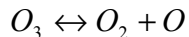
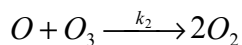


Question 1:

A possible mechanism for the decomposition of Ozone is:



with forward and reverse rate constants  $k_1$  and  $k_{-1}$



Using the steady-state approximation for O , which of the following rate laws is consistent with the proposed mechanism?

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1.  $\frac{d[O_2]}{dt} = \frac{3k_1k_2[O_3]}{(k_{-1}[O_2] + k_2[O_3])}$
2.  $\frac{d[O_2]}{dt} = \frac{2k_1k_2[O_3]^2}{(k_{-1} + k_2)}$
3.  $\frac{d[O_2]}{dt} = \frac{3k_1k_2[O_3]^2}{(k_{-1}[O_2] + k_2[O_3])}$
4.  $\frac{d[O_2]}{dt} = \frac{3k_1k_2[O_3]}{(k_{-1}[O_2] + k_2[O_3]^2)}$
5. none of the above

Answer 1:

The rate equation of decomposition of Ozone consistent with the proposed mechanism is:

$$\frac{d[O_2]}{dt} = v_1 - v_{-1} + 2v_2 = k_1[O_3] - k_{-1}[O_2][O] + 2k_2[O][O_3]$$

Using the steady –state approximation for [O]:

$$\frac{d[O]}{dt} = v_1 - v_{-1} - v_2 = k_1[O_3] - k_{-1}[O_2][O] - k_2[O][O_3] = 0$$

steady-state concentration of [O] is given as

$$[O] = \frac{k_1[O_3]}{k_2[O_3] + k_{-1}[O_2]}$$

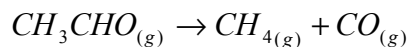
Substituting the SSA solution for [O] into the rate equation ,rate law becomes:

$$\frac{d[O_2]}{dt} = \frac{3k_1k_2[O_3]^2}{(k_{-1}[O_2] + k_2[O_3])}$$

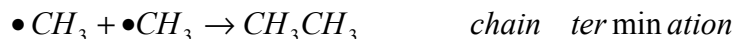
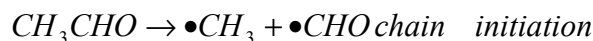
Therefore the right answer is answer 3.

Question 2:

The pyrolysis of acetaldehyde (thermal decomposition in absence of air)



Is proposed to proceed by the chain reaction mechanism:



Apply the SSA to the reactive intermediates  $\bullet\text{CH}_3$  and  $\bullet\text{CH}_3\text{CO}$ , to find the rate equation for the formation of  $\text{CH}_4$ . This rate equation is of the form

$$d[\text{CH}_4]/dt = k[\text{CH}_3\text{CHO}]^n$$

The order n is:

1. -1
2. -1/2
3. 0
4. 1/2
5. 1
6. 3/2
7. 2
8. 5/2
9. 3
10. none of the above

Answer:

The rate equation for the pyrolysis of acetaldehyde is:

$$\frac{d[\text{CH}_4]}{dt} = v_2 = k_2[\text{CH}_3\text{CHO}][\text{CH}_3]$$

Applying the SSA upon intermediates  $\bullet\text{CH}_3$  and  $\bullet\text{CH}_3\text{CO}$  will give the steady-state concentration of  $\bullet\text{CH}_3$

$$\frac{d[\bullet\text{CH}_3]}{dt} = v_1 - v_2 + v_3 - 2v_4 = 0$$

$$\frac{d[\bullet\text{CH}_3\text{CHO}]}{dt} = v_2 - v_3 = 0$$

$$v_1 = 2v_4$$

$$\Rightarrow k_1[\text{CH}_3\text{CHO}] = 2k_4[\bullet\text{CH}_3]^2$$

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

Submitting the concentration of  $\bullet\text{CH}_3$  into the rate equation ,rate equation becomes:

$$\frac{d[\text{CH}_4]}{dt} = k_2 \sqrt{\frac{k_1}{2k_4}}[\text{CH}_3\text{CHO}]^{3/2}$$

The order n is therefore 3/2, and the correct answer is number 6.

Question 3:

In aqueous solution at  $T^{\circ}\text{C}$ , the decomposition of  $\text{H}_2\text{O}_2$  in the absence of a catalyst has rate constant  $k_1$  ( $\text{L/mol s}$ ), and  $E_{a1}$  ( $\text{kJ/mol}$ ). In the presence of the enzyme catalase, activation energy is  $E_{a2}$  ( $\text{kJ/mol}$ ). If the frequency factors  $A$  are about the same in both cases, estimate the rate constant (in  $\text{L/mol s}$ ) for the reaction catalyzed by catalase.

According to the Arrhenius equation the rate constant in the absence of the catalyst is :

$$k_1(T) = A \cdot e^{-\frac{E_{a1}}{RT}}$$

and the one for the reaction with the catalyst is:

$$k_2(T) = A \cdot e^{-\frac{E_{a2}}{RT}}$$

Since both reactions are done at the same temperature, frequency factors  $A$  are about the same in both cases and the ratio of the two rate constants is given as:

$$\frac{k_2(T)}{k_1(T)} = e^{-\frac{1}{RT}(E_{a2}-E_{a1})}$$

The rate constant for the reaction with the catalyst at temperature  $T^{\circ}\text{C}$  is then:

$$k_2(T) = k_1(T) \cdot e^{\frac{1}{RT}(E_{a1}-E_{a2})}$$

Question 4:

The rate equation for a reaction is found experimentally to be

$$-\frac{d[A]}{dt} = \frac{k_1[A]}{(k_2 + k_3[B])}$$

Indicate which of the following statements is/are correct?

1. This is a one step reaction.
2. The mechanism for this reaction must involve more than a single step.
3. Increasing the concentration of B will slow down the reaction.
4. This is a typical rate equation for an overall first-order reaction.
5. It appears that B is an enzyme(i.e. speeds up the reaction)

Answer:

1. FALSE  
Since rate of the reaction shows the complicated concentration A and B dependence the reaction involves more than single step.
2. TRUE
3. TRUE  
If the concentration of B is increased, according to the rate equation, denominator is increased and rate of the reaction is decreased.
4. FALSE  
Overall order of the reaction is sum of orders upon A and B. Since the rate equation is complicated, the order with respect to A is 1; the order with respect to B is not defined. In the special case that  $k_2 \ll k_3[B]$ , the order in B is  $-1$  and the overall order of the reaction is 0. In the special case that  $k_2 \gg k_3[B]$ , the order in B is 0 and the overall order of the reaction is 1.
5. FALSE  
Since increase in the concentration B is slowing down the reaction, B is an inhibitor.