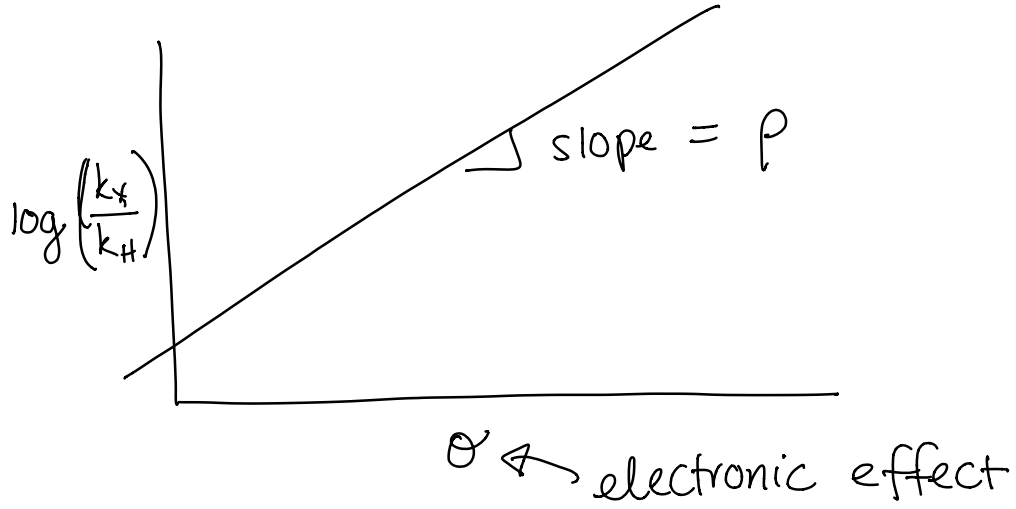
Lecture 20: Mechanistic Experiments

Announcements:
- PS 5 returned today.
- Midterm 2 on Thurs.

