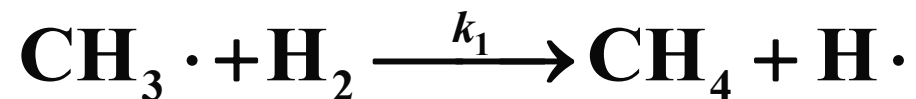




Ex. 26

Mechanism of the reaction $\text{C}_2\text{H}_6 + \text{H}_2 \longrightarrow 2\text{CH}_4$ can be presented as

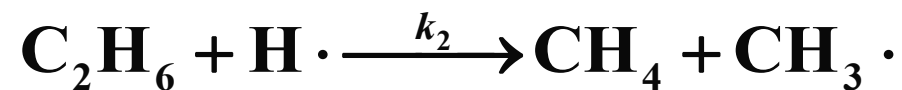
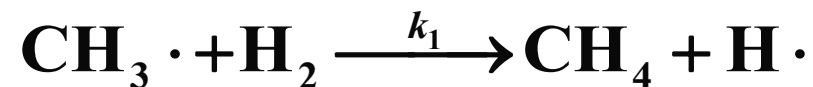
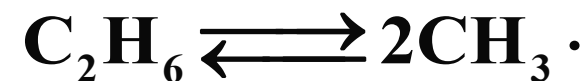


Try to prove
$$\frac{d[\text{CH}_4]}{dt} = 2k_1 K^{1/2} [\text{C}_2\text{H}_6]^{1/2} [\text{H}_2]$$



Ex. 26

$$\frac{d[\text{CH}_4]}{dt} = k_1[\text{CH}_3 \cdot][\text{H}_2] + k_2[\text{H} \cdot][\text{C}_2\text{H}_6]$$



$$d[\text{H} \cdot] / dt = k_1[\text{CH}_3 \cdot][\text{H}_2] - k_2[\text{H} \cdot][\text{C}_2\text{H}_6] = 0 \quad \text{H} \cdot \text{ is at steady state}$$

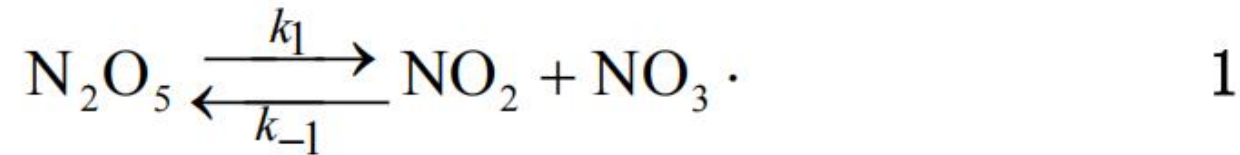
$$[\text{CH}_3 \cdot]^2 / [\text{C}_2\text{H}_6] = K \quad \text{Equilibrium constant } K$$

$$\begin{aligned} \frac{d[\text{CH}_4]}{dt} &= k_1[\text{CH}_3 \cdot][\text{H}_2] + k_2[\text{H} \cdot][\text{C}_2\text{H}_6] = 2k_1[\text{CH}_3 \cdot][\text{H}_2] \\ &= 2k_1 K^{1/2} [\text{C}_2\text{H}_6]^{1/2} [\text{H}_2] \end{aligned}$$



Ex. 27

Mechanism of the decomposition reaction of N_2O_5 can be presented as



(1) If NO and NO_3 are active intermediates, try to give the production rate of O_2 by

