How do we distinguish Single step reactions from multi
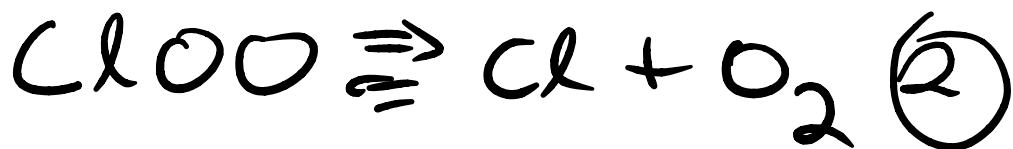
$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

$$OClO \rightleftharpoons Cl + O_2$$

actually

$$OClO \rightleftharpoons ClOO \quad \text{①}$$
$$ClOO \rightleftharpoons Cl + O_2 \quad \text{②}$$

$$v_f^1 \gg v_b^1 \qquad v_f^2 \gg v_b^2$$
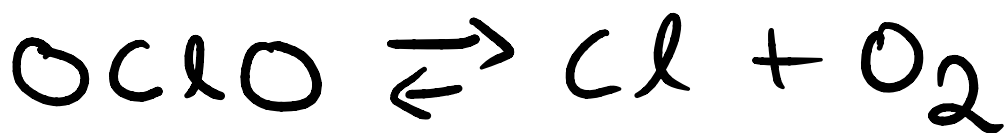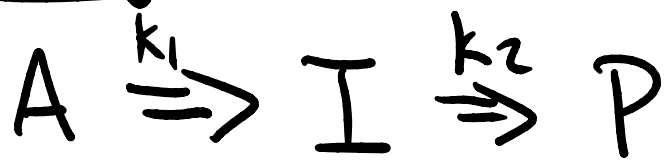
$$\underset{A}{OClO} \xrightarrow{k_1} \underset{I}{ClOO} \xrightarrow{k_2} \underset{P}{Cl + O_2}$$

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

$$\frac{d[I]}{dt} = k_1[A] - k_2[I]$$

$$\frac{d[P]}{dt} = k_2[I]$$

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

$$\frac{d[I]}{dt} = k_1[A] - k_2[I]$$

$$d[P]/dt = k_2[I]$$

[prob 29-5]

$$[A](t) = [A]_0 e^{-k_1 t}$$

$$[I](t) = \frac{k_1[A]_0}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$[P](t) = [A]_0 - [I] - [A]$$

Start with $[A]_0$

$$[P](t) = [A]_0\left(1 + \frac{1}{k_1-k_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right)$$

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P \qquad [A](t) = [A]_0 e^{-k_1 t}$$

Question is : can we tell I exists

$$k_2 \gg k_1$$

← big k

small k

$$[P](t) \approx [A]_0\left(1 - \frac{1}{k_2}\left(k_2 e^{-k_1 t}\right)\right) \text{ looks like}$$

$$\approx [A]_0\left(1 - e^{-k_1 t}\right) \leftarrow \text{single step reaction}$$

$$[P](t) = [A]_0 \left(1 + \frac{1}{k_1 - k_2} \left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t} \right) \right)$$

$$A \overset{k_1}{\Rightarrow} I \overset{k_2}{\Rightarrow} P \qquad [A](t) = [A]_0 e^{-k_1 t}$$
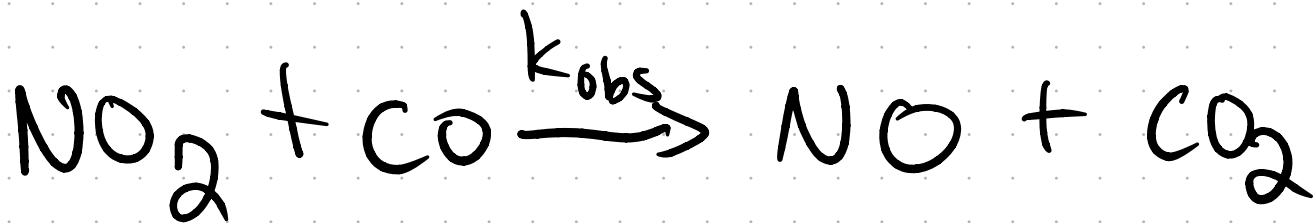
$$k_1 \gg k_2 \qquad [P](t) = [A]_0 \left(1 - \frac{1}{k_1} \cdot k_1 e^{-k_2 t} \right)$$