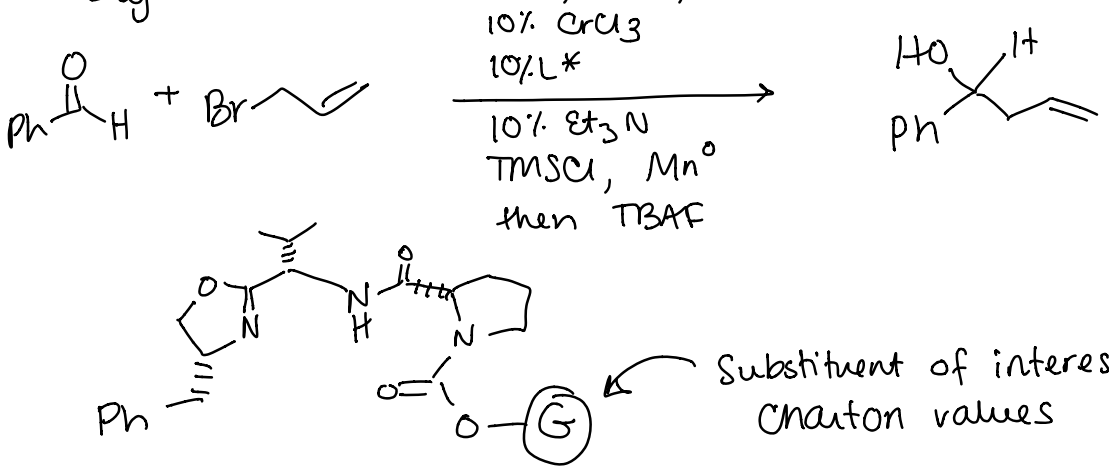
Today:
- More mechanistic experiments

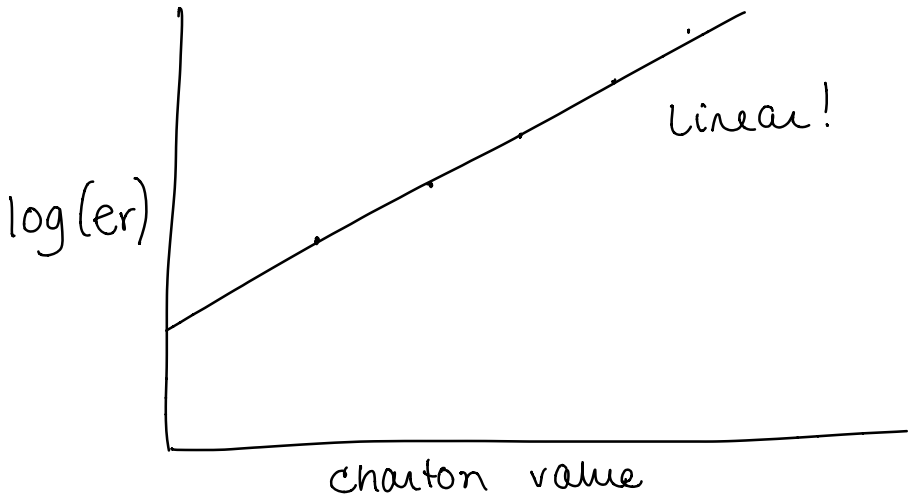
Hammett Correlation:

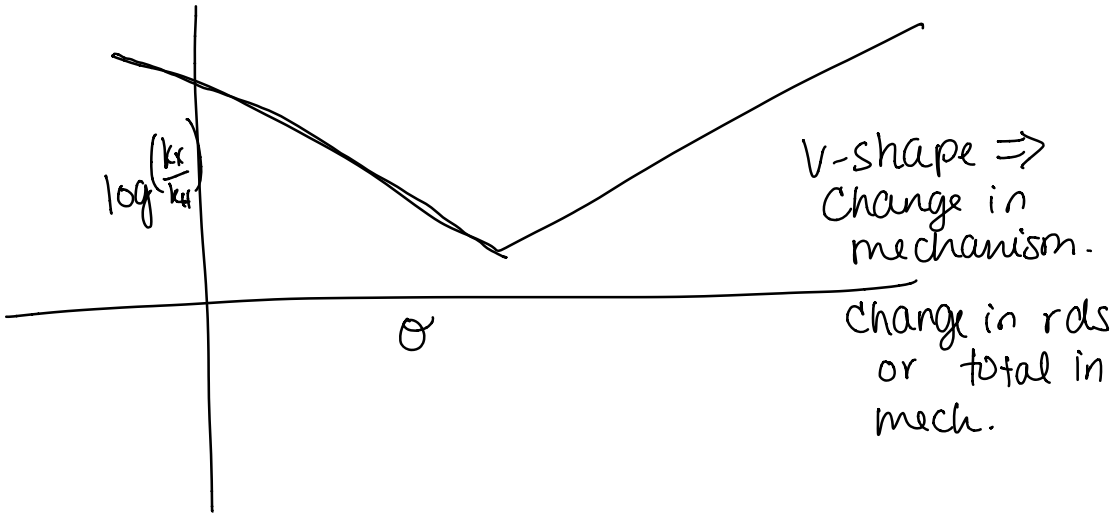


Other LFER:

Sigman ACIE 2008, 47, 771. Steric bulk & ee?




log(er)
Linear!
charton value


$\log\left(\frac{k_r}{k_u}\right)$
0
V-shape ⇒
Change in
mechanism.
Change in rds
or total in
mech.

Isotope Effects

→ KIE related to change in mass → H vs. D

→ ① Detect if X–H / X–D bond is broken in or before rds.

② Detect changes in hybridization @ X–H/D in rds.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

