# Chap. 10. The kinetics of complex reactions

## Chain reaction

A chain of reactions where the intermediates generated in one step generate inrermediates in a subsequent reaction

#### Examples: radical chain reaction, explosion, polymerization

**Eq.1:**  $CH_3CHO(g) \rightarrow CH_4(g) + CO(g), \quad v = k[CH_3CHO]^{3/2}$ 

Initiation:  $CH_3CHO \rightarrow CH_3 + CHO$ ,  $v = k_i[CH_3CHO]$ 

Propogation:  $CH_3CHO + \cdot CH_3 \rightarrow CH_3CO \cdot + CH_4$ ,  $v = k_p[CH_3CHO][\cdot CH_3]$ 

Propogation:  $CH_3CO \rightarrow CH_3 + CO, v = k'_p[CH_3CO]$ 

Termination:  $\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3, \quad v = k_t [\cdot CH_3]^2$ 

#### **Steady state approximations**

 $\frac{d}{dt}[\cdot \mathrm{CH}_3] = k_i[\mathrm{CH}_3\mathrm{CHO}] - k_p[\cdot \mathrm{CH}_3][\mathrm{CH}_3\mathrm{CHO}] + k'_p[\mathrm{CH}_3\mathrm{CO}\cdot] - 2k_t[\cdot \mathrm{CH}_3]^2 = 0$  $\frac{d}{dt}[\mathrm{CH}_3\mathrm{CO}\cdot] = k_p[\cdot \mathrm{CH}_3][\mathrm{CH}_3\mathrm{CHO}] - k'_p[\mathrm{CH}_3\mathrm{CO}\cdot] = 0$ 



**Eg.2:**  $H_2(g) + Br_2(g) \rightarrow 2HBr(g), \quad \frac{d}{dt}[HBr] = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'[HBr]}$ 

Initiation:  $Br_2 + M \rightarrow Br \cdot + Br \cdot + M$ ,  $v = k_i [Br_2][M]$ 

Propagation:  $\operatorname{Br} + \operatorname{H}_2 \to \operatorname{HBr} + \operatorname{H}_2$ ,  $v = k_p[\operatorname{Br} \cdot][\operatorname{H}_2]$  $\operatorname{H} + \operatorname{Br}_2 \to \operatorname{HBr} + \operatorname{Br}_2$ ,  $v = k'_p[\operatorname{H} \cdot][\operatorname{Br}_2]$ 

Retardation:  $H \cdot + HBr \rightarrow H_2 + Br \cdot$ ,  $v = k_r [H \cdot] [HBr]$ reduces the net rate of formation of product

Termination:  $Br \cdot + Br \cdot + M \to Br_2 + M^*$ ,  $v = k_t [Br \cdot]^2 [M]$ quencher, removes the energy of recombination

 $\frac{d}{dt}[\mathrm{HBr}] = k_p[\mathrm{Br}\cdot][\mathrm{H}_2] + k'_p[\mathrm{H}\cdot][\mathrm{Br}_2] - k_r[\mathrm{H}\cdot][\mathrm{HBr}]$ 

#### **Steady state approximations**

$$\frac{d}{dt}[\mathbf{H}\cdot] = k_p[\mathbf{B}\cdot\cdot][\mathbf{H}_2] - k'_p[\mathbf{H}\cdot][\mathbf{B}\mathbf{r}_2] - k_r[\mathbf{H}\cdot][\mathbf{H}\mathbf{B}\mathbf{r}] = 0$$
  
$$\frac{d}{dt}[\mathbf{B}\cdot\cdot] = 2k_i[\mathbf{B}\mathbf{r}_2][\mathbf{M}] - k_p[\mathbf{B}\cdot\cdot][\mathbf{H}_2] + k'_p[\mathbf{H}\cdot][\mathbf{B}\mathbf{r}_2] + k_r[\mathbf{H}][\mathbf{H}\mathbf{B}\mathbf{r}] - 2k_t[\mathbf{B}\cdot\cdot]^2[\mathbf{M}] = 0$$

## **Enzyme - Biological Catalyst**

**Reduces the activation energy with great specificity** 

### **Michaelis-Menten mechanism**

$$E + S \stackrel{k_a}{\underset{k_a'}{\leftrightarrow}} ES \stackrel{k_b}{\rightarrow} P \qquad v = k_b[ES] = \frac{k_b[E]_0}{1 + K_M/[S]_0}$$

## **Steady state approximation**

$$\frac{d}{dt}[ES] = k_a[E][S] - k'_a[ES] - k_b[ES] = 0$$
Michaelis constant:  $K_M = \frac{k'_a + k_b}{k_a} = \frac{[E][S]}{[ES]} = \frac{([E]_0 - [ES])[S]}{[ES]}$ 

$$\implies [ES] = \frac{[E]_0[S]}{K_M + [S]} \approx \frac{[E]_0[S]_0}{K_M + [S]_0}$$
For  $[S]_0 \gg K_M$ ,  $v \Rightarrow v_{max} = k_b[E]_0$ 

For  $[S]_0 >> K_M, v \to v_{max} = k_b [E]_0$ 

Lineweaver-Burk plot:	1	1	$K_M$	1
	$\overline{v} =$	$=\overline{v_{max}}$	$\overline{v_{max}}$	[S] <sub>0</sub>



## **Catalytic constant or turnover frequency**

# of catalytic cycles (turnovers) performed by the active site in a given interval divided by the duration of the interval.

$$k_{cat} = k_b = rac{v_{max}}{[{
m E}]_0}$$
Catalytic efficiency:  ${\cal E} = rac{k_{cat}}{K_M} = rac{k_a k_b}{k_a' + k_b}$ 



## **Mechanism of Enzyme Inhibition**

$$E + S \stackrel{k_a}{\underset{k_a'}{\leftrightarrow}} ES \stackrel{k_b}{\rightarrow} E + P$$
Inhibition
$$EI \leftrightarrow E + I \qquad ESI \leftrightarrow ES + I$$
steps:
$$K_I = \frac{[E][I]}{[EI]} \qquad K'_I = \frac{[ES][I]}{[ESI]}$$

$$[E]_0 = \alpha[E] + \alpha'[ES], \text{ where } \alpha = 1 + \frac{[I]}{K_I} \text{ and } \alpha' = 1 + \frac{[I]}{K'_I}$$

$$[\mathrm{ES}] = \frac{[\mathrm{E}]_0}{(\alpha K_M / [\mathrm{S}]_0 + \alpha')} \longrightarrow v = k_b [\mathrm{ES}] = \frac{v_{max}}{(\alpha K_M / [\mathrm{S}]_0 + \alpha')}$$

## **Photochemistry**

#### **Quantum Yield**

 $\phi = \frac{\text{number of events}}{\text{number of photons absorbed}} = \frac{\text{rate of process}}{\text{rate of photon absorption}}$ 

$$\sum_{i} \phi_{i} = \sum_{i} \frac{v_{i}}{I_{abs}} = 1$$

Without photochemical reaction, With photochemical reaction,  $\phi_f + \phi_{IC} + \phi_{ISC} + \phi_P = 1$ 

$$\phi_f + \phi_{IC} + \phi_{ISC} + \phi_P + \phi_R = 1$$

Absorption: 
$$S + h\nu_i \to S^*$$
,  $v_{abs} = I_{abs}$   
Fluorescence:  $S^* \to S + h\nu_f$ ,  $v_f = k_f[S^*]$   
Internal conversion:  $S^* \to S$ ,  $v_{IC} = k_{IC}[S^*]$   
Intersystem crossing:  $S^* \to T^*$ ,  $v_{ISC} = k_{ISC}[S^*]$ 

After light is turned off,  $[S^*] = [S^*]_0 e^{-t/\tau_0}$ ,  $\tau_0 = rac{1}{k_f + k_{ISC} + k_{IC}}$ 



# In the presence of steady radiation,

$$\frac{d[S^*]}{dt} = I_{abs} - k_f[S^*] - k_{ISC}[S^*] - k_{IC}[S^*] = 0$$

$$\implies I_{abs} = (k_f + k_{ISC} + k_{IC})[S^*]$$

$$\phi_f = \frac{k_f[S^*]}{(k_f + k_{ISC} + k_{IC})[S^*]} = \frac{k_f}{k_f + k_{ISC} + k_{IC}}$$

$$\rightarrow$$
  $\tau_0 = \frac{\phi_f}{k_f}$ 

In the presence of quenching and steady radiation,

$$S^* + Q \to S + Q, \quad v_Q = k_Q[Q][S^*]$$
$$I_{abs} = (k_f + k_{IC} + k_{ISC} + k_Q[Q])[S^*]$$

$$\phi_f = \frac{k_f[S^*]}{I_{abs}} = \frac{k_f}{k_f + k_{ISC} + k_{IC} + k_Q[Q]}$$



#### **Stern-Volmer equation**

$$\frac{\phi_{f,0}}{\phi_f} = 1 + \left(\frac{k_Q}{k_f + k_{ISC} + k_{IC}}\right)[Q] = 1 + \tau_0 k_Q[Q]$$
$$\implies \quad \frac{1}{\tau} = \frac{1}{\tau_0} + k_Q[Q]$$



 $\frac{\text{Resonance energy transfer}}{S^* + Q \to S + Q^*}, \quad k_F = \frac{1}{\tau_0} \left(\frac{R_0}{R}\right)^6$  $E_T = 1 - \frac{\phi_f}{\phi_{f,0}} = 1 - \frac{\tau}{\tau_0} = 1 - \frac{R^6}{R_0^6 + R^6} = \frac{R_0^6}{R_0^6 + R^6}$