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

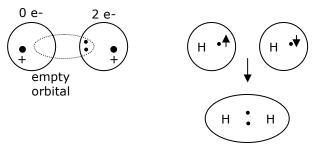


Figure 3. Bond formation. On the left, an empty orbital receives two electrons from another orbital. On the right, half-filled orbitals on the H atom mix to form a filled bonding orbital with two electrons.

Boltzmann Distribution

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

 $E \gg k_{\scriptscriptstyle R} T \rightarrow \text{very unlikely}$

$$E_{\scriptscriptstyle A} + E_{\scriptscriptstyle B} > E_{\scriptscriptstyle Activation}_{\scriptscriptstyle Barrier}$$



Small fraction will collide correctly and react

$$k(T) \sim Ae^{-E_a/k_BT}$$

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

Reactive Intermediates

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

Example:

$$\begin{matrix} O \\ RC-OR + H_2O \end{matrix} \rightleftharpoons RC-OH + ROH$$

$$R \rightarrow 0^{-} + H_2O \rightleftharpoons R \rightarrow 0H^{-} + OH^{-}$$

$$\frac{d \begin{bmatrix} O^{-} \\ RC^{-}OR \end{bmatrix}}{dt} \approx 0 \qquad \begin{bmatrix} O^{-} \\ RC^{-}OR \end{bmatrix} \approx \frac{k_{1} \begin{bmatrix} OH^{-} \end{bmatrix} \begin{bmatrix} O \\ RC^{-}OR \end{bmatrix}}{k_{-1} + k_{2}}$$

$$\frac{d \begin{bmatrix} RO^{-} \end{bmatrix}}{dt} \approx 0 \qquad \begin{bmatrix} RO^{-} \end{bmatrix} \approx \frac{k_{2} \begin{bmatrix} O^{-} \\ RC^{-}OR \end{bmatrix}}{OH}$$

$$r_{ROH} = k_{3} \begin{bmatrix} RO^{-} \end{bmatrix} \begin{bmatrix} acid \end{bmatrix} = k_{2} \begin{bmatrix} O^{-} \\ RC^{-}OR \end{bmatrix} = \underbrace{k_{1}k_{2}}_{C-} \begin{bmatrix} OH^{-} \end{bmatrix} \begin{bmatrix} O \\ RC^{-}OR \end{bmatrix}$$

Rate Limiting Step

-Only 1 rate constant of keff is really relevant

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

RC-OR + H₂O
$$\rightleftharpoons$$
 RC-OH + ROH

$$H^{+} + RC-OR \xrightarrow{k_{1}} RC-OR \xrightarrow{k_{2}} ROH + ROH$$

$$(acid catalyzed) \qquad (SS) \qquad RC-OR \xrightarrow{k_{2}} ROH + ROH$$

$$R^{+} + H_{2}O \xrightarrow{k_{3}} ROH + H^{+}$$

$$\frac{d \begin{bmatrix} OH \\ RC-OR \end{bmatrix}}{dt} \approx 0 \qquad \begin{bmatrix} OH \\ RC-OR \end{bmatrix} \approx \frac{k_{1} \begin{bmatrix} H^{+} \end{bmatrix} \begin{bmatrix} O \\ RC-OR \end{bmatrix}}{k_{-1} + k_{2}}$$

$$\frac{d \begin{bmatrix} R^{+} \end{bmatrix}}{dt} \approx 0 \qquad \begin{bmatrix} R^{+} \end{bmatrix} \approx \frac{k_{2} \begin{bmatrix} OH \\ RC-OR \end{bmatrix}}{k_{3} [H_{2}O]}$$

$$r_{ROH} = k_3 \left[\mathbf{R}^+ \right] \left[\mathbf{H}_2 \mathbf{O} \right] = k_2 \left[\mathbf{R}_+^{\mathsf{OH}} - \mathbf{O} \mathbf{R} \right] = \underbrace{\frac{k_1 k_2}{k_{-1} + k_2}}_{\mathbf{k}_{eff}} \left[\mathbf{H}^+ \right] \left[\mathbf{R}_-^{\mathsf{O}} - \mathbf{O} \mathbf{R} \right]$$

Ethylene (in plastics)
$$C_2H_6 \rightarrow H_2 + C_2H_4$$
 Ethyl radical
$$C_2H_6 + H^{"} \rightarrow H_2 + C_2H_5^{"}$$

$$C_2H_5^{"} \rightarrow C_2H_4 + H^{"}$$

$$-r_{C_2H_6} = k_1 \left[H^{"} \right] \left[C_2H_6 \right]$$

$$C_2H_6 \xrightarrow{slow} 2CH_3^{\bullet}$$
 inefficient, but important (radical creation) $CH_3^{\bullet} + C_2H_6 \rightarrow CH_4 + C_2H_5^{\bullet}$ $2C_2H_5^{\bullet} \rightarrow C_2H_6 + C_2H_4$ (radical destruction) (disproportionation)

 $C_2H_6 + C_2H_4 \rightarrow 2C_2H_5^{\bullet}$ reverse disproportionation also happens