$$= [A]_0 \left(1 - e^{-k_2 t} \right)$$

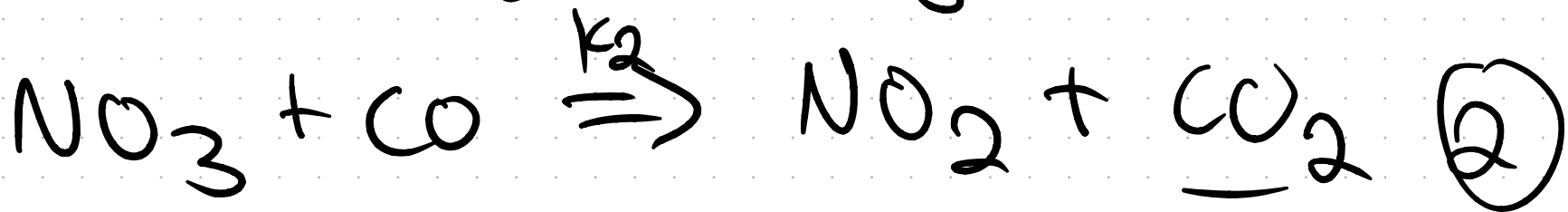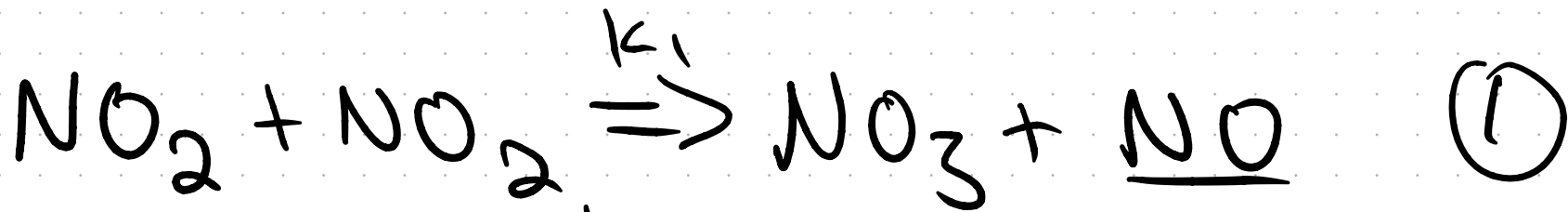Compare $-\dfrac{d[A]}{dt}$ & $\dfrac{d[P]}{dt}$ different rates

Rate determining steps

If one step very slow - set rate law
that is observed

$$NO_2 + CO \xrightarrow{k_{obs}} NO + CO_2$$

expect is $v = k[NO_2][CO]$ ✗ not correct

$$NO_2 + NO_2 \xRightarrow{k_1} NO_3 + \underline{NO} \quad ①$$

$$NO_3 + CO \xRightarrow{k_2} NO_2 + \underline{CO}_2 \quad ②$$

$$v_1 << v_2 \qquad v = k_1[NO_2]^2$$

$A \Rightarrow I \Rightarrow P$

$k_1 \qquad k_2$

Steady state approximation

If $k_1 >> k_2$

$k_2 >> k_1$

Steady state

$$A \Rightarrow I \Rightarrow P$$

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

$$\frac{d[I]}{dt} = k_1[A] - k_2[I] = 0$$

SS, solve for I

$\downarrow$
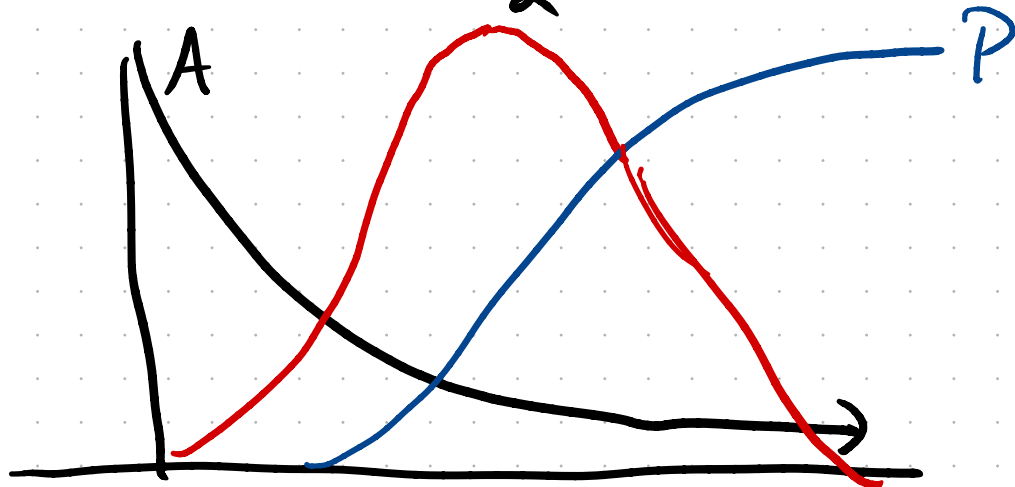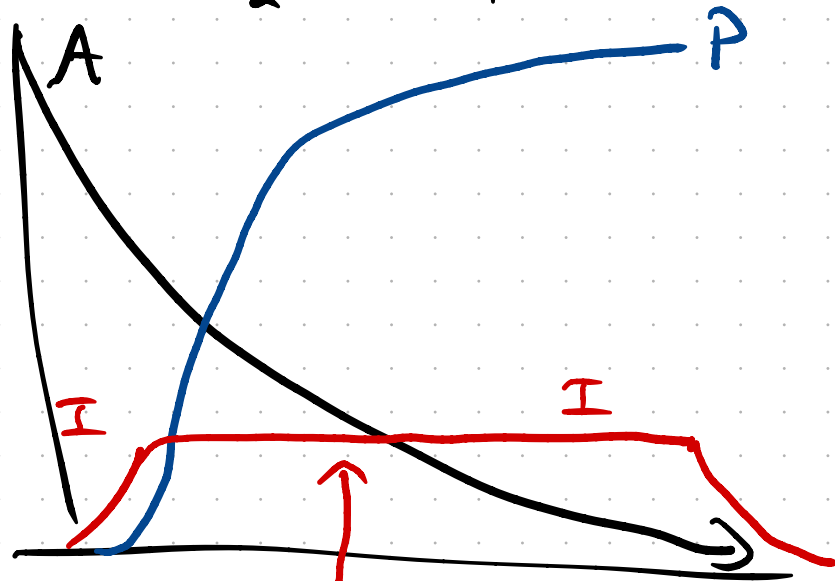
$$\frac{d[P]}{dt} = k_2[I]$$