Steady State Approximation

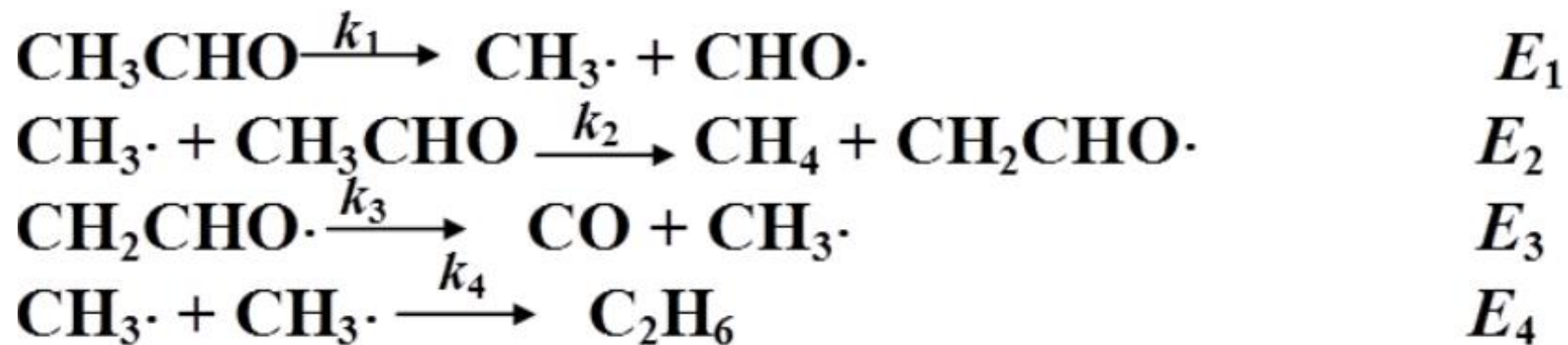
(2) Suppose the step 2 is the rate-controlled step, try to give the production rate of O_2

under the **Pre-Equilibrium Approximation**



Ex. 28

Mechanism of the reaction $\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$ can be presented as



Try to give the express of $\frac{d\mathbf{c}_{\text{CH}_4}}{dt}$ and the apparant activation energy of the reaction?



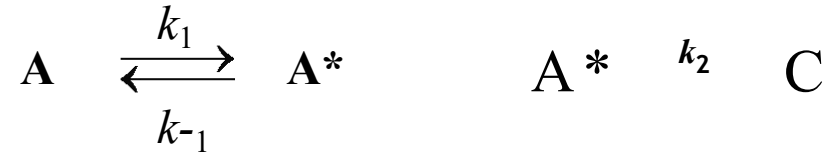
Ex. 29

For reaction $A \rightarrow C$, there are two possible reaction mechanisms:

(1) the reaction took place directly, and displayed the characterizations of first order reaction.

the half time at 294K is 1000min, while at $T=340K$, the time needed to reduce the concentration of A to $1/1024 C_{A0}$ is 0.1min.

(2) the reaction took place by two steps:



the activation energies of each step were $E_{a,1}=125.52\text{kJ/mol}$, $E_{a,-1}=120.3\text{kJ/mol}$ and

$E_{a,2}=167.36\text{kJ/mol}$

Try to determine which one is the most possible mechanism at $T=500K$?



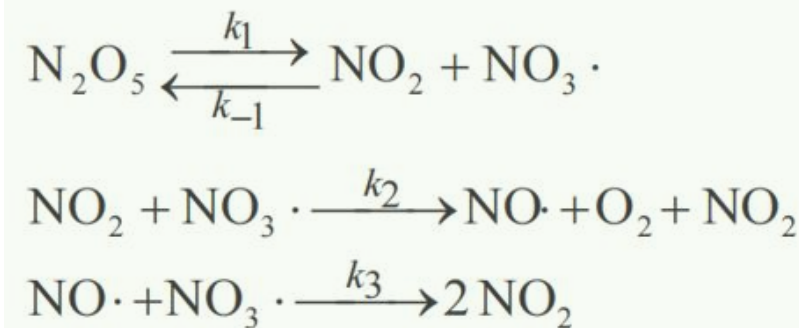
Ex. 27

$$(1) \quad \frac{d[\text{O}_2]}{dt} = k_2 [\text{NO}_2][\text{NO}_3]$$

$$\begin{cases} \frac{d[\text{NO}]}{dt} = k_2 [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}][\text{NO}_3] = 0 \\ \frac{d[\text{NO}_3]}{dt} = k_1 [\text{N}_2\text{O}_5] - k_{-1} [\text{NO}_2][\text{NO}_3] - k_2 [\text{NO}_2][\text{NO}_3] - k_3 [\text{NO}][\text{NO}_3] = 0 \end{cases}$$

