ASSIGNMENT 2 (SOLUTION)

Answer 1

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

$$2R \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R_2^*$$

$$R_2^* + X \xrightarrow{k_3} R_2 + X$$

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

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

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

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 $k_3 C_X >> k_2$,

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

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

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

$$\frac{dC_{R_2}}{dt} = \frac{k_1 k_3 C_R^2 C_X}{k_1 + k_3 C_X} \approx \frac{k_1 k_3}{k_2} C_X C_R^2;$$ therefore the reaction is 3rd order.

Answer 2

Using the steady-state hypothesis we get,

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

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

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

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

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

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

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

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

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

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

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

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

Also, $\frac{dC_{H_2O}}{dt} = k_2 C_{OH} C_{H_2} + k_5 C_H C_{OH} C_M$

$= 2 k_2 C_{OH} C_{H_2}$ (From Eq. (5))

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