$$[I]_{ss} = \frac{k_1}{k_2}[A]$$

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

$$\frac{d[I]}{dt} = k_1[A] - k_2\left(\frac{k_1}{k_2}(A)\right) = 0$$
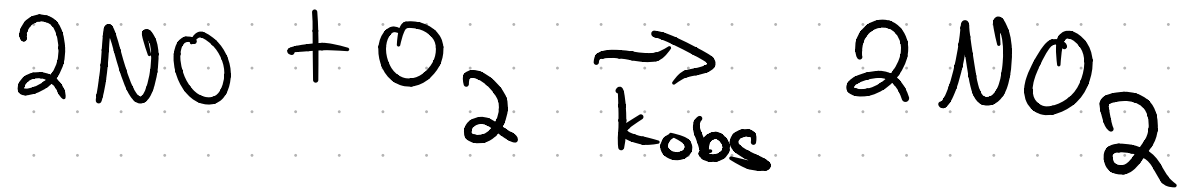
$$\frac{d[P]}{dt} = k_2 I$$

$$[A](t) = [A]_0 e^{-k_1 t}$$

$$[I]_{ss}(t) = \frac{k_1}{k_2}[A] = \frac{k_1}{k_2}[A]_0 e^{-k_1 t}$$

$$\frac{d[P]}{dt} = k_1[A]_0 e^{-k_1 t} \Rightarrow [P](t) = [A]_0 \left(1 - e^{-k_1 t}\right)$$

$$\frac{d[I]_{ss}}{dt} = -k_1^2 [A]_0 e^{-k_1 t} \frac{1}{k_2}$$

$$\approx 0 \quad \frac{k_1^2}{k_2}[A]_0 \approx 0$$

Rate Law $\rightarrow$ Mechanism

$$2NO + O_2 \xrightarrow{k_{obs}} 2NO_2$$

$$v(t) = k_{obs} [NO]^2 [O_2] \xleftarrow{\text{not a single step}}$$

Mechanism 1

$$NO + O_2 \underset{k_b^1}{\overset{k_f^1}{\rightleftharpoons}} NO_3 \quad \text{fast} \quad ①$$

$$NO_3 + NO \underset{k_f^2}{\Longrightarrow} 2NO_2 \quad \begin{array}{c} \text{rate} \\ \text{determining} \end{array} ②$$

$$k_b^2 \approx 0$$
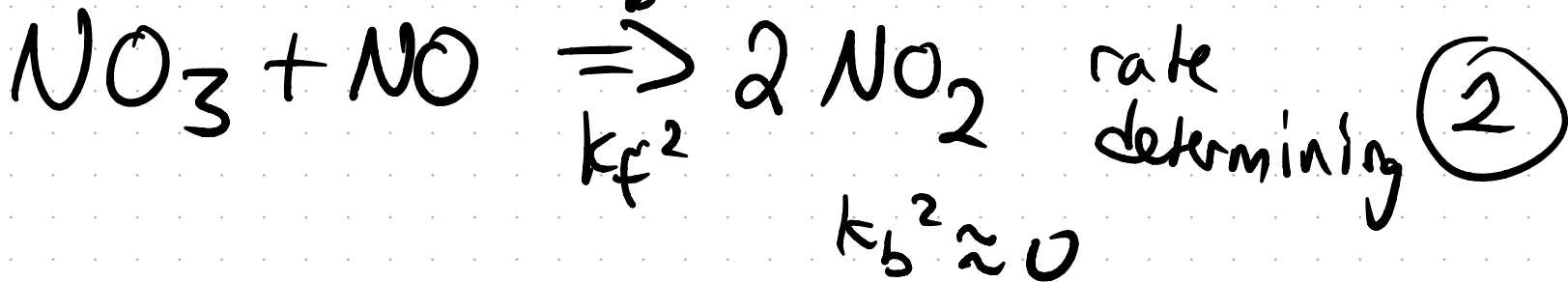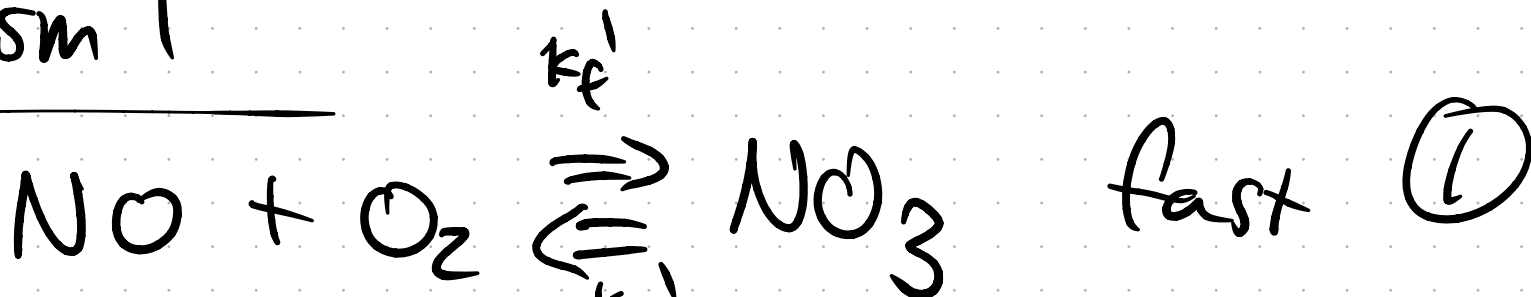
$$@ \, Eq \quad \frac{k_f^1}{k_b^1} = \frac{[NO_3]}{[NO][O_2]} \quad \text{detailed balance}$$

