

LIB Steady-State Solutions

① (a)
$$\frac{d[\text{CH}_4]}{dt} = k_p [\text{CH}_3\text{CHO}] [\cdot\text{CH}_3]$$

Only step 2a produces CH_4 . No reaction consumes CH_4 .

(b)
$$\begin{aligned} \frac{d[\cdot\text{CH}_3]}{dt} &= \left(\begin{array}{c} \text{Rate of Production} \\ \text{of } \cdot\text{CH}_3 \end{array} \right) - \left(\begin{array}{c} \text{Rate of Consumption} \\ \text{of } \cdot\text{CH}_3 \end{array} \right) \\ &= k_i [\text{CH}_3\text{CHO}] + k'_p [\cdot\text{CH}_3\text{CO}] - k_p [\text{CH}_3\text{CHO}] [\cdot\text{CH}_3] - 2k_t [\cdot\text{CH}_3]^2 \\ &= 0 \end{aligned}$$

Similarly, $\cdot\text{CH}_3$ coefficient of 2 b/c two molecules of $\cdot\text{CH}_3$ are consumed in the termination step

$$\frac{d[\text{CH}_3\text{CO}\cdot]}{dt} = -k'_p [\text{CH}_3\text{CO}\cdot] + k_p [\text{CH}_3\text{CHO}] [\cdot\text{CH}_3] = 0$$

(c) Using the hint,

$$\frac{d[\cdot\text{CH}_3]}{dt} + \frac{d[\text{CH}_3\text{CO}\cdot]}{dt} \approx 0 + 0 = 0 = k_i [\text{CH}_3\text{CHO}] - 2k_t [\cdot\text{CH}_3]^2$$

(Two terms beautifully cancel out upon addition!)

Thus, $2k_t [\cdot\text{CH}_3]^2 = k_i [\text{CH}_3\text{CHO}]$

$$[\cdot\text{CH}_3] = \sqrt{\frac{k_i}{2k_t} [\text{CH}_3\text{CHO}]}$$

Only take positive root \rightarrow we can't have "negative concentration"

Plugging into part (a),

$$\frac{d[\text{CH}_4]}{dt} = k_p [\text{CH}_3\text{CHO}] [\cdot\text{CH}_3] = k_p [\text{CH}_3\text{CHO}] \sqrt{\frac{k_i}{2k_t} [\text{CH}_3\text{CHO}]}$$

$$\boxed{\frac{d[\text{CH}_4]}{dt} = \frac{k_p \sqrt{k_i}}{\sqrt{2k_t}} [\text{CH}_3\text{CHO}]^{3/2}}$$

Order of acetaldehyde is $3/2$

② Rate of formation of B: $\frac{d[B]}{dt} = k_2 [A^*]$

(a) Steady-state equation for intermediate $[A^*]$:

$$\frac{d[A^*]}{dt} = 0 = k_1 [A][He] - k_{-1} [A^*][He] - k_2 [A^*] = 0$$

$$k_1 [A][He] = [A^*] (k_{-1} [He] + k_2)$$

$$[A^*] = \frac{k_1 [A][He]}{k_{-1} [He] + k_2}$$

Substituting, we have

$$\boxed{\frac{d[B]}{dt} = \frac{k_2 k_1 [A][He]}{k_{-1} [He] + k_2}}$$

(b) When $[He]$ is small, k_2 dwarfs $k_{-1} [He]$, so $k_{-1} [He] + k_2 \approx k_2$

$$\text{so } \boxed{\frac{d[B]}{dt} \approx \frac{k_2 k_1 [A][He]}{k_2} = k_1 [A][He]}$$

When $[He]$ is large, $k_{-1} [He]$ dwarfs k_2 , so $k_{-1} [He] + k_2 \approx k_{-1} [He]$

$$\text{so } \boxed{\frac{d[B]}{dt} \approx \frac{k_2 k_1 [A][He]}{k_{-1} [He]} = \frac{k_2 k_1}{k_{-1}} [A]}$$

(c) We are essentially "working backwards" in this problem. Observing the rate law from part (a), $\frac{d[B]}{dt} = \frac{k_1 k_2 [A][He]}{k_{-1} [He] + k_2}$, the key observation here is that if we substitute $[He]$ with $[A]$, we get exactly the kinetic behavior described.

$$\boxed{\frac{d[B]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1} [A] + k_2}}$$

2nd order when $[A]$ is small
1st order when $[A]$ is large

Basically, this rate law simply corresponds with replacing He with

A everywhere in the mechanism:

