A few remaining topics in kinetics

Last time, we developed Transition State Theory

$$k = \left(\frac{kT}{h}\right) K^{\ddagger}$$

($K^{\ddagger}$: all coordinates except reaction coordinate)

$$= \left(\frac{k_B T}{h}\right) \left(\frac{q^{\ddagger}}{q_{Reactants}}\right) e^{\Delta D^{\ddagger}/k_B T}$$

Since $\Delta G^{\ddagger} = -k_B T \ln K^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

($\Delta H^{\ddagger}$: enthalpy of activated state relative to reactants)

we also have

$$k = \left(\frac{k_B T}{h}\right) e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

Today we'll talk a bit about some special situations:

1) Consider:

$$CH \rightarrow (CH)^{\ddagger} \rightarrow C + H$$

$$CD \rightarrow (CD)^{\ddagger} \rightarrow C + D$$

the rates for breaking CH bonds are ~ 8 times faster than CD bonds (and around 60 times faster than CT bonds!)

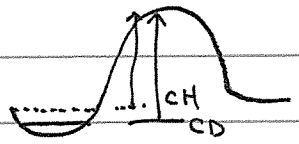
Why?

$$\frac{k_H}{k_D} = \frac{\left(\frac{k_B T}{h}\right) \frac{q^{\ddagger}_{CH}}{q_{CH}} e^{\Delta D^{\ddagger}_{CH}/k_B T}}{\left(\frac{k_B T}{h}\right) \frac{q^{\ddagger}_{CD}}{q_{CD}} e^{\Delta D^{\ddagger}_{CD}/k_B T}}$$

Although the total mass changes a little bit, most of the differences will show up in the exponential terms

$$\frac{k_H}{k_D} = \underbrace{\left(\frac{m_{CD}}{m_{CH}}\right)^{3/2}}_{\text{trans}} \underbrace{\frac{\mu_{CD}}{\mu_{CH}}}_{\text{rot}} \cdot \underbrace{e^{-\left(\frac{h\nu_{CD}}{2} + h\nu_{CH}/2\right)/kT}}_{\text{vibrational}} \cdots$$

The vibrational part is the most important. This is essentially the difference in energy to get from the ground vibrational level to the TS:



Now, the vibrational frequencies are pretty simple

$$\nu_{CD} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{CD}}} \qquad \& \qquad \nu_{CH} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{CH}}}$$

$$\nu_{CD} - \nu_{CH} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{CH}}}\left(\sqrt{\frac{\mu_{CH}}{\mu_{CD}}} - 1\right)$$

$$\mu_{CH} = \frac{m_C m_H}{m_C + m_H} \approx \tfrac{6}{7} m_H$$

$$\mu_{CD} = \frac{m_C m_D}{m_C + m_D} \approx m_D = 2m_H = 2\mu_{CH}$$

$$\therefore \quad \nu_{CD} - \nu_{CH} = \nu_{CH}\left(\frac{1}{\sqrt{2}} - 1\right)$$

$$\therefore \quad \frac{k_H}{k_D} \approx e^{-h\nu_{CH}\left(\frac{1}{\sqrt{2}} - 1\right)/2k_BT} \qquad \left(\nu_{CH} \approx 2900\ cm^{-1}\right)$$

so @ 300K,

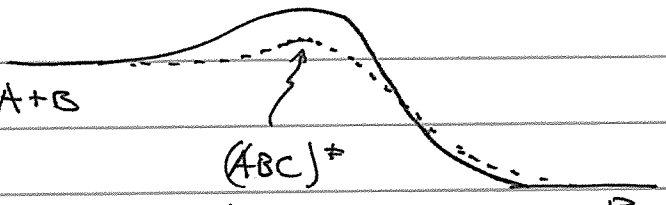
$$\frac{k_H}{k_D} \simeq 7.68!$$

← zero point energy of reactant causes an 8-fold increase in reaction rate!

This is called the primary kinetic isotope effect

for bare CH & CD: ← the rates are even larger because of rotational effects, but for a single CH bound in a much larger molecule, only the vibrational part matters.

Catalysts



$A + B \xrightarrow{k_0} P$ ← uncatalyzed reaction

← Catalysts work (presumably) by stabilizing the transition state

$$K_c^{\ddagger} = \frac{[(ABC)^{\ddagger}]}{[A][B][C]}$$

↑ catalyst concentration

$$K^{\ddagger}_{uncatalyzed} = \frac{[(AB)^{\ddagger}]}{[A][B]}$$

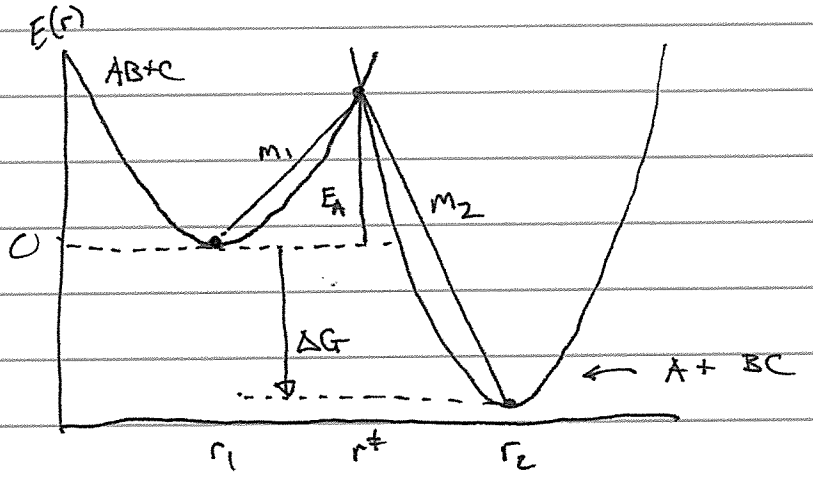
$$\frac{k_{catalyzed}}{k_0} = \frac{(k_B T/h)\, K_c^{\ddagger}}{(k_B T/h)\, K^{\ddagger}_{uncatalyzed}} = \frac{[(ABC)^{\ddagger}]}{[(AB)^{\ddagger}][C]} = K_B$$

K_B: binding constant of catalyst to TS

Good catalysts: 1) Bind tightly to TS
2) Don't bind to reactants
3) Don't bind to products!

Evans - Polanyi model

$A^{r}\!\cdots B\cdots\cdots C$ ← consider this simple reaction



m_1 & m_2 are slopes of straight lines from reactant & product structures to TS

$$E_{AB}(r) = m(r - r_1)$$ ← slope of line 1

$$r^{\ddagger} = \frac{E_a}{m_1} + r_1$$

likewise for BC molecule: $E_{BC}(r) = m_2 (r - r^{\ddagger}) + E_A$

This implies: $\Delta G = m_2 (r_2 - r^{\ddagger}) + E_a$

$$= m_2 \left(r_2 - \left(\frac{E_a}{m_1} + r_1\right)\right) + E_a$$

Or:

$$E_a = \frac{m_1}{m_1 - m_2}\left[\Delta G - m_2 (r_2 - r_1)\right]$$

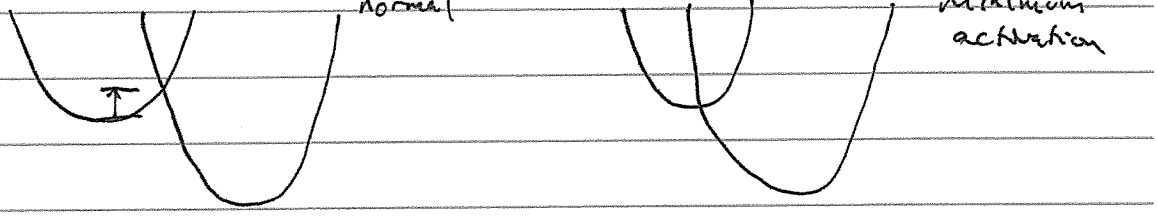
estimate of activation energy from simple linear formulae & measurable ΔG values!

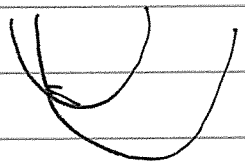
The linear Evans-Polanyi model was later extended to parabolas by Rudy Marcus to explain electron transfer reactions:

$$E_{AB}(r) = m_1(r - r_1)^2 + b$$

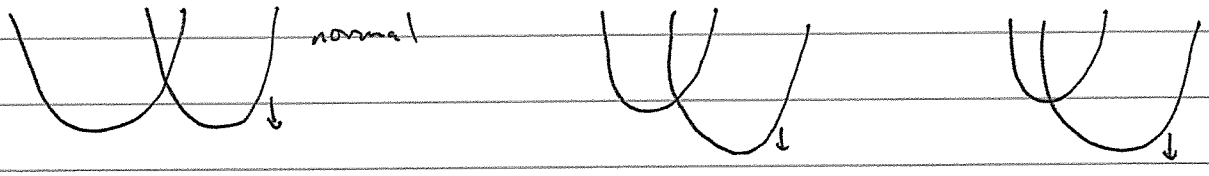
He found:

$$E_a \sim (\text{constant} + \Delta G)^2$$

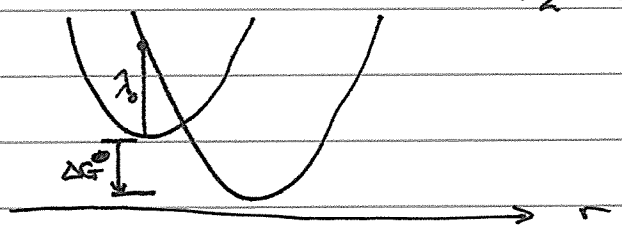




"inverted" region sometimes increasing product stability can slow down a reaction



$E_1 = m_1(r - r_1)^2$ $\qquad$ $E_2 = m_2(r - r_2)^2 + c$



$$\Delta G^{\ddagger} \text{ or } E_A = \frac{(\lambda_o + \Delta G_o)^2}{4\lambda_o}$$

ΔG_o = difference in free energy in reactant & product wells

λ_o = product energy measured at reactant coordinate

Marcus theory:

$$k_{et} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda_o k_B T}} e^{-(\lambda + \Delta G_o)^2 / 4\lambda k_B T}$$

$|H_{AB}|^2$ is a "coupling" term that measures probability of jumping from one diabatic surface to the other

Marcus won the Nobel prize in 1992 for this theory of intersecting parabolas & for predicting the inverted region!