Consistent
w/ overall rate law

$$NO + O_2 \underset{k_b^1}{\overset{k_f^1}{\rightleftharpoons}} NO_3 \quad \text{fast} \quad ①$$

$$NO_3 + NO \underset{k_f^2}{\Longrightarrow} 2 NO_2 \quad \begin{array}{l}\text{rate}\\ \text{determining}\end{array} ②$$

$$k_b^2 \approx 0$$
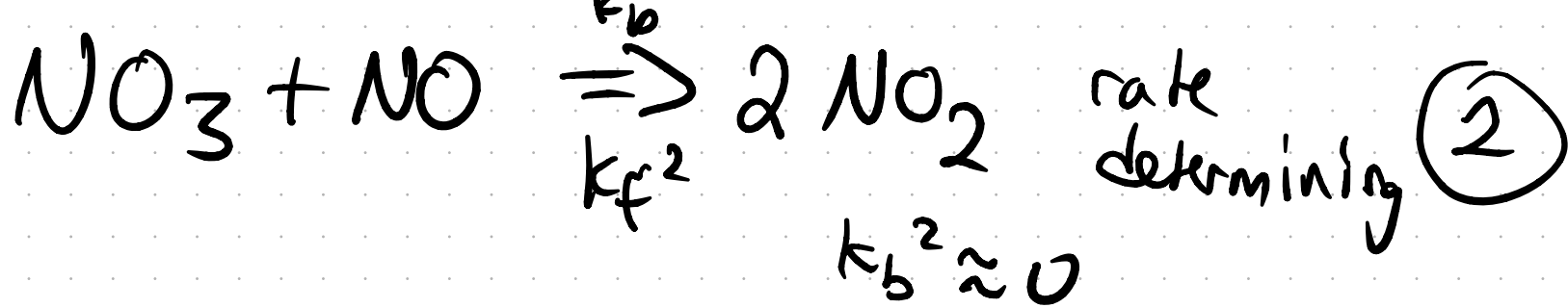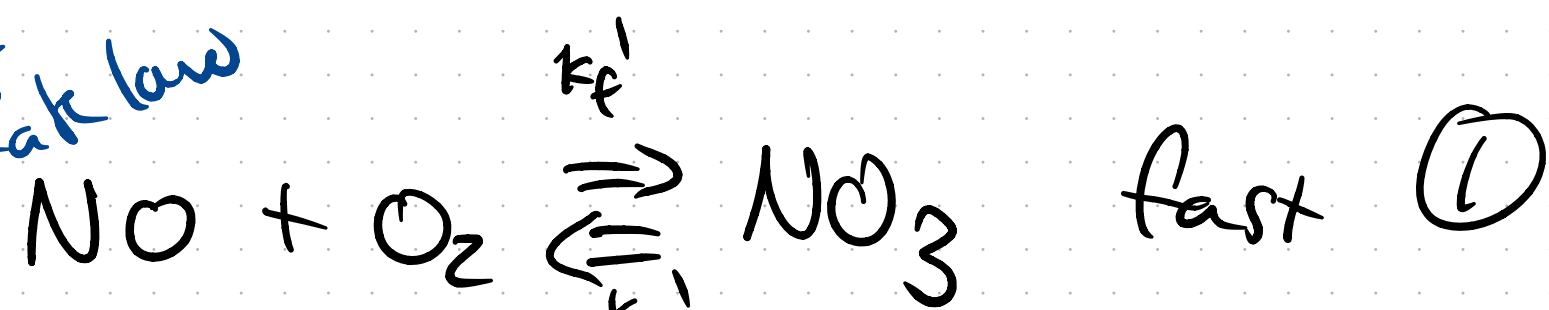
@ $Eq \quad \dfrac{k_f^1}{k_b^1} = \dfrac{[NO_3]}{[NO][O_2]} \quad$ detailed balance

2nd is rate determining

$$v_{rate} = \dfrac{1}{2} \dfrac{d[NO_2]}{dt} = k_2 [NO_3][NO]$$

$$= \boxed{k_2 \dfrac{k_f^1}{k_b^1}} [NO]^2 [O_2]$$

$\sim k_{obs}$

Mechanism 1

$$NO + O_2 \underset{k_b^1}{\overset{k_f^1}{\rightleftharpoons}} NO_3 \quad \text{fast} \quad \textcircled{1}$$

$$NO_3 + NO \underset{k_f^2}{\Longrightarrow} 2 NO_2 \quad \begin{array}{l}\text{rate} \\ \text{determining}\end{array} \quad \textcircled{2}$$

$$k_b^2 \approx 0$$

Mechanism 2

$$NO + NO \underset{k_b^1}{\overset{k_f^1}{\rightleftharpoons}} N_2O_2 \quad \begin{array}{l}\text{steady} \\ \text{State}\end{array}$$

$$N_2O_2 + O_2 \underset{k_f^2}{\Longrightarrow} 2 NO_2$$

$$\text{rate} = \frac{1}{2}\frac{d[NO_2]}{dt} = k_f^2 [N_2O_2][O_2]$$

① $NO + NO \underset{k_b^1}{\overset{k_f^1}{\rightleftharpoons}} N_2O_2$ steady state

