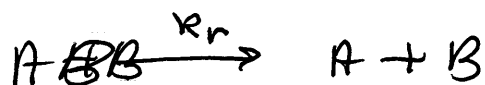


Diffusion Controlled Rxn



a) $k_r \gg k_p$

$$K = \frac{[AB]}{[A][B]} = \frac{k_d}{k_r}$$

$$[AB] = \frac{k_d}{k_r} [A][B]$$

$$\text{rate} = k_p [AB] = \frac{k_p k_d}{k_r} [A][B]$$

b) $k_r \approx k_p$

$$\frac{d[AB]}{dt} = k_d [A][B] - k_r [AB] - k_p [AB] = 0$$

$$[AB] = \frac{k_d}{k_r + k_p} [A][B]$$

$$\text{rate} = \frac{k_p k_d}{k_r + k_p} [A][B]$$

$$k_p \gg k_r$$

$$\text{rate} = k_d [A][B]$$

Solutions

$$R_0 = k^{fm} + k^{phy}$$

$$k_{\text{diff}} \gg k^{\text{pk}}_s$$

SLOWEST STEP IS DIFFUSION

$$k_d \approx k^{\text{pk}}_s = 4\pi(D_{AB})N_A(r_A+r_B)$$

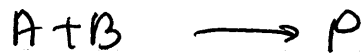
$$D \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

$$r_A+r_B \sim 5 \text{ \AA}$$

$$k_d \sim 10^{10} \text{ M s}^{-1}$$

$$D = \frac{kT}{6\pi\eta r}$$

Activated Complex



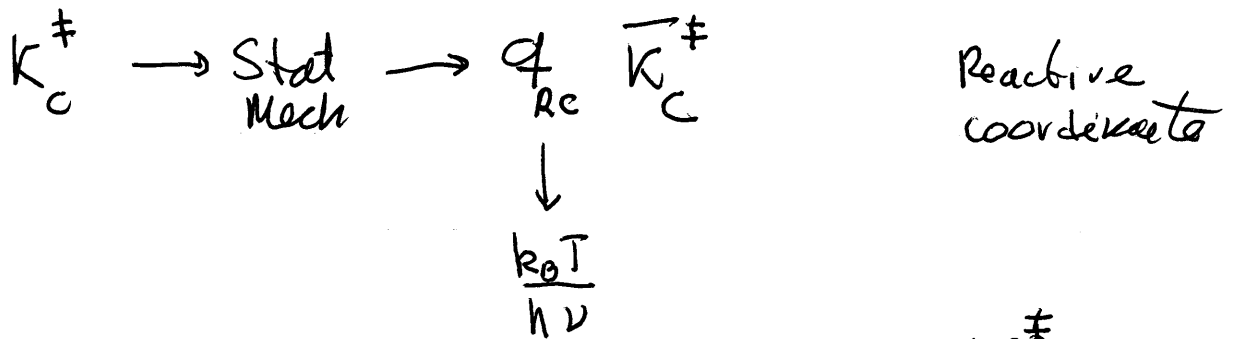
$$K_c^{\ddagger} = \frac{[AB^{\ddagger}] / c^{\circ}}{\frac{[A]}{c^{\circ}} \frac{[B]}{c^{\circ}}} = \frac{[AB^{\ddagger}] c^{\circ}}{[A][B]}$$

$$v_{\text{obs}} = k_2 [AB^{\ddagger}] = \left(\frac{k_2 K_c^{\ddagger}}{c^{\circ}} \right) [A][B]$$

QM \rightarrow Activated complex $\xrightarrow{\text{vib}} \text{vib} \rightarrow \nu$

$$k_2 = k \nu$$

$k =$ transition coeff.



$$k^{\text{obs}} = k \frac{k_B T}{h c^{\circ}} \bar{K}_c^{\ddagger} = k \frac{k_B T}{h c^{\circ}} \ominus^{-\frac{\Delta G^{\ddagger}}{RT}}$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger}$$

$$k^{\text{obs}} = \frac{k k_B T}{h c^{\circ}} \ominus^{\frac{\Delta S^{\ddagger}}{R}} \ominus^{-\frac{\Delta H^{\ddagger}}{RT}}$$

In general we define

$$E_a \equiv RT^2 \frac{d \ln k}{dT}$$