k_2}$

But...

① Changes [A], [B], [Pd+] over rxn course → change in rds

② May not have clearly defined rds

③ Catalyst "resting state" may not be naked catalyst.
↳ & may change over rxn course.

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

what is [cat]?

cat = Naked catalyst

$$[\text{cat}]_{\text{total}} = [\text{cat}]_T = [\text{cat}] + [\text{cat}\cdot\text{A}]$$

$$[\text{cat}] = [\text{cat}]_T - [\text{cat}\cdot\text{A}]$$

$$\text{rate} = k_2 [\text{cat}\cdot\text{A}] \cancel{[\text{B}]} = \frac{k_1 k_2 [\text{A}]\cancel{[\text{B}]}\left([\text{cat}]_T - [\text{cat}\cdot\text{A}]\right)}{k_{-1} + k_2}$$

Solve for $[\text{cat}\cdot\text{A}]$:

$$k_2[\text{cat}\cdot\text{A}]$$

... to be continued ...