② $N_2O_2 + O_2 \underset{k_f^2}{\Rightarrow} 2NO_2$
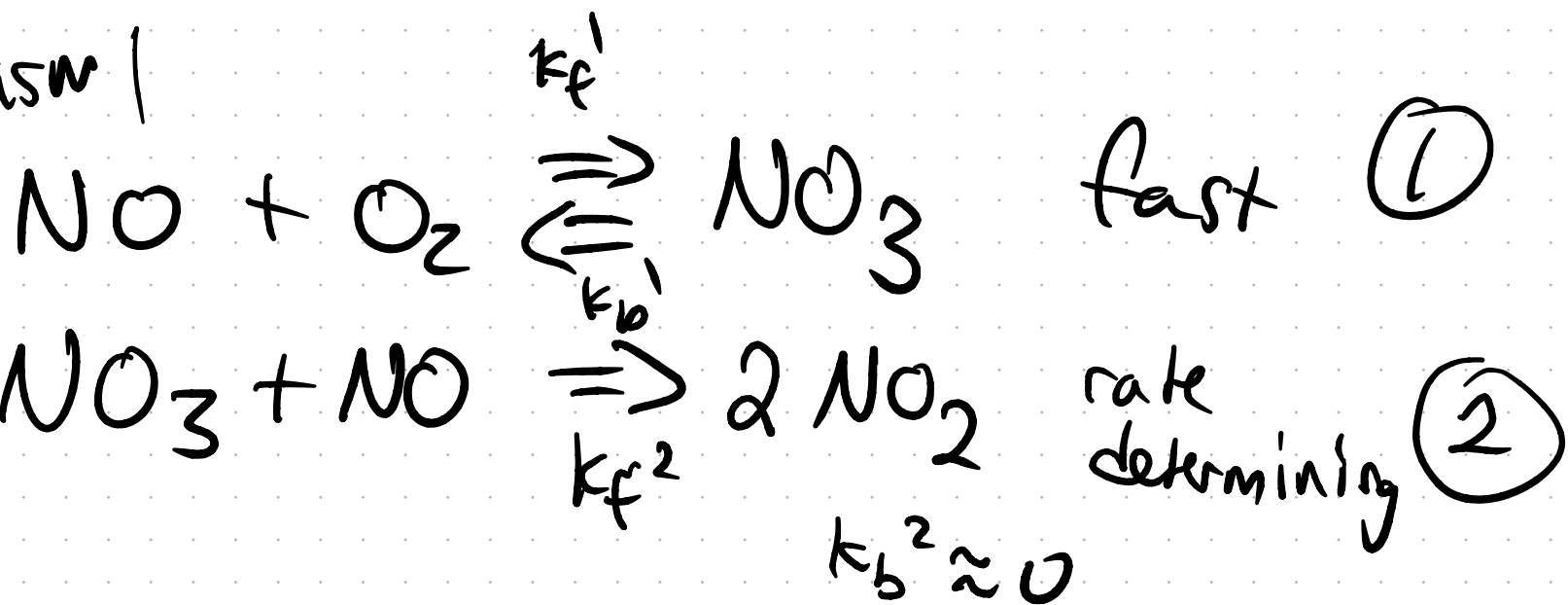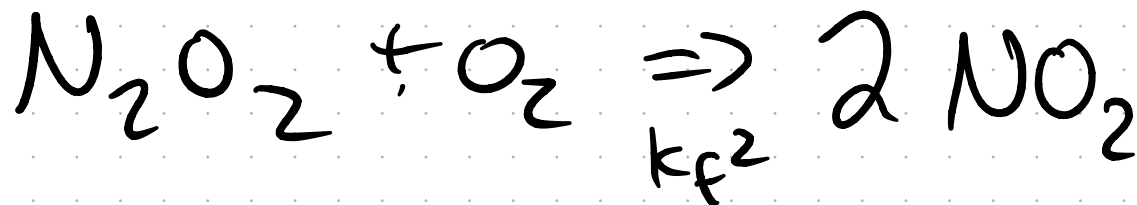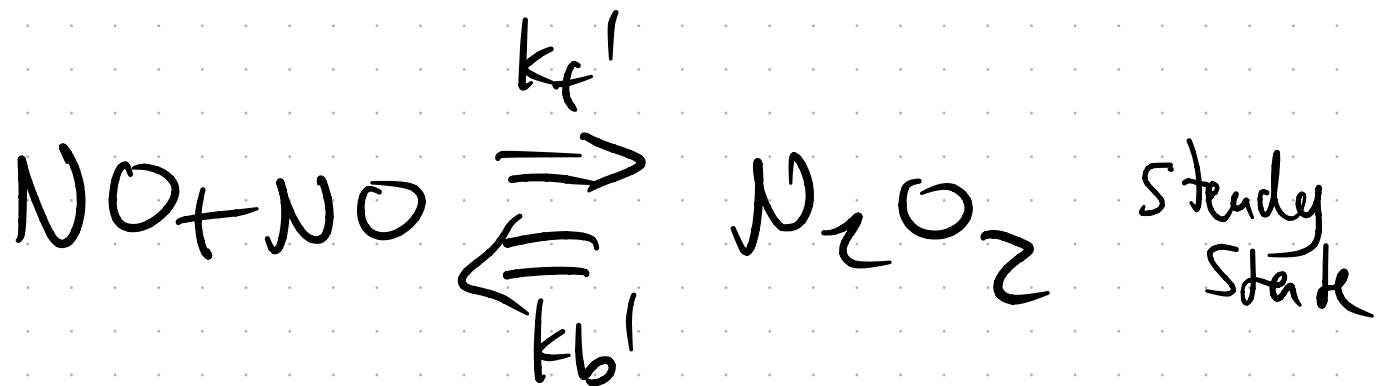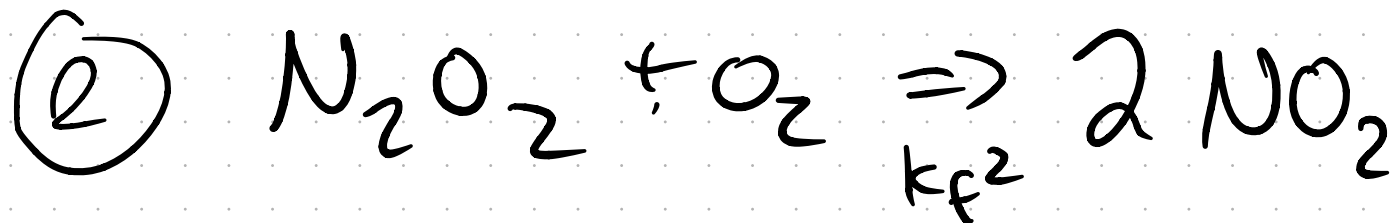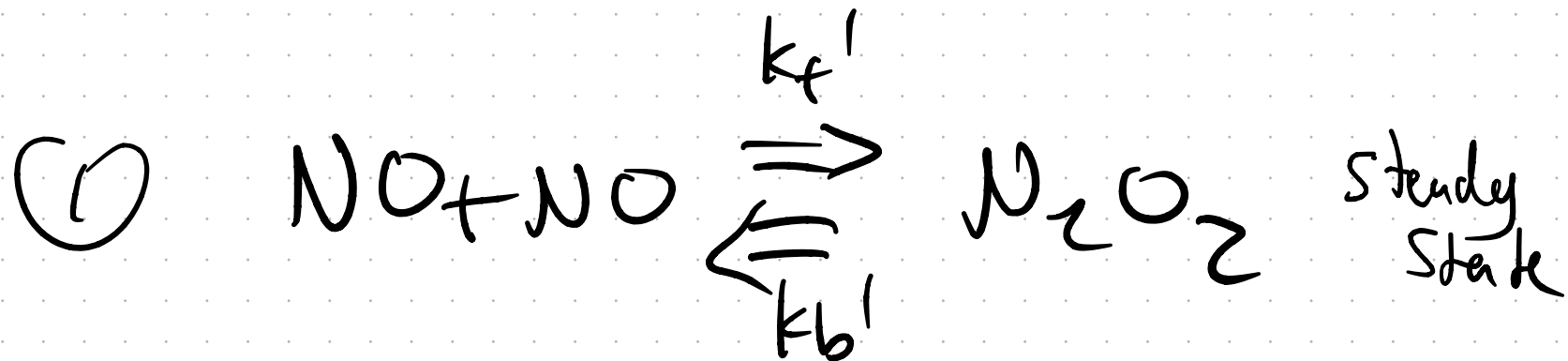
$\text{rate} = \frac{1}{2}\frac{d[NO_2]}{dt} = k_f^2 [N_2O_2][O_2]$