spring force constant

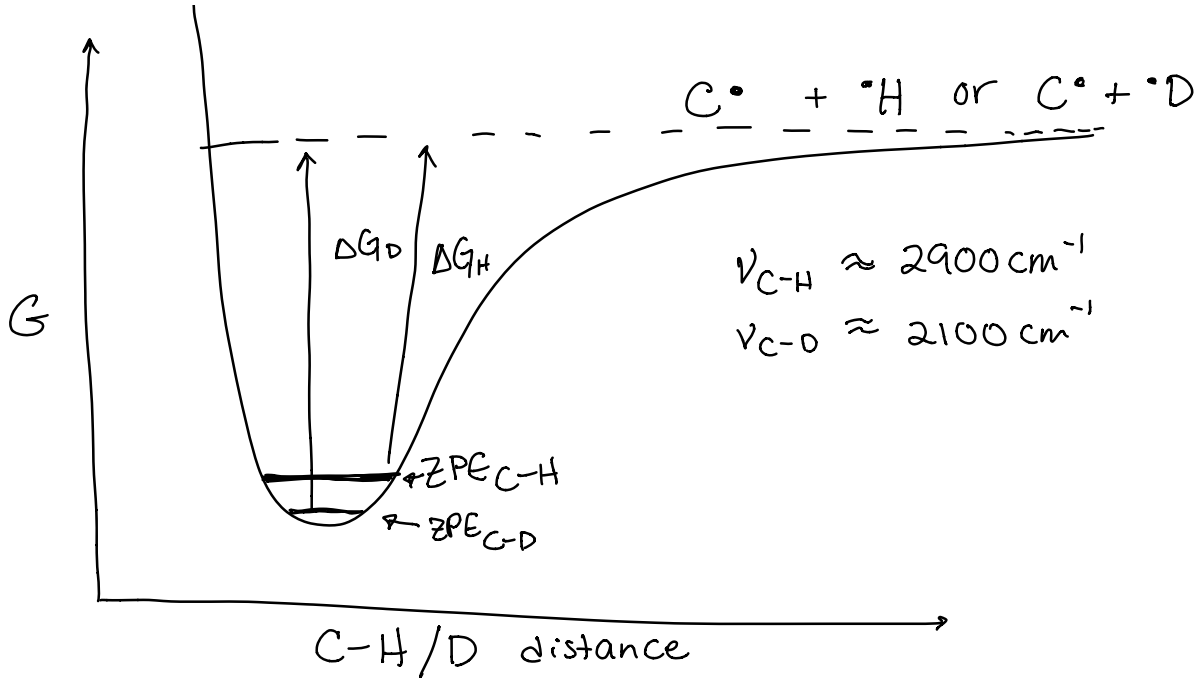
ν = frequency of vibration

μ = reduced mass $= \frac{m_A m_B}{m_A + m_B}$

Heavier mass ⟹ Lower frequency

C–H vs C–D

C–D: lower frequency
more stable / stronger bond



$\nu_{C-H} \approx 2900\ cm^{-1}$

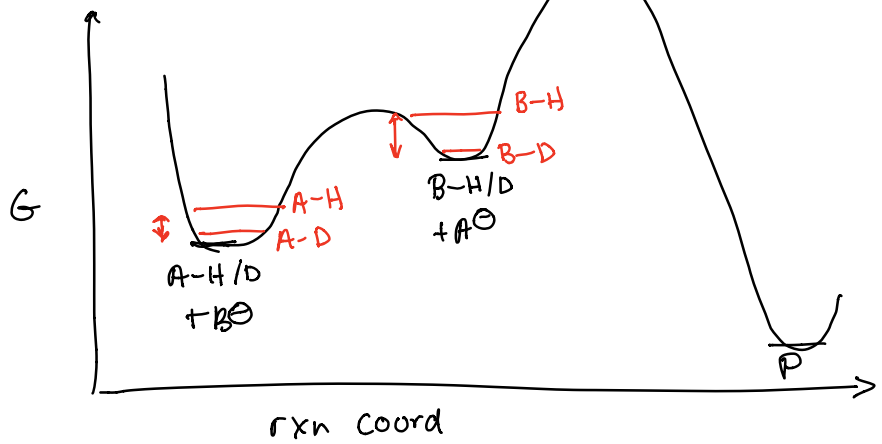
$\nu_{C-D} \approx 2100\ cm^{-1}$

$$\frac{k_H}{k_D} = KIE = e^{-\Delta E / k_B T}$$

max KIE ≈ 6.5 for "normal" organic reaction.

Equilibrium Isotope Effects

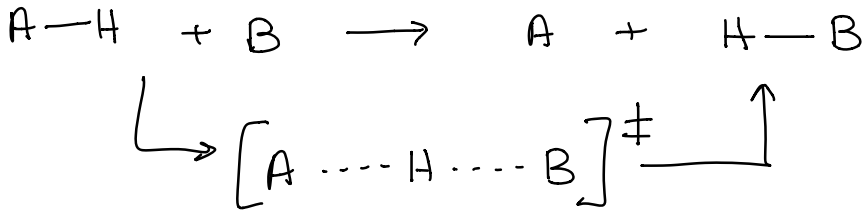
$$A\text{–}H/D + B^{\ominus} \rightleftharpoons A^{\ominus} + B\text{–}H/D \longrightarrow P$$



Kinetic Isotope Effects (KIE)

When C-H/D is not fully cleaved.

