Chem 311
12/14/07

Kinetics and Energetics

Arrhenius: $k = Ae^{-E_a/RT}$ ← E_a: activation energy
(empirical)

A: pre-exponential factor (same units as k)

$$\ln k = \ln A - \frac{E_a}{RT}$$

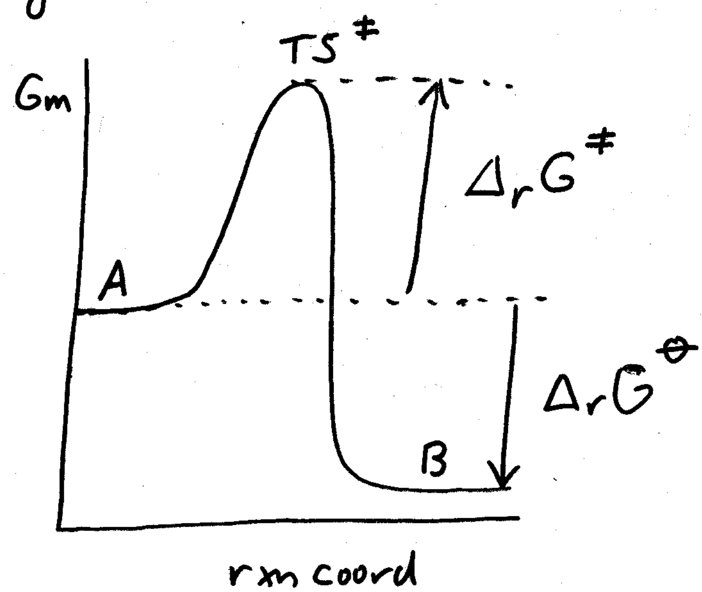
$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$

$$y = m x + b$$

use to fit k vs. T data (assumes $E_a \neq f(T)$)

Eyring: In each ES of a mechanism, the reactant(s) pass(es) thru a <u>transition state</u> (TS) to form product(s)

eg $A \rightarrow B$ with $\Delta_r G^\ominus < 0$ ("exergonic")



Thermo: $K = e^{-\Delta_r G^\ominus / RT}$

Kinetics: $k = B e^{-\Delta_r G^\ddagger / RT}$

(by analogy)

