

1. Consider the following mechanism.



(a) Write the overall reaction and list all catalysts and intermediates



(b) Using the steady-state approximation, find the rate of formation of D.

$$\frac{d[B]}{dt} = k_1[A] - k_2[A][B] = 0 \implies [B] = \frac{k_1}{k_2}$$
$$\frac{d[D]}{dt} = k_2[A][B] = k_1[A]$$

(c) Using the steady-state approximation, find the rate of formation of E.

$$\frac{d[C]}{dt} = k_1[A] - k_3[C] = 0 \implies [C] = \frac{k_1[A]}{k_3}$$
$$\frac{d[E]}{dt} = k_3[C] = k_1[A]$$

(d) What is the rate of this reaction and what is its order?

$v(t) = k_1[A]$, first order

2. Consider the following mechanism for the formation of NO_3 from NO and O_2 .



Write the rate law, ignoring higher-order intermediate terms.

$$v(t) = k_3[\text{O}^\bullet][\text{NO}_2]$$

Steady-state for intermediate:

$$\begin{aligned} \frac{d[\text{O}^\bullet]}{dt} &= k_1[\text{O}_2] - \cancel{k_{-1}[\text{O}^\bullet]^2} - k_2[\text{O}^\bullet][\text{NO}] - k_3[\text{O}^\bullet][\text{NO}_2] = 0 \\ \frac{d[\text{NO}_2]}{dt} &= k_2[\text{O}^\bullet][\text{NO}] - k_3[\text{O}^\bullet][\text{NO}_2] = 0 \end{aligned}$$

Eliminate one variable by subtracting system of equations:

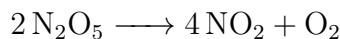
$$\begin{aligned} 0 &= k_1[\text{O}_2] - 2k_2[\text{O}^\bullet][\text{NO}] \implies [\text{O}^\bullet] = \frac{k_1}{2k_2} \cdot \frac{[\text{O}_2]}{[\text{NO}]} \\ 0 &= k_2[\text{O}^\bullet][\text{NO}] - k_3[\text{O}^\bullet][\text{NO}_2] \implies [\text{NO}_2] = \frac{k_2}{k_3}[\text{NO}] \end{aligned}$$

Substitute into rate law:

$$v(t) = k_3 \left(\frac{k_1}{2k_2} \cdot \frac{[\text{O}_2]}{[\text{NO}]} \right) \cdot \left(\frac{k_2}{k_3}[\text{NO}] \right)$$

$$v(t) = \frac{k_1}{2}[\text{O}_2]$$

3. Consider the following mechanism.



Write the rate law for this reaction and state the conditions that it would be overall first order.

Rate of formation of O_2 is easier since only present in one step

$$v(t) = k_2[\text{NO}_3]$$

Apply steady-state to intermediates NO_3 and NO :

$$\frac{d[\text{NO}_3]}{dt} = 2k_1[\text{N}_2\text{O}_5] - 2k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_3] - k_3[\text{NO}_3][\text{NO}] = 0$$

$$\frac{d[\text{NO}]}{dt} = k_2[\text{NO}_3] - k_3[\text{NO}_3][\text{NO}] = 0$$

Eliminate one variable by subtracting system of equations:

$$0 = 2k_1[\text{N}_2\text{O}_5] - 2k_{-1}[\text{NO}_2][\text{NO}_3] - 2k_2[\text{NO}_3]$$

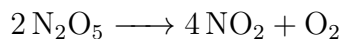
$$k_1[\text{N}_2\text{O}_5] = [\text{NO}_3] (k_{-1}[\text{NO}_2] + k_2)$$

$$[\text{NO}_3] = \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2}$$

$$v(t) = k_3 \cdot \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2}$$

Would be first order if $k_2 \gg k_{-1}[\text{NO}_2]$

4. Consider the following mechanism.



Write the rate law for this reaction and show that it is first order.

Rate of formation of O_2 is easier since only present in one step

$$v(t) = k_2[\text{NO}_3][\text{NO}_2]$$

Apply steady-state to intermediates NO_3 and NO :

$$\frac{d[\text{NO}_3]}{dt} = 2k_1[\text{N}_2\text{O}_5] - 2k_{-1}[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_3][\text{NO}_2] - k_3[\text{NO}_3][\text{NO}] = 0$$

$$\frac{d[\text{NO}]}{dt} = k_2[\text{NO}_3][\text{NO}_2] - k_3[\text{NO}_3][\text{NO}] = 0$$

Eliminate one variable by subtracting system of equations:

$$0 = 2k_1[\text{N}_2\text{O}_5] - 2k_{-1}[\text{NO}_2][\text{NO}_3] - 2k_2[\text{NO}_3][\text{NO}_2]$$

$$k_1[\text{N}_2\text{O}_5] = [\text{NO}_3] (k_{-1}[\text{NO}_2] + k_2[\text{NO}_2])$$

$$[\text{NO}_3] = \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}_2]}$$

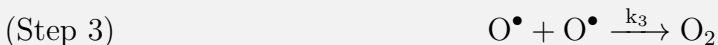
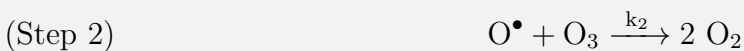
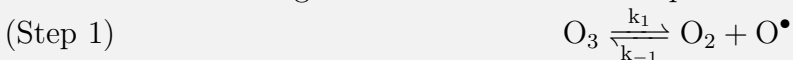
$$v(t) = k_3 \cdot \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1}[\text{NO}_2] + k_2[\text{NO}_2]} \cdot [\text{NO}_2]$$

$$= k_3 \cdot \frac{k_1[\text{N}_2\text{O}_5]}{k_{-1} + k_2}$$

Would be first order if $k_2 \gg k_{-1}[\text{NO}_2]$

Homework Problem 37

1. Consider the following mechanism for the decomposition of ozone.



Write the rate law, ignoring higher-order intermediate terms. You do not need the most simplified form, stop after eliminating the intermediate.

$$\frac{d[\text{O}^\bullet]}{dt} = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}^\bullet] - k_2[\text{O}^\bullet][\text{O}_3] - k_3[\text{O}^\bullet]^2 = 0$$

Drop the quadratic term and factor $[\text{O}^\bullet]$:

$$\begin{aligned} k_1[\text{O}_3] &= [\text{O}^\bullet](k_{-1}[\text{O}_2] + k_2[\text{O}_3]) \\ [\text{O}^\bullet] &= \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \end{aligned}$$

Rate based on formation of O_2 :

$$v(t) = \frac{d[\text{O}_2]}{dt} = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}^\bullet] + k_2[\text{O}^\bullet][\text{O}_3] + k_3[\text{O}^\bullet]^2$$

Substitute $[\text{O}^\bullet]$, ignoring the second order term:

$$v(t) = k_1[\text{O}_3] - k_{-1}[\text{O}_2] \cdot \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} + k_2[\text{O}_3] \cdot \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}$$

If you chose to simplify further

$$\begin{aligned} &= k_1[\text{O}_3] \left[1 + \frac{-k_{-1}[\text{O}_2] + k_2[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \right] \\ &= k_1[\text{O}_3] \cdot \frac{k_{-1}[\text{O}_2] + k_2[\text{O}_3] - k_{-1}[\text{O}_2] + k_2[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \\ &= k_1[\text{O}_3] \cdot \frac{3k_2[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \end{aligned}$$

$$v(t) = \frac{2k_1k_2[\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]}$$