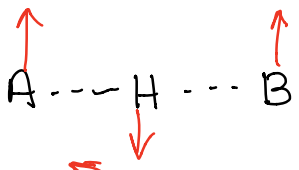
Consider linear TS:



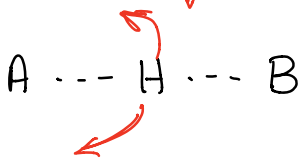
Vibrational Frequencies:

1) Asymmetric Stretch = rxn coord
↑ no frequency in TS

2) Bending

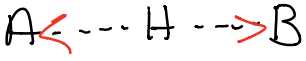


3) Wag



Similar in SM & TS

4) Symmetric Stretch

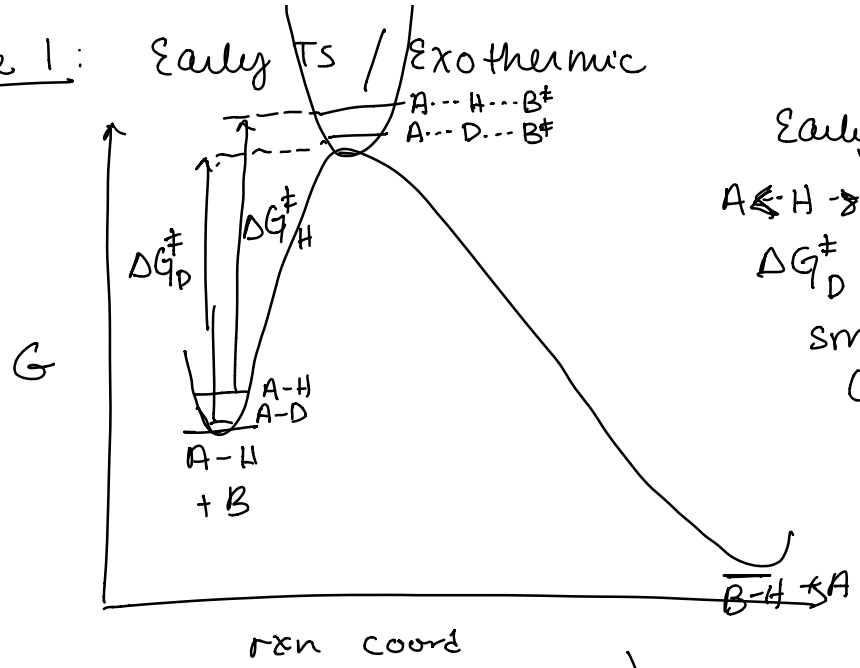


New to TS

Not in A-H or B-H

↳ Can be affected by isotopes.