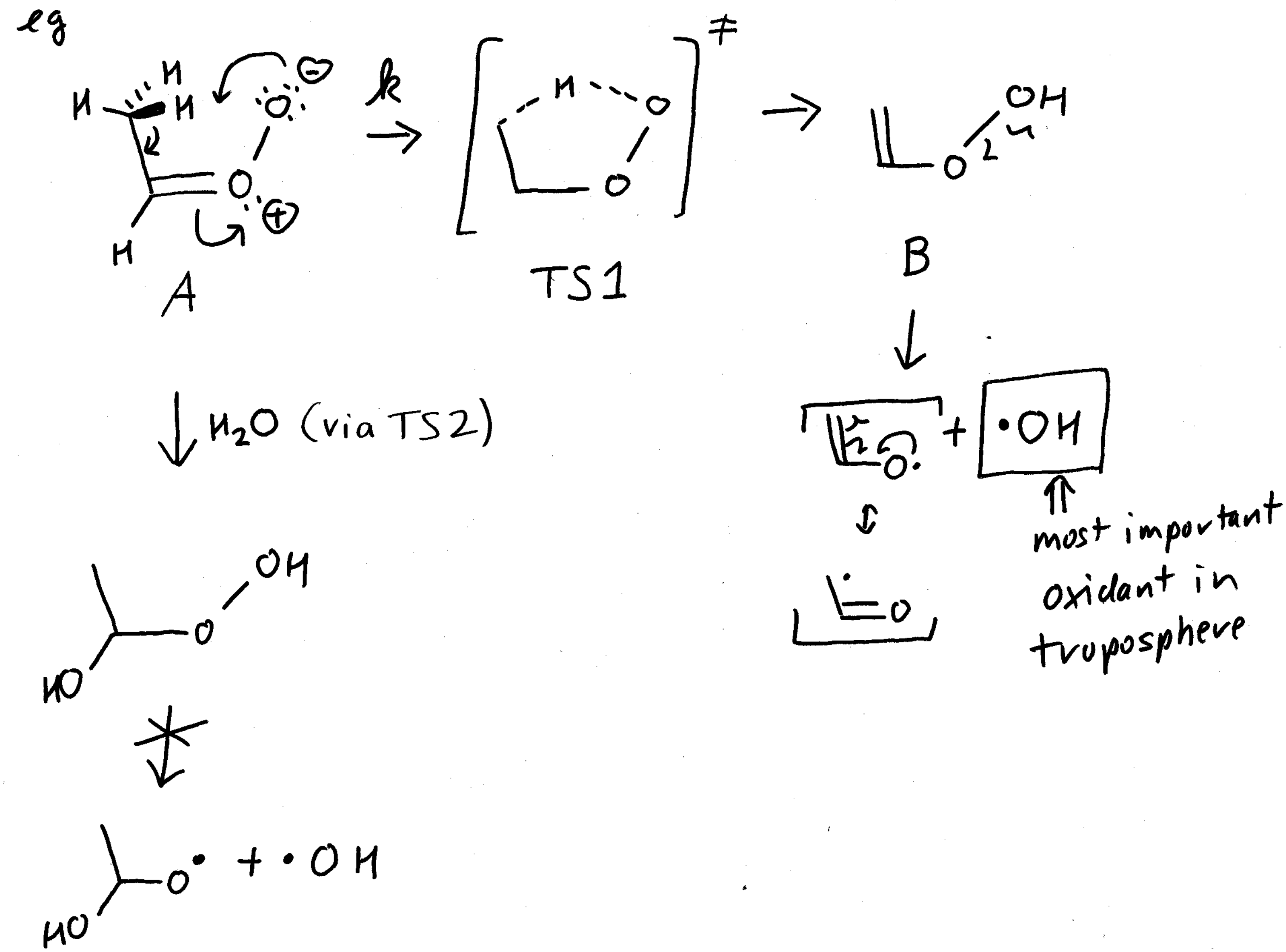
where $$-\frac{\Delta_r G^\ddagger}{RT} = -\frac{(\Delta_r H^\ddagger - T\Delta_r S^\ddagger)}{RT} = \frac{\Delta_r S^\ddagger}{R} - \frac{\Delta_r H^\ddagger}{RT}$$

$$\therefore\ k = B e^{\Delta_r S^\ddagger / R} e^{-\Delta_r H^\ddagger / RT}$$ Eyring eqn

↑ (B): use stat mech to evaluate

---

eg



State of the art quantum mechanical calculation:

$$\Delta_r H^{\ddagger} = G_m(TS1) - G_m(A) = (75 \pm 5)\ \text{kJ mol}^{-1}$$

(7% relative uncertainty)

What is the corresponding uncertainty in k (e_k)?

Chem 222: For $y = f(x)$, $e_y = \left|\frac{dy}{dx}\right| e_x$

Here, $$\frac{dk}{d\Delta_r H^{\ddagger}} = B e^{\Delta_r S^{\ddagger}/R}\left(-\frac{1}{RT}\right) e^{-\Delta_r H^{\ddagger}/RT} = -\frac{k}{RT}$$

so $$e_k = \frac{k}{RT} e_{\Delta_r H^{\ddagger}} \quad \text{or} \quad \frac{e_k}{k} = \text{relative uncertainty} = \frac{e_{\Delta_r H^{\ddagger}}}{RT}$$

At 22₀ K (min T in troposphere)

$$\frac{e_k}{k} = \left(\frac{5 \times 10^3\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}}{8.3\ \cancel{\text{J}}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{K}^{-1}}}\right)\left(\frac{1}{22_0\ \cancel{\text{K}}}\right) \cong 3 \text{ or } 300\%\ (!)$$

relative uncertainty