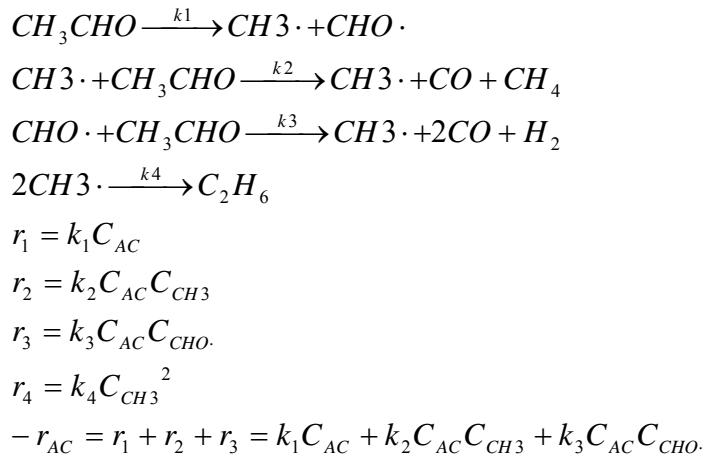


1.

(a)



Active intermediates $CH_3\cdot$ $CHO\cdot$

$$-r_{CH3\cdot} = -r_1 + r_2 - r_2 - r_3 + 2r_4 = -k_1 C_{AC} - k_3 C_{CHO} C_{AC} + k_4 C_{CH3\cdot}^2 = 0$$

$$-r_{CHO\cdot} = -r_1 + r_3 = -k_1 C_{AC} + k_3 C_{CHO} C_{AC} = 0$$

$$C_{CHO\cdot} = \frac{k_1}{k_3}$$

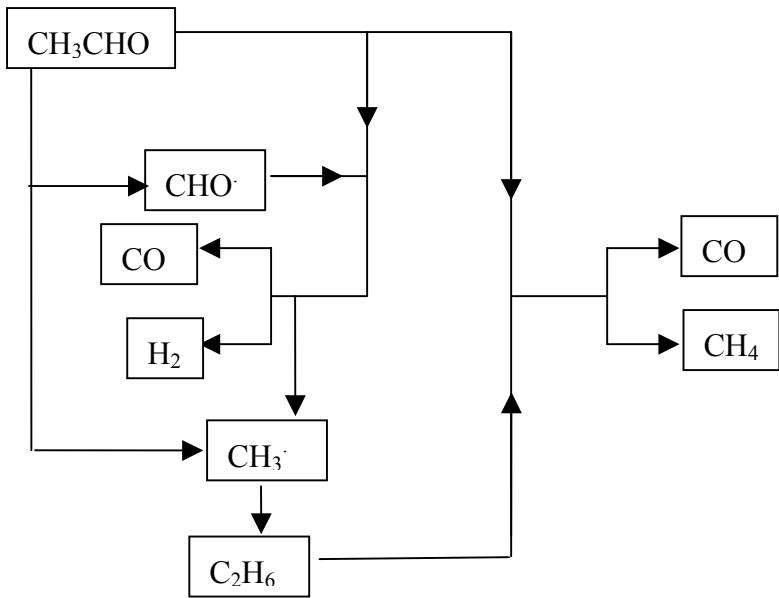
$$C_{CH3\cdot} = \sqrt{\frac{2k_1}{k_4}} C_{AC}$$

$$-r_{ac} = k_1 C_{AC} \left[2 + \frac{2k_2}{\sqrt{k_1 k_4}} \sqrt{C_{AC}} \right]$$

(b)

$$k_2 \sqrt{\frac{2}{k_1 k_4}} \gg 1 \text{ or } C_{AC} \gg 1 \Rightarrow -r_{AC} \propto (C_{AC})^{3/2}$$

(c)



2.

(a)

$$\frac{1}{V} \frac{dN_s}{dt} = \frac{dC_s}{-dt} = r_s = \frac{-V_{\max} C_s}{K_m + C_s}$$

$$\int_{C_{s0}}^{C_s} \left[\frac{K_m}{C_s} + 1 \right] dC_s = - \int_0^t V_{\max} dt = K_m \ln \frac{C_s}{C_{s0}} + C_s - C_{s0} = -V_{\max} t$$

$$\frac{1}{t} \ln \frac{C_s}{C_{s0}} = - \frac{C_{s0} - C_s}{K_m t} + \frac{V_{\max}}{K_m}$$

$$\text{Plot } \frac{1}{t} \ln \frac{C_s}{C_{s0}} \text{ v.s. } \frac{C_{s0} - C_s}{t} \rightarrow \frac{1}{t} \ln \frac{C_s}{C_{s0}} = -28.208 \frac{C_{s0} - C_s}{t} + 0.018$$

$$\text{slope} = -28.208 = -1/K_m \rightarrow K_m = 0.035 \text{ g mol/l}$$

$$0.018 = V_{\max}/K_m \rightarrow V_{\max} = 6.372 \times 10^{-4} \text{ gmol/L min}$$