Case 1: Early TS / Exothermic



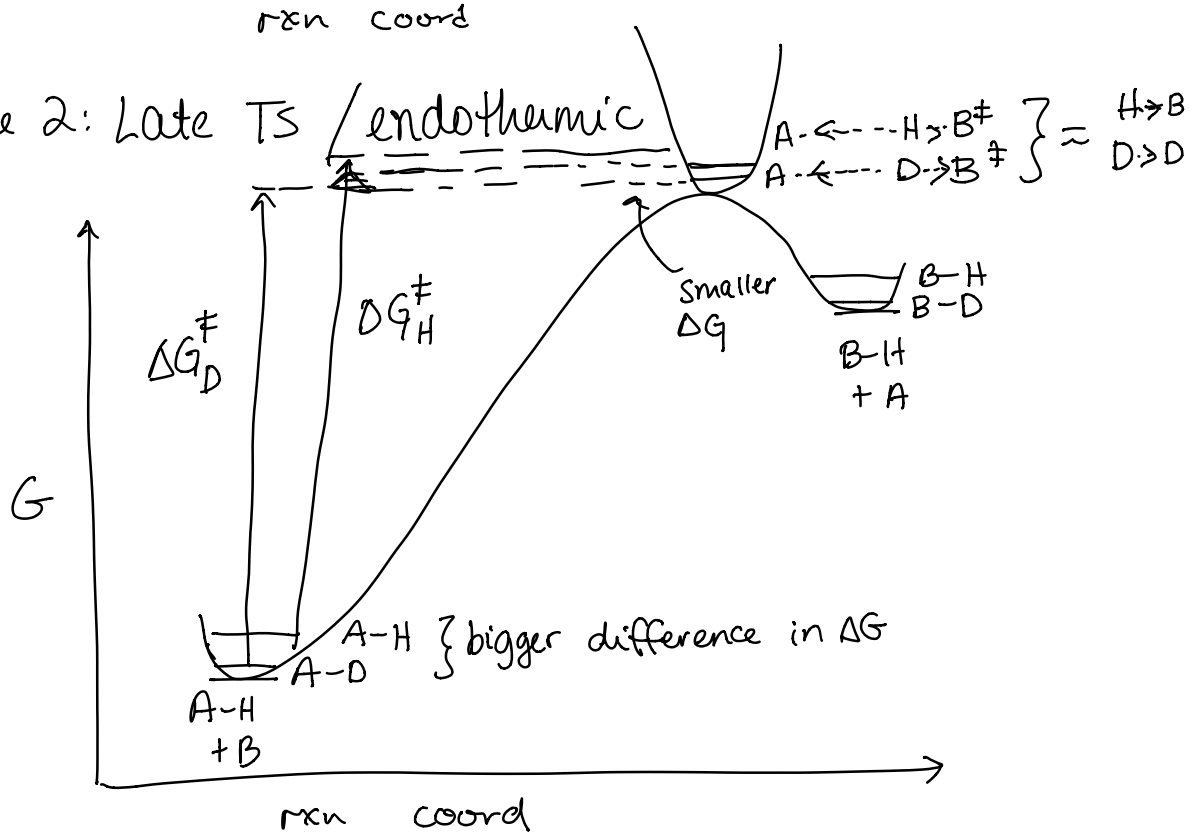
Early TS ≈ SM

A⟵H ⟶ ------ B ≈ A⟵H

$\Delta G^{\ddagger}_{D} \simeq \Delta G^{\ddagger}_{H}$

small KIE (close to 1)

Case 2: Late TS / endothermic

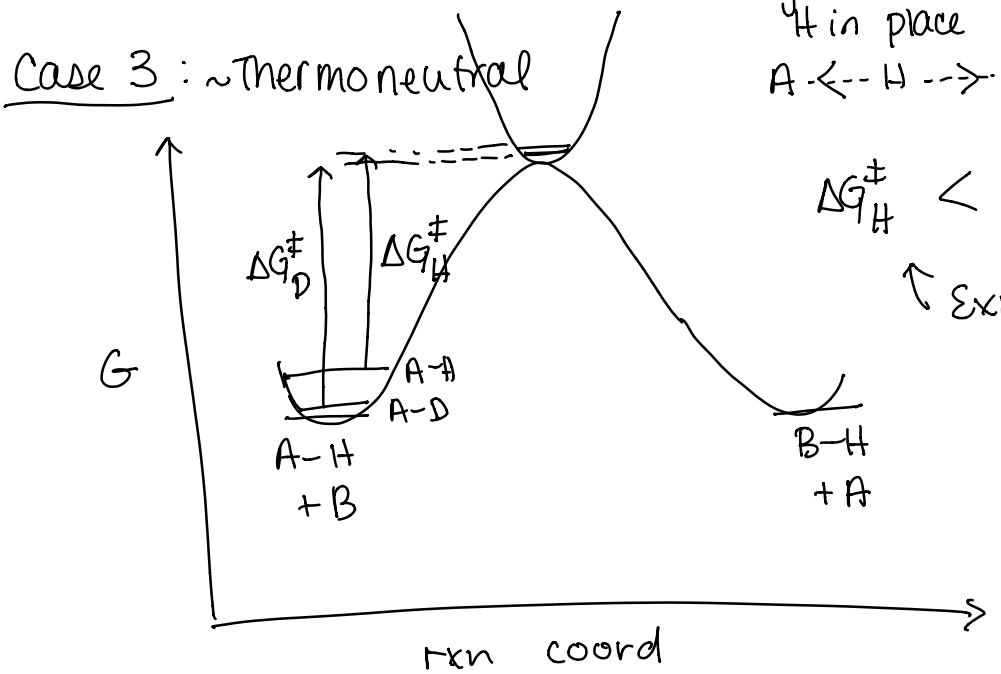


If $H \rightarrow B \approx H \rightarrow A$, then small KIE.

If $H \rightarrow B \neq H \rightarrow A$, then you will probably see KIE.

$\Delta G^{\ddagger}_{H} < \Delta G^{\ddagger}_{D} \Rightarrow$ faster for A-H than A-D.

Case 3 : ~Thermoneutral



symm. stretch holds H in place

A <-- H --> B

$\Delta G^{\ddagger}_H < \Delta G^{\ddagger}_D$

↑ Expect KIE 2 – 7

↑ Typical for Primary KIE's

↑ 1°

$$KIE = \frac{k_H}{k_D}$$