

## Reaction Mechanism Examples

① The Chlorination of an organic molecule R:



Mechanism:

- 1)  $Cl_2 \xrightarrow{k_1} 2Cl$
- 2)  $Cl + R \xrightarrow{k_2} RCl$
- 3)  $RCl + Cl_2 \xrightarrow{k_3} P + Cl$
- 4)  $Cl + Cl \xrightarrow{k_4} Cl_2$

• Goal: what is  $k$  in terms of  $k$ 's for mechanism steps?  
What are  $x$  +  $y$ ?

• Assume Steady State Approx for intermediates.

① Write rates for each step:

$$v_1 = k_1 [Cl_2]$$

$$v_2 = k_2 [Cl][R]$$

$$v_3 = k_3 [RCl][Cl_2]$$

$$v_4 = k_4 [Cl]^2$$

$$\textcircled{2} \quad \frac{d[Cl]}{dt} = 2k_1 [Cl_2] - k_2 [Cl][R] + k_3 [RCl][Cl_2] - 2k_4 [Cl]^2 = 0$$

$$\frac{d[RCl]}{dt} = k_2 [Cl][R] - k_3 [RCl][Cl_2] = 0$$

$$\frac{d[P]}{dt} = k_3 [RCl][Cl_2]$$

→ tells me:  $k_2 [Cl][R] = k_3 [RCl][Cl_2]$

so,  $\frac{d[Cl]}{dt} = 0 = 2k_1 [Cl_2] - 2k_4 [Cl]^2$

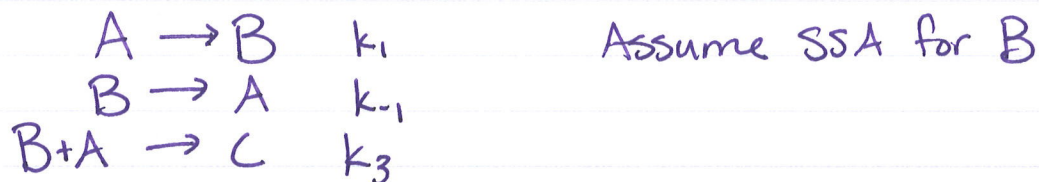
so,  $k_1 [Cl_2] = k_4 [Cl]^2$

$$[Cl] = \left(\frac{k_1}{k_4}\right)^{1/2} [Cl_2]^{1/2}$$

$$\frac{d[P]}{dt} = k_3 [RCI] [C_2] = k_2 \underbrace{[CI]}_{\text{sub!}} [R]$$

$$\frac{d[P]}{dt} = k_2 \left( \frac{k_1}{k_4} \right)^{1/2} [CI]^{1/2} [R]$$

- ② Write the rate law for the rxn  $2A \rightarrow C$  given the mechanism:



What are we looking for?

Rate Law can be written as:  $-\frac{1}{2} \frac{d[A]}{dt}$  or  $\frac{d[C]}{dt}$   
we will choose the easiest later.

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B] - k_3[A][B]$$

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_3[A][B] = 0$$

$$\frac{d[C]}{dt} = k_3[A][B]$$

$$\rightarrow k_1[A] = (k_{-1} + k_3[A])[B]$$

$$\frac{k_1[A]}{k_{-1} + k_3[A]} = [B]$$

$$\frac{d[C]}{dt} = \frac{k_1 \cdot k_3 [A]^2}{k_{-1} + k_3[A]}$$

Ugly! But, this is valid as it is only in terms of  $[A]$  +  $k$ 's

2b) When will the rate be pseudo-second order?

$$\text{When does } \frac{k_1 k_3 [A]^2}{k_{-1} + k_3 [A]} \approx k' [A]^2 ?$$

When  $k_{-1} \gg k_3 [A]$ , the rate is

$$\frac{d[C]}{dt} = \frac{k_1 k_3}{k_{-1}} [A]^2$$

So when  $[A]$  <sup>(or  $k_3$ )</sup> is very small or  $k_{-1}$  is large the rxn is 2nd order. Note that in both cases,  $[B]$  will essentially be  $\emptyset$

2c) When will the rate be pseudo-first order?

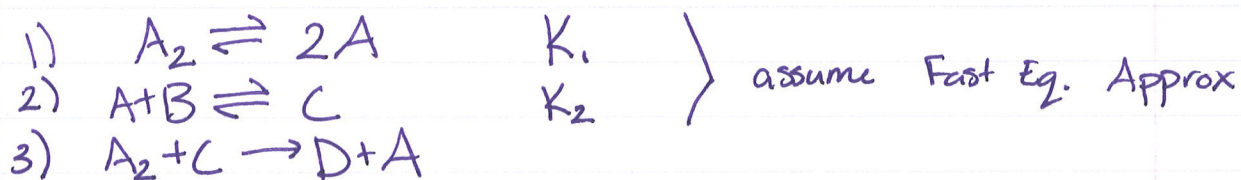
You will see 1st-order kinetics if  $k_3 [A] \gg k_{-1}$

$$\frac{d[C]}{dt} = k_1 [A]$$

So, you would either need  $[A]$  <sup>or  $k_3$</sup>  to be large, or  $k_{-1}$  to be very small.



③ The Rxn  $A_2 + B \rightarrow D$  proceeds by the mechanism:



Find the rate law for this rxn.

Fast Equilibrium means:

$$\bullet k_1[A_2] = k_{-1}[A]^2 \quad K_1 = \frac{[A]^2}{[A_2]}$$

$$\text{so } K_1 = \frac{k_1}{k_{-1}} = \frac{[A]^2}{[A_2]}$$

$$\bullet k_2[A][B] = k_{-2}[C] \quad K_2 = \frac{[C]}{[A][B]}$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{[C]}{[A][B]}$$

Rate for overall rxn:

$$\frac{d[D]}{dt} = k_3[A_2][C]$$

↑ must write in terms of  $A_2 + B$

$$[C] = K_2[A][B] \quad [A] = \sqrt{K_1[A_2]}$$

$$[C] = K_2 \sqrt{K_1} [A_2]^{1/2} [B]$$

$$\frac{d[D]}{dt} = k_3[A_2] K_2 \sqrt{K_1} [A_2]^{1/2} [B]$$

$$\frac{d[D]}{dt} = k_3 K_2 \sqrt{K_1} [A_2]^{3/2} [B] = \frac{k_3 k_2}{k_{-2}} \left( \frac{k_1}{k_{-1}} \right)^{1/2} [A_2]^{3/2} [B]$$