

Lecture 4: Reaction Mechanisms and Rate Laws

Fundamentals of Chemical Reactions

- PSSA (SS, QSSA, PSSH)
- long chain approximation
- rate-limiting step

A+B

Stable molecules: neutral, closed shells

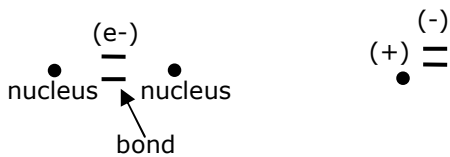


Figure 1. Stable molecules.

Pauli Exclusion Principle

-You can't put 2 identical e^- in the same exact spot

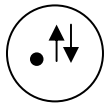


Figure 2. Two electrons in an orbital have opposite spin.

Bond Forming

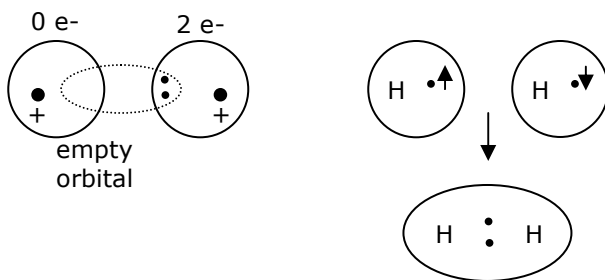


Figure 3. Bond formation. On the left, an empty orbital receives two electrons from another orbital. On the right, half-filled orbitals on the H atom mix to form a filled bonding orbital with two electrons.

Boltzmann Distribution

$$p(E) \sim e^{-E/k_B T} \quad k_B = \frac{R}{N_A}$$

$E \gg k_B T \rightarrow$ very unlikely

$$E_A + E_B > E_{\text{Activation Barrier}}$$



Small fraction will collide correctly and react

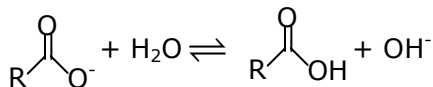
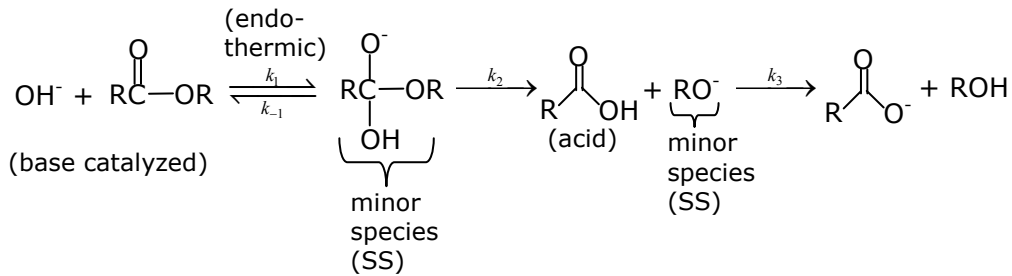
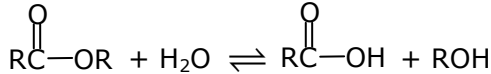
$$k(T) \sim A e^{-E_a/k_B T}$$

A is the prefactor, proportional to the number of ways the molecules get together with sufficient energy to react.

Reactive Intermediates

- charged \longrightarrow acid/base chemistry
- empty orbital \longrightarrow metal catalyst
- single e- orbital \longrightarrow free radical

Example:



$$\frac{d \left[\begin{array}{c} \text{O}^- \\ | \\ \text{RC}-\text{OR} \\ | \\ \text{OH} \end{array} \right]}{dt} \approx 0 \quad \left[\begin{array}{c} \text{O}^- \\ | \\ \text{RC}-\text{OR} \\ | \\ \text{OH} \end{array} \right] \approx \frac{k_1 [\text{OH}^-] \left[\begin{array}{c} \text{O} \\ || \\ \text{RC}-\text{OR} \end{array} \right]}{k_{-1} + k_2}$$

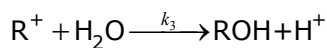
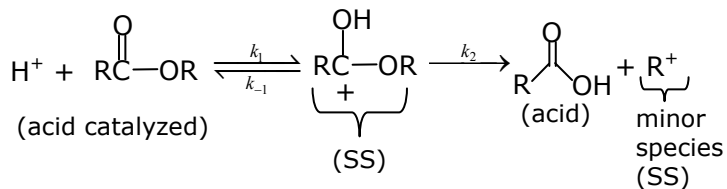
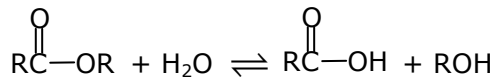
$$\frac{d [\text{RO}^-]}{dt} \approx 0 \quad [\text{RO}^-] \approx \frac{k_2 \left[\begin{array}{c} \text{O}^- \\ | \\ \text{RC}-\text{OR} \\ | \\ \text{OH} \end{array} \right]}{k_3 [\text{acid}]}$$

$$r_{\text{ROH}} = k_3 [\text{RO}^-] [\text{acid}] = k_2 \left[\begin{array}{c} \text{O}^- \\ | \\ \text{RC}-\text{OR} \\ | \\ \text{OH} \end{array} \right] = \underbrace{\frac{k_1 k_2}{k_{-1} + k_2}}_{k_{\text{eff}}} [\text{OH}^-] \left[\begin{array}{c} \text{O} \\ || \\ \text{RC}-\text{OR} \end{array} \right]$$

Rate Limiting Step

-Only 1 rate constant of k_{eff} is really relevant

-What do you have most of in a reaction mix? This is the material preceding the rate limiting step.

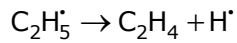
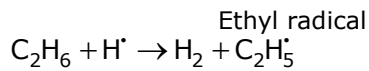
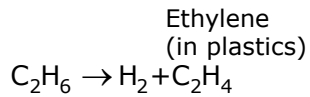


$$\frac{d \left[\begin{array}{c} \text{OH} \\ | \\ \text{RC}-\text{OR} \\ + \end{array} \right]}{dt} \approx 0 \quad \left[\begin{array}{c} \text{OH} \\ | \\ \text{RC}-\text{OR} \\ + \end{array} \right] \approx \frac{k_1 [\text{H}^+] \left[\begin{array}{c} \text{O} \\ || \\ \text{RC}-\text{OR} \end{array} \right]}{k_{-1} + k_2}$$

$$\frac{d [\text{R}^+]}{dt} \approx 0 \quad [\text{R}^+] \approx \frac{k_2 \left[\begin{array}{c} \text{OH} \\ | \\ \text{RC}-\text{OR} \\ + \end{array} \right]}{k_3 [\text{H}_2\text{O}]}$$

$$r_{ROH} = k_3 [R^+] [H_2O] = k_2 \left[\begin{array}{c} \text{OH} \\ | \\ \text{RC}^+ - \text{OR} \end{array} \right] = \frac{k_1 k_2}{k_{-1} + k_2} [H^+] \left[\begin{array}{c} \text{O} \\ || \\ \text{RC} - \text{OR} \end{array} \right]$$

k_{eff}



$$-r_{C_2H_6} = k_1 [H^\cdot] [C_2H_6]$$

