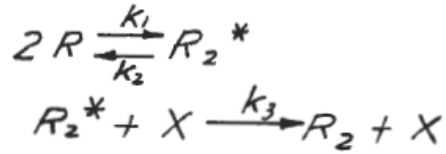


## ASSIGNMENT 2 (SOLUTION)

### Answer 1

The energy-transfer mechanism during radical or atom recombination is described by the following chemical steps:



According to the law of mass action, the rate of change of the concentration of  $R_2^*$  can be written as

$$\frac{dC_{R_2^*}}{dt} = k_1 C_R^2 - k_2 C_{R_2^*} - k_3 C_{R_2^*} C_X$$

Under steady-state condition,  $\frac{dC_{R_2^*}}{dt} = 0$ .  
Therefore,  $C_{R_2^*} = \frac{k_1 C_R^2}{k_2 + k_3 C_X}$

The rate of production of R is

$$\begin{aligned} \frac{dC_R}{dt} &= -2k_1 C_R^2 + 2k_2 C_{R_2^*} = -2k_1 C_R^2 + \frac{2k_1 k_2 C_R^2}{k_2 + k_3 C_X} \\ &= -\frac{2k_1 k_3 C_X C_R^2}{k_2 + k_3 C_X} \end{aligned}$$

The rate of consumption of R is equal to

$$\frac{2k_1 k_3 C_X C_R^2}{k_2 + k_3 C_X}$$

When the concentration of X is sufficiently large such that  $k_3 C_X \gg k_2$ ,

$$\frac{dC_{R_2}}{dt} = k_3 C_{R_2^*} C_X = \frac{k_1 k_3 C_R^2 C_X}{k_2 + k_3 C_X} \approx k_1 C_R^2,$$

thus, the order of recombination reaction is 2nd order.

When the pressure is very low,  $k_3 C_X \ll k_2$ , then

$$\frac{dC_{R_2}}{dt} = \frac{k_1 k_3 C_R^2 C_X}{k_1 + k_3 C_X} \approx \frac{k_1 k_3}{k_2} C_X C_R^2; \text{ therefore the}$$

reaction is 3rd order.

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Answer 2

Using the steady-state hypothesis we get,

$$\frac{dC_{OH}}{dt} = 2k_1 C_{H_2} C_{O_2} - k_2 C_{OH} C_{H_2} + k_3 C_H C_{O_2} + k_4 C_O C_{H_2} - k_5 C_H C_{OH} C_M = 0 \quad (1)$$

$$\frac{dC_H}{dt} = k_2 C_{OH} C_{H_2} - k_3 C_H C_{O_2} + k_4 C_O C_{H_2} - k_5 C_H C_{OH} C_M = 0 \quad (2)$$

$$\frac{dC_O}{dt} = k_3 C_H C_{O_2} - k_4 C_O C_{H_2} = 0 \quad (3)$$

$$\text{From Eq. (3), } k_3 C_H C_{O_2} = k_4 C_O C_{H_2} \quad (4)$$

Substituting Eq. (4) in (2) we get,

$$k_2 C_{OH} C_{H_2} = k_5 C_H C_{OH} C_M$$

$$\text{Therefore, } C_H = k_2 C_{H_2} / k_5 C_M \quad (5)$$

Substituting Eqs. (4) and (5) into (1), we get,

$$k_1 C_{H_2} C_{O_2} - k_2 C_{OH} C_{H_2} + k_3 C_H C_{O_2} = 0 \quad (6)$$

Substituting Eq. (5) into (6) we get,

$$k_1 C_{H_2} C_{O_2} - k_2 C_{OH} C_{H_2} + k_2 k_3 C_{H_2} C_{O_2} / k_5 C_M = 0$$

$$\text{Therefore } C_{OH} = [k_1 + k_2 k_3 / k_5 C_M] C_{O_2} / k_2 \quad (7)$$

$$\text{Also, } \frac{dC_{H_2O}}{dt} = k_2 C_{OH} C_{H_2} + k_5 C_H C_{OH} C_M = 2k_2 C_{OH} C_{H_2} \quad (\text{From Eq. (5)})$$

$$\therefore \frac{dC_{H_2O}}{dt} = 2k_2 C_{O_2} C_{H_2} \left( \frac{k_1}{k_2} + \frac{k_3}{k_5 C_M} \right)$$

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