P9-4

$$CH_3CHO \xrightarrow{k_1} CH_3\cdot + CHO\cdot$$

$$CH_3\cdot + CH_3CHO \xrightarrow{k_2} CH_3\cdot + CO + CH_4$$

$$CHO\cdot + CH_3CHO \xrightarrow{k_3} CH_3\cdot + 2CO + H_2$$

$$2CH_3\cdot \xrightarrow{k_4} C_2H_6$$

$$-r_{AC} = r_1 + r_2 + r_3$$

$$= k_1 C_{AC} + k_2 C_{AC} C_{CH_3\cdot} + k_3 C_{AC} C_{CHO\cdot}$$

$$= C_{AC}\left[k_1 + k_2 C_{CH_3\cdot} + k_3 C_{CHO\cdot}\right] \quad \text{— (1)}$$

Active Intermediate

$CH_3\cdot$, $CHO\cdot$

$$-r_{CH_3\cdot} = -r_1 + r_2 - r_3 + \frac{1}{2} r_4$$

$$0 = -k_1 C_{AC} - k_3 C_{CHO\cdot} C_{AC} + \frac{1}{2} k_4 C_{CH_3\cdot}^2 \quad \text{— (2)}$$

$$-r_{CHO\cdot} = -r_1 + r_3$$

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

$$\Rightarrow \quad C_{CHO\cdot} = \frac{k_1}{k_3} \quad \text{— (3)}$$

Substituting (3) in (2)

$$0 = -k_1 C_{Ac} - k_3 C_{Ac} \frac{k_1}{k_3} + \frac{1}{2} k_4 C_{CH_3\cdot}^2$$

$$\Rightarrow \frac{1}{2} k_4 C_{CH_3\cdot}^2 = C_{Ac}\left[2k_1\right]$$

$$C_{CH_3\cdot} = 2 C_{Ac}^{1/2} \left(\frac{k_1}{k_4}\right)^{1/2} \quad \text{——} \quad (4)$$

Substitute (3) and (4) in (1)

$$-r_{Ac} = C_{Ac}\left[k_1 + 2k_2\left(\frac{k_1}{k_4}\right)^{1/2} C_{Ac}^{1/2} + \quad k_1\right]$$

$$\boxed{-r_{Ac} = 2k_1 C_{Ac}\left[1 + \frac{k_2}{\sqrt{k_1 k_4}}\sqrt{C_{Ac}}\right]}$$

(b) For

$$-r_{Ac} = k C_{CH_3CHO}^{3/2}$$

$$\Rightarrow C_{Ac} >> 1 \quad \text{or}$$

$$\frac{k_2}{\sqrt{k_1 k_4}} >> 1$$

(c)