1. Consider the following mechanism.

(Step 1) $\mathrm{A} \xrightarrow{\mathrm{k_1}} \mathrm{B} + \mathrm{C}$

(Step 2) $\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{k_2}} \mathrm{D}$

(Step 3) $\mathrm{C} \xrightarrow{\mathrm{k_3}} \mathrm{E}$

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

$2\,\mathrm{A} \longrightarrow \mathrm{D} + \mathrm{E}$, no catalysts, B, C are 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.

(Step 1) $$O_2 \xrightleftharpoons[k_{-1}]{k_1} 2\,O^\bullet$$

(Step 2) $$O^\bullet + NO \xrightarrow{k_2} NO_2$$

(Step 3) $$O^\bullet + NO_2 \xrightarrow{k_3} NO_3$$

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

$$v(t) = k_3[O^\bullet][NO_2]$$

Steady-state for intermediate:

$$\frac{d[O^\bullet]}{dt} = k_1[O_2] - \cancel{k_{-1}[O^\bullet]^2} - k_2[O^\bullet][NO] - k_3[O^\bullet][NO_2] = 0$$
$$\frac{d[NO_2]}{dt} = k_2[O^\bullet][NO] - k_3[O^\bullet][NO_2] = 0$$

Eliminate one variable by subtracting system of equations:

$$0 = k_1[O_2] - 2k_2[O^\bullet][NO] \implies [O^\bullet] = \frac{k_1}{2k_2} \cdot \frac{[O_2]}{[NO]}$$
$$0 = k_2[O^\bullet][NO] - k_3[O^\bullet][NO_2] \implies [NO_2] = \frac{k_2}{k_3}[NO]$$

Substitute into rate law:

$$v(t) = k_3\left(\frac{k_1}{2k_2} \cdot \frac{[O_2]}{[NO]}\right) \cdot \left(\frac{k_2}{k_3}[NO]\right)$$
$$\boxed{v(t) = \frac{k_1}{2}[O_2]}$$

3. Consider the following mechanism.

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

(Step 1) $$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

(Step 2) $$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

(Step 3) $$NO_3 \xrightarrow{k_2} NO + O_2$$

(Step 4) $$NO_3 + NO \xrightarrow{k_3} 2\,NO_2$$

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

$$v(t) = k_2[NO_3]$$

Apply steady-state to intermediates NO_3 and NO:

$$\frac{d[NO_3]}{dt} = 2k_1[N_2O_5] - 2k_{-1}[NO_2][NO_3] - k_2[NO_3] - k_3[NO_3][NO] = 0$$
$$\frac{d[NO]}{dt} = k_2[NO_3] - k_3[NO_3][NO] = 0$$

Eliminate one variable by subtracting system of equations:

$$0 = 2k_1[N_2O_5] - 2k_{-1}[NO_2][NO_3] - 2k_2[NO_3]$$
$$k_1[N_2O_5] = [NO_3]\left(k_{-1}[NO_2] + k_2\right)$$
$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2}$$
$$v(t) = k_3 \cdot \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2}$$

Would be first order if $k_2 \gg k_{-1}[NO_2]$

4. Consider the following mechanism.

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

(Step 1) $$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

(Step 2) $$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

(Step 3) $$NO_3 + NO_2 \xrightarrow{k_2} NO + NO_2 + O_2$$

(Step 4) $$NO_3 + NO \xrightarrow{k_3} 2\,NO_2$$

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

$$v(t) = k_2[NO_3][NO_2]$$

Apply steady-state to intermediates NO_3 and NO:

$$\frac{d[NO_3]}{dt} = 2k_1[N_2O_5] - 2k_{-1}[NO_2][NO_3] - k_2[NO_3][NO_2] - k_3[NO_3][NO] = 0$$
$$\frac{d[NO]}{dt} = k_2[NO_3][NO_2] - k_3[NO_3][NO] = 0$$

Eliminate one variable by subtracting system of equations:

$$\begin{aligned}
0 &= 2k_1[N_2O_5] - 2k_{-1}[NO_2][NO_3] - 2k_2[NO_3][NO_2] \\
k_1[N_2O_5] &= [NO_3]\left(k_{-1}[NO_2] + k_2[NO_2]\right) \\
[NO_3] &= \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2]} \\
v(t) &= k_3 \cdot \frac{k_1[N_2O_5]}{k_{-1}[NO_2] + k_2[NO_2]} \cdot [NO_2] \\
&= k_3 \cdot \frac{k_1[N_2O_5]}{k_{-1} + k_2}
\end{aligned}$$

Would be first order if $k_2 \gg k_{-1}[NO_2]$

Homework Problem 37

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

(Step 1) $$O_3 \xrightleftharpoons[k_{-1}]{k_1} O_2 + O^\bullet$$

(Step 2) $$O^\bullet + O_3 \xrightarrow{k_2} 2\ O_2$$

(Step 3) $$O^\bullet + O^\bullet \xrightarrow{k_3} O_2$$

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

$$\frac{d[O^\bullet]}{dt} = k_1[O_3] - k_{-1}[O_2][O^\bullet] - k_2[O^\bullet][O_3] - k_3[O^\bullet]^2 = 0$$

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

$$k_1[O_3] = [O^\bullet]\Big(k_{-1}[O_2] + k_2[O_3]\Big)$$

$$[O^\bullet] = \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$

Rate based on formation of O_2:

$$v(t) = \frac{d[O_2]}{dt} = k_1[O_3] - k_{-1}[O_2][O^\bullet] + k_2[O^\bullet][O_3] + k_3[O^\bullet]^2$$

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

$$\boxed{v(t) = k_1[O_3] - k_{-1}[O_2] \cdot \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} + k_2[O_3] \cdot \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]}}$$

If you chose to simplify further

$$= k_1[O_3]\left[1 + \frac{-k_{-1}[O_2] + k_2[O_3]}{k_{-1}[O_2] + k_2[O_3]}\right]$$

$$= k_1[O_3] \cdot \frac{k_{-1}[O_2] + k_2[O_3] - k_{-1}[O_2] + k_2[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$

$$= k_1[O_3] \cdot \frac{3k_2[O_3]}{k_{-1}[O_2] + k_2[O_3]}$$

$$\boxed{v(t) = \frac{2k_1k_2\,[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}}$$