$$[\text{NO}_3] = \frac{k_1 [\text{N}_2\text{O}_5]}{(k_{-1} + 2k_2) [\text{NO}_2]} \quad \frac{d[\text{O}_2]}{dt} = \frac{k_1 k_2}{k_{-1} + 2k_2} [\text{N}_2\text{O}_5]$$

$$(2) \quad K = \frac{[\text{NO}_2][\text{NO}_3]}{[\text{N}_2\text{O}_5]} = \frac{k_1}{k_{-1}} \quad \frac{d[\text{O}_2]}{dt} = k_2 [\text{NO}_2][\text{NO}_3] = \frac{k_1 k_2}{k_{-1}} [\text{N}_2\text{O}_5]$$





Ex. 28

$$(1) \quad \frac{dc_{\text{CH}_4}}{dt} = k_2 [\text{CH}_3 \cdot] [\text{CH}_3\text{CHO}]$$

$$\begin{aligned} \frac{d[\text{CH}_3 \cdot]}{dt} &= k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3 \cdot] [\text{CH}_3\text{CHO}] \\ &\quad + k_3 [\text{CH}_2\text{CHO} \cdot] - 2k_4 [\text{CH}_3 \cdot]^2 = 0 \end{aligned}$$

$$\frac{d[\text{CH}_2\text{CHO} \cdot]}{dt} = k_2 [\text{CH}_3 \cdot] [\text{CH}_3\text{CHO}] - k_3 [\text{CH}_2\text{CHO} \cdot] = 0$$

$$[\text{CH}_3 \cdot] = \sqrt{\frac{k_1 [\text{CH}_3\text{CHO}]}{2k_4}}$$

$$\begin{aligned} \therefore \frac{d[\text{CH}_4]}{dt} &= k_2 [\text{CH}_3\text{CHO}] \sqrt{k_1 [\text{CH}_3\text{CHO}] / 2k_4} \\ &= k_2 (k_1 / 2k_4)^{1/2} [\text{CH}_3\text{CHO}]^{3/2} \end{aligned}$$

$$(2) \quad E_a = \frac{1}{2} E_1 + E_2 - \frac{1}{2} E_4$$



Ex. 29

(1)

$$k(294 \text{ K}) = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1000 \text{ min}} = 6.93 \times 10^{-4} \text{ min}^{-1}$$

$$k(340 \text{ K}) = \frac{1}{t} \ln \frac{1}{1-y} = \frac{1}{0.10 \text{ min}} \ln \frac{1}{1 - \frac{1023}{1024}} = 69.31 \text{ min}^{-1}$$

$$\ln \frac{k(T_2)}{k(T_1)} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{69.31}{6.93 \times 10^{-4}} = \frac{E_a}{R} \left(\frac{1}{294 \text{ K}} - \frac{1}{340 \text{ K}} \right)$$

$$E_a(1) = 208.0 \text{ kJ} \cdot \text{mol}^{-1}$$

(2)

$$r_2 = k_2[A^*] = \frac{k_1 k_2}{k_{-1}}[A] = k[A]$$

$$k = \frac{k_1 k_2}{k_{-1}}$$

$$k_1[A] = k_{-1}[A^*], \quad [A^*] = \frac{k_1}{k_{-1}}[A],$$

$$E_a(2) = E_{a,1} + E_{a,2} - E_{a,-1} = (125.52 + 167.36 - 120.30) \text{ kJ} \cdot \text{mol}^{-1} = 172.58 \text{ kJ} \cdot \text{mol}^{-1}$$