Intermediates

How can we distinguish single step from multistep rxns?

$$A \xRightarrow{k_1} I \xRightarrow{k_2} P$$

Example: ① 

② 

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

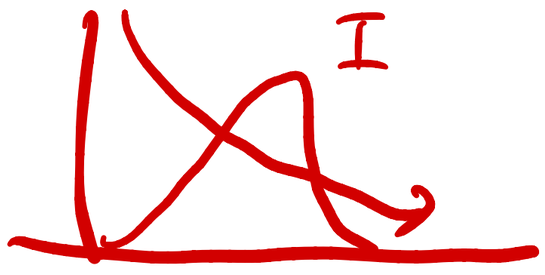
(prob 29-5)

$$\frac{d[A]}{dt} = -k_1[A] \quad \leftarrow \quad [A](t) = [A]_0 e^{-k_1 t}$$

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

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

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



$$P(t) = A_0 - I - A$$

$$= A_0\left(1 + \frac{1}{k_1 - k_2}\left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t}\right)\right)$$

$$P(t) = A_0 - I - A$$
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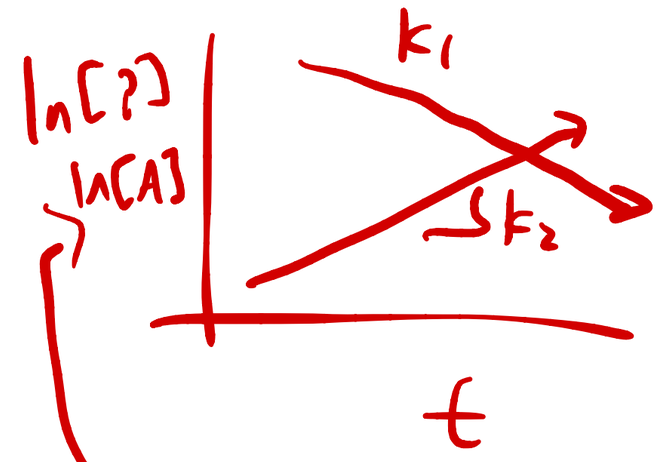

Single step

$$[P] = [A_0] - [A] = [A]_0\left(1 - e^{-k_1 t}\right)$$

if $k_2 >> k_1$

$$P(t) \approx [A]_0\left(1 + \frac{1}{-k_2}\left(k_2 e^{-k_1 t} - \approx 0\right)\right)$$

$$\approx [A]_0\left(1 - e^{-k_1 t}\right)$$

if $k_1 >> k_2$ $\quad P(t) \approx [A]_0\left(1 - e^{-k_2 t}\right)$ ← measure $-\frac{dA}{dt}$ $\quad dP/dt \neq$

Rate determining Step

If you have a very slow step,
it determines the apparent rxn mechanism
(rate law)

Example:

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

not

$$r = k[NO_2][CO]$$

$$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO \quad \leftarrow \text{slow step}$$

$$NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$$

Observed:

$$r = k_1[NO_2]^2$$

If sufficient [CO]

Steady state approximation for intermediates

$$A \Rightarrow I \Rightarrow P$$

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

$$\frac{d[I]}{dt} = k_1[A] - k_2[I] \approx 0, \quad [I]_{ss} = \frac{k_1[A]}{k_2}$$

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

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

$$\frac{dP}{dt} = [A]_0 k_1 e^{-k_1 t}$$

integrate $\rightarrow$ $[P](t) = [A]_0 (1 - e^{-k_1 t})$

when true? $\frac{d[I]}{dt} = -\frac{k_1^2[A_0]}{k_2} e^{-k_1 t}$

small

when $\frac{k_1^2}{k_2}[A]_0$ is small

Rate law $\rightarrow$ mechanism

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

$$r(t) = k_{obs}[NO]^2[O_2]$$

Possible mechanisms

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

$$NO_3 + NO \overset{k_f^2}{\Rightarrow} 2NO_2 \quad \text{rate dep} \quad (2)$$

$$NO + O_2 \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} NO_3 \qquad \text{fast} \quad (1)$$

$$NO_3 + NO \xrightarrow{k_f^2} 2NO_2 \qquad \text{rate dep} \quad (2)$$

@eq $\dfrac{k_f'}{k_b'} = \dfrac{[NO_3]}{[NO][O_2]}$

$$r = \frac{1}{2}\frac{d[NO_2]}{dt} = k_2[NO_3][NO]$$

$$= k_2 k_f'/k_b' [NO]^2[O_2]$$

Choice 2

$$NO + NO \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} N_2O_2 \quad \text{(steady state)}$$

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

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

$$\frac{d[N_2O_2]}{dt} = -k_b'[N_2O_2] + k_f'[NO]^2 + k_f^2[N_2O_2][O_2]$$

$$[N_2O_2]_{ss} \approx \frac{k_f'[NO]^2}{k_b' + k_f^2[O_2]}$$

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

$$[N_2O_2]_{ss} \approx \frac{k_f'[NO]^2}{k_b + k_f^2[O_2]}$$

$$\text{rate} \approx \frac{k_f^2 k_f'[NO]^2[O_2]}{k_b' + k_f^2[O_2]} \approx \frac{k_f^2 k_f'}{k_b'}[NO]^2[O_2]$$

$$k_{obs}$$

if $k_f^2[O_2]$ is small

Lindemann Mechanism

Molecules have to have enough energy to overcome activaton barriers

In gas phase, comes from direct collisions

$$CH_3-NC \xrightarrow[k]{} CH_3-CN \qquad (E_a \ 131 \ \frac{kJ}{mol})$$

At high conc:

$$r = k[CH_3NC]$$

low:

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

Lindemann Mechanism

"activated state"

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

$$A^* \xrightarrow[k_2]{} B$$

$[A^*]$ is small

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

$$\frac{d[A^*]}{dt} = k_f[A][M] - k_2[A^*] - k_b[A^*][M]$$