(b)

$V_{\max} = [E_t]$, If the enzyme concentration is increased by a factor of three, then

$$V_{\max} = 3(6.372 \times 10^{-4}) = 1.91 \times 10^{-3}$$

$$K_m \ln \frac{C_s}{C_{s0}} + C_s - C_{s0} = -V_{\max} t$$

$$0.035 \ln \frac{C_s}{0.02} + C_s - 0.02 = -1.91 \times 10^{-3} \times 20 = -0.0382$$

$$\ln \frac{C_s}{0.02} = \frac{-0.0182 - C_s}{0.035}$$

$$C_s = 0.02 \exp \left(\frac{-0.0182 - C_s}{0.035} \right)$$

$$C_s = 0.00915 \text{ mol/L}$$

3.

Assume the rate law is of the form $-r_{VI} = \frac{kP^2_{VTIPO}}{1 + K_{VI} P_{VTIPO}^2}$

At high temperature $K \downarrow$ as $T \uparrow$ and therefore $KP^2_{VTIPO} \ll 1$

$$-r_{VI} = kP^2_{VTIPO}$$

$$\frac{-r_{VI}}{P^2_{VTIPO}} = k$$

$$\text{Run 1 } \frac{0.028}{(0.05)^2} = 11.2$$

$$\text{Run 2 } \frac{0.45}{(0.2)^2} = 11.28$$

$$\text{Run 3 } \frac{7.2}{(0.8)^2} = 11.25$$

At low temperature and low pressure

$$-r_{VI} = kP^2_{VTIPO}$$

$$\frac{-r_{VI}}{P^2_{VTIPO}} = k$$

$$\text{Run 1 } \frac{0.004}{(0.1)^2} = 0.4$$

$$\text{Run 2 } \frac{0.015}{(0.2)^2} = 0.375$$

At high pressure $KP^2_{VTIPO} \gg 1$

$$-r_{VI} = \frac{kP^2_{VTIPO}}{KP^2_{VTIPO}} = \frac{k}{K}$$

at $P_{VTIPO} = 1.5$, $-r_{VI} = 0.095$

at $P_{VTIPO} = 2$, $-r_{VI} = 0.1$

Now find the activation energy

At low pressure and high temperature $k=11.2$

At low pressure and low temperature $k=0.4$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{11.2}{0.4}\right) = \frac{E}{R} \left(\frac{1}{393} - \frac{1}{473}\right)$$

$$\frac{E}{R} = 7738$$

$$E = 15375 \frac{\text{cal}}{\text{mol}}$$

4.

$$r_{TiO_2} = k_s f_{I,S}$$

$$f_{I,S} = P_1 K_I f_V$$

$$1 = f_V + f_{I,S} = f_V (1 + K_I P_I)$$

$$f_{I,S} = \frac{K_I P_I}{1 + K_I P_I}$$

$$K_P = \frac{P_I P_{P1}}{P_{TTIP}^2}$$

$$P_I = \frac{K_P P_{TTIP}^2}{P_{P1}}$$

$$r_{TiO_2} = \frac{k_s K_I P_I}{1 + K_I P_I} = \frac{k_s K_I \frac{K_P P_{TTIP}^2}{P_{P1}}}{1 + K_I \frac{K_P P_{TTIP}^2}{P_{P1}}} = \frac{k_s K_I K_P P_{TTIP}^2}{P_{P1} + K_I K_P P_{TTIP}^2} = \frac{k P_{TTIP}^2}{P_{P1} + K P_{TTIP}^2}$$

Low P_{TTIP} $\rightarrow P_{TTIP}^2 K_P K_I \ll P_{P1}$ \rightarrow reaction is second order

High P_{TTIP} $\rightarrow P_{TTIP}^2 K_P K_I \gg P_{P1}$ \rightarrow reaction is zero order

High temperature K_I very small such that $P_{TTIP}^2 K_P K_I \ll P_{P1}$ \rightarrow reaction is second order .