turns out $[N_2O_2]_{ss} = \dfrac{k_f^1 [NO]^2}{k_b^1 + k_f^2 [O_2]}$
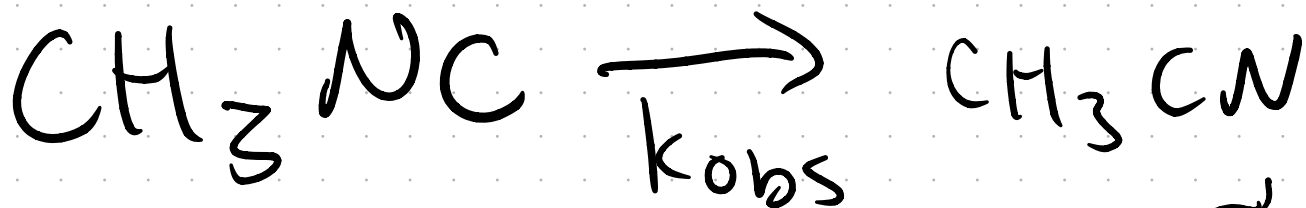
if $k_f^2 [O_2]$ small

$\approx k_f^1 [NO]^2 / k_b^1$

Mechanism 2

$$v = \frac{k_2 k_f'}{k_b'} [NO]^2 [O_2]$$

Also consistent

Experiments favor Mechanism 2

Unimolecular rxn example:

$$CH_3NC \xrightarrow{k_{obs}} CH_3CN$$

info1

$$E_a = 131 \text{ kJ/mol} \longrightarrow k_0 e^{-E_a/k_BT}$$

info 2

At high concentration

$$v = k[CH_3NC]$$

low concentration

$$v = k[CH_3NC]^2$$

Lindemann Mechanism

$$A + M \underset{k_b}{\overset{k_f}{\rightleftharpoons}} A^* + M$$

$$A^* \overset{k_f^2}{\Rightarrow} B$$
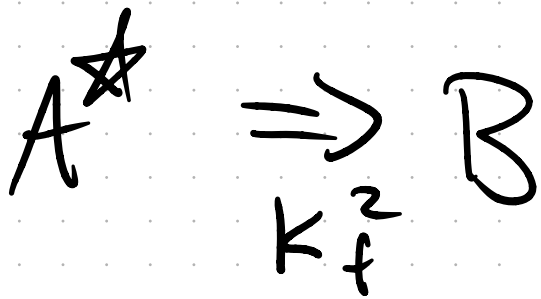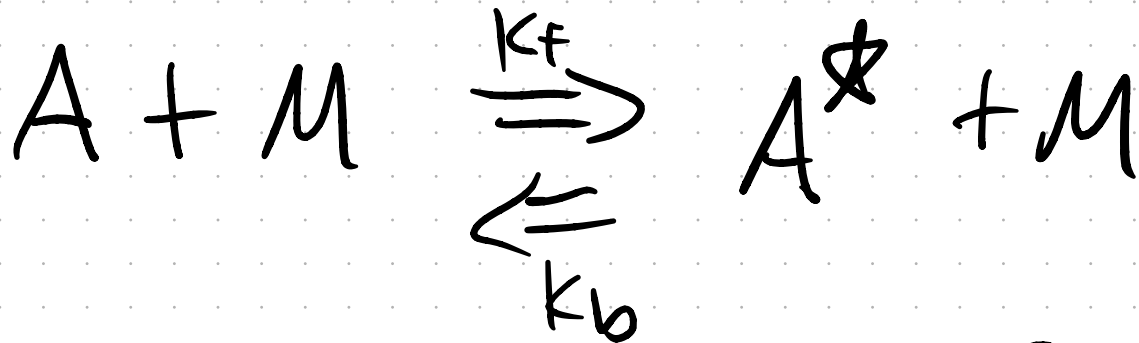
$[A^*]$ is small

$$\frac{d[A^*]}{dt} \approx 0$$

$$\frac{d[B]}{dt} = k_f^2 [A^*]$$

$$0 = \frac{d[A]^*}{dt} = k_f' [A][M] - k_b' [A^*][M] - k_f^2 [A^*]$$

$$0 = \frac{d[A]^*}{dt} = k_f' [A][M] - k_b' [A^*][M]$$
$$- k_f^2 [A^*]$$

$$[A^*] = \frac{k_f' [A][M]}{k_f^2 + k_b'[M]}$$

$$\frac{d[B]}{dt} = k_f^2 [A^*] = \frac{k_f' k_f^2}{k_f^2 + k_b'[M]} [A][M]$$

$$= k_{obs}[A] \qquad k_{obs} = \frac{k_f' k_f^2 [M]}{k_f^2 + k_b'[M]}$$

$$k_{obs} = \frac{k_f^1 k_f^2 [M]}{k_f^2 + k_b^1 [M]}$$

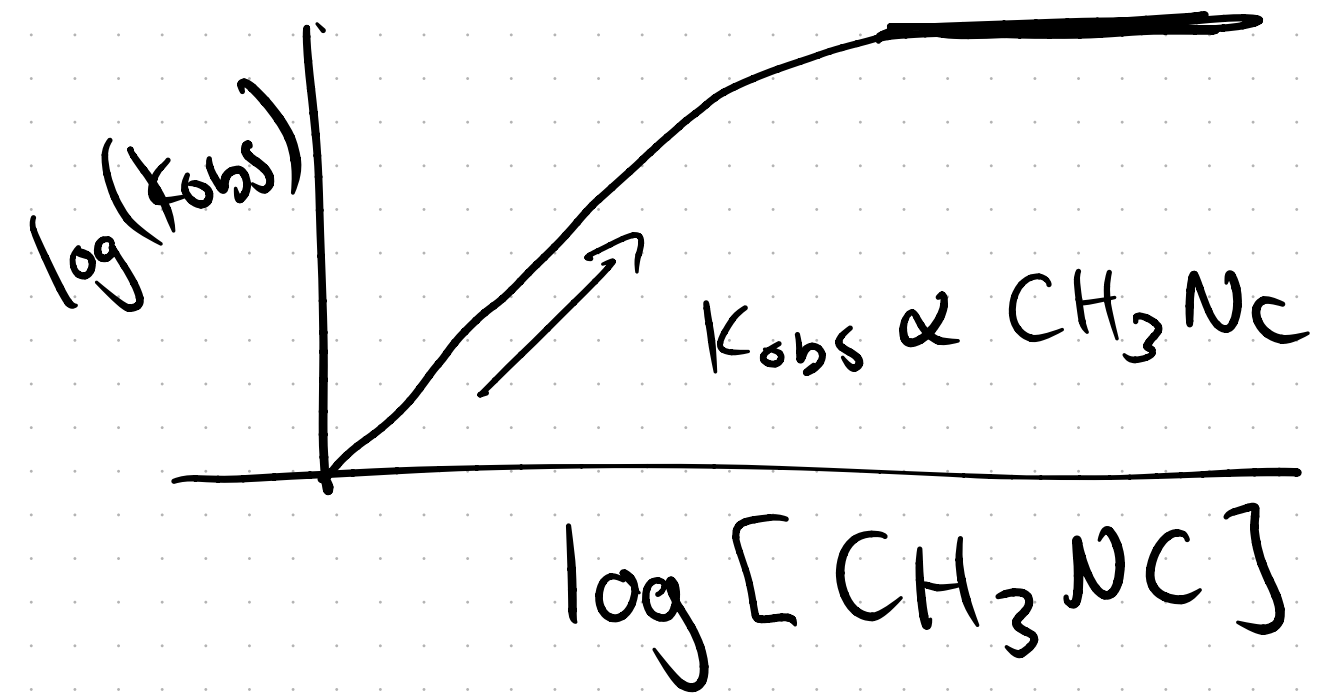high $[M]$, $k_{obs} = \frac{k_f^1 k_f^2 [M]}{k_b^1 [M]} = \frac{k_f^1 k_f^2}{k_b^1}$

no $\overrightarrow{[M]}$ dep

low $[M]$

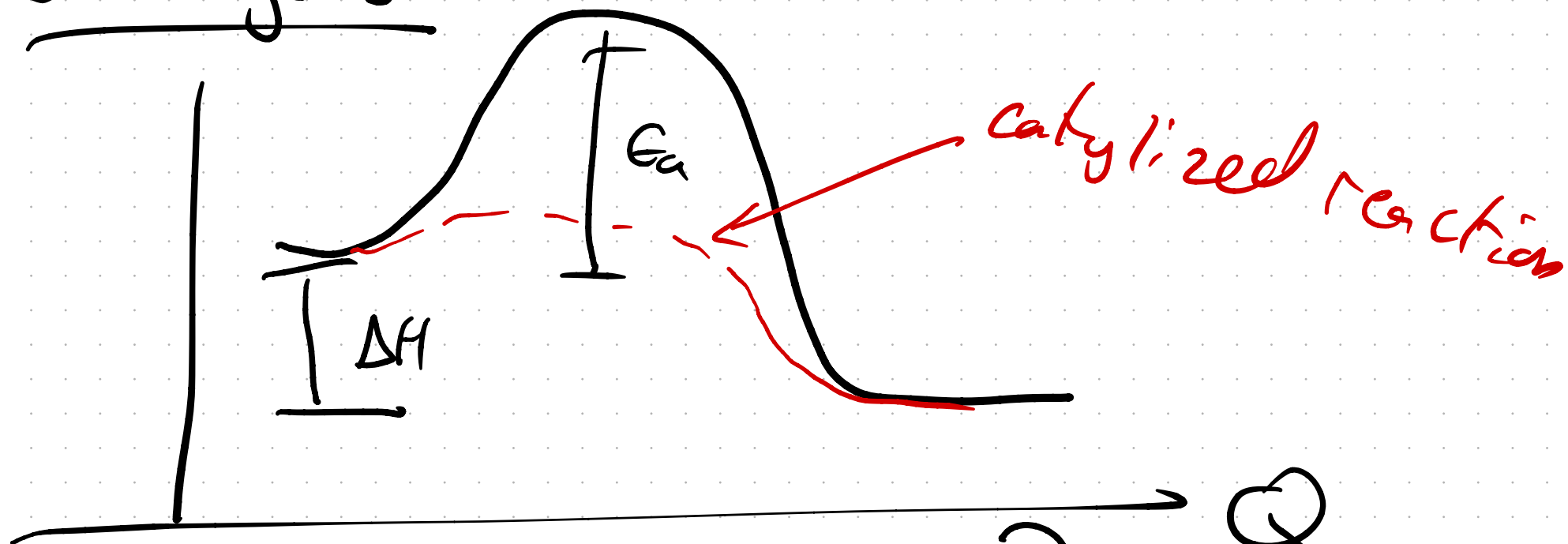$k_{obs} = k_f^1 [M]$, second order reaction at low conc

what about CH_3NC

$$v = k_{obs}[CH_3NC]$$

at low conc $\quad v = k'_{obs}[CH_3NC]^2$

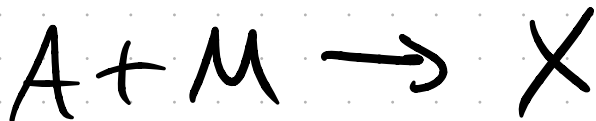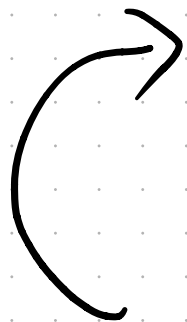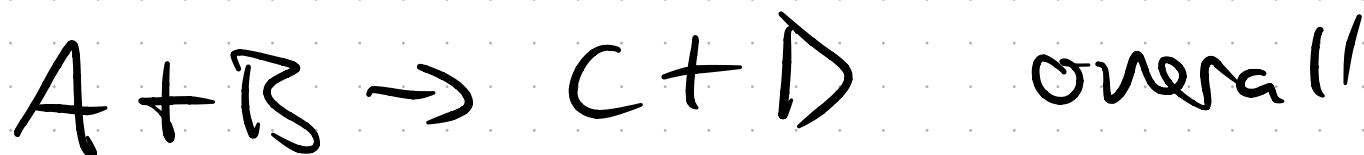[Skip chain reactions 29-7]

Catalysts

effectively lower barrier
* different reactive paths

About catalysts

Catlysts participates in reaction but is not used up

consumed & produced

$$A + B \rightarrow C + D \quad \text{overall}$$

$$\Downarrow$$

$$A + M \rightarrow X$$

$$+ \quad X + B \rightarrow C + D + M$$

2 types of catylists

homogeneous ← in same phase

heterogeneous ← a different
                  phase

Enzymes are biological catalysts

Accelerate reactions by many
  orders of magnitude

Very specific & stero selective