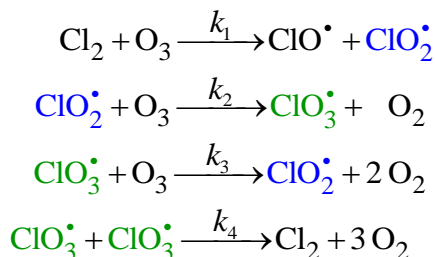


Problem 3-02 Mechanism

Mechanism of ozone decomposition in the presence of ozone can be described by the following reaction steps:



Radical ClO^\bullet decomposes to elements without causing a chain reaction. The rate of the first initiation step is negligibly small in comparison with the rest. Write the equation describing the time decrease of ozone concentration.

$$\left[-\frac{d[\text{O}_3]}{d\tau} = 2 k_3 \cdot \left(\frac{k_1}{k_4} \right)^{1/2} \cdot [\text{Cl}_2]^{1/2} \cdot [\text{O}_3]^{3/2} \right]$$

Solution:

Decrease of ozone concentration with time:

$$-\frac{d[\text{O}_3]}{d\tau} = k_1 \cdot [\text{Cl}_2] \cdot [\text{O}_3] + k_2 \cdot [\text{ClO}_2^\bullet] \cdot [\text{O}_3] + k_3 \cdot [\text{ClO}_3^\bullet] \cdot [\text{O}_3] \quad (1)$$

Unstable intermediates:

$$\left. \begin{aligned} \frac{d[\text{ClO}_2^\bullet]}{d\tau} &= 0 = r_1 - r_2 + r_3 \\ \frac{d[\text{ClO}_3^\bullet]}{d\tau} &= 0 = r_2 - r_3 - r_4 \end{aligned} \right\} \begin{aligned} &r_1 = r_4 \\ &k_1 \cdot [\text{Cl}_2] \cdot [\text{O}_3] = k_4 \cdot [\text{ClO}_3^\bullet]^2 \Rightarrow [\text{ClO}_3^\bullet] = \left(\frac{k_1}{k_4} \cdot [\text{Cl}_2] \cdot [\text{O}_3] \right)^{1/2} \end{aligned}$$

$$-\frac{d[\text{ClO}_2^\bullet]}{d\tau} = 0 = k_1 \cdot [\text{Cl}_2] \cdot [\text{O}_3] - k_2 \cdot [\text{ClO}_2^\bullet] \cdot [\text{O}_3] + k_3 \cdot [\text{ClO}_3^\bullet] \cdot [\text{O}_3] =$$

$$0 = k_1 \cdot [\text{Cl}_2] \cdot [\text{O}_3] - k_2 \cdot [\text{ClO}_2^\bullet] \cdot [\text{O}_3] + k_3 \cdot \left(\frac{k_1}{k_4} \cdot [\text{Cl}_2] \cdot [\text{O}_3] \right)^{1/2} \cdot [\text{O}_3]$$

$$[\text{ClO}_2^\bullet] = \frac{k_1 \cdot [\text{Cl}_2] \cdot [\text{O}_3]}{k_2 \cdot [\text{O}_3]} + \frac{k_3}{k_2 \cdot [\text{O}_3]} \cdot \left(\frac{k_1}{k_4} \cdot [\text{Cl}_2] \cdot [\text{O}_3] \right)^{1/2} \cdot [\text{O}_3] = \frac{k_1}{k_2} \cdot [\text{Cl}_2] + \frac{k_3}{k_2} \cdot \left(\frac{k_1}{k_4} \cdot [\text{Cl}_2] \cdot [\text{O}_3] \right)^{1/2}$$

Substituting $[\text{ClO}_2^\bullet]$ and $[\text{ClO}_3^\bullet]$ into eq. (1):

$$\begin{aligned} -\frac{d[\text{O}_3]}{d\tau} &= k_1 \cdot [\text{Cl}_2] \cdot [\text{O}_3] + k_2 \cdot [\text{ClO}_2^\bullet] \cdot [\text{O}_3] + k_3 \cdot [\text{ClO}_3^\bullet] \cdot [\text{O}_3] = \\ &= k_1 \cdot [\text{Cl}_2] \cdot [\text{O}_3] + k_2 \cdot \frac{k_1}{k_2} \cdot [\text{Cl}_2] \cdot [\text{O}_3] + \frac{k_3}{k_2} \cdot \left(\frac{k_1}{k_4} \cdot [\text{Cl}_2] \cdot [\text{O}_3] \right)^{1/2} \cdot [\text{O}_3] + \\ &\quad + k_3 \cdot \left(\frac{k_1}{k_4} \cdot [\text{Cl}_2] \cdot [\text{O}_3] \right)^{1/2} \cdot [\text{O}_3] \\ &= 2 k_1 \cdot [\text{Cl}_2] \cdot [\text{O}_3] + 2 k_3 \cdot \left(\frac{k_1}{k_4} \right)^{1/2} \cdot [\text{Cl}_2]^{1/2} \cdot [\text{O}_3]^{3/2} \end{aligned}$$

The rate of the first initiation step is negligibly small in comparison with the rest:

$$-\frac{d[\text{O}_3]}{d\tau} = 2 k_3 \cdot \left(\frac{k_1}{k_4} \right)^{1/2} \cdot [\text{Cl}_2]^{1/2} \cdot [\text{O}_3]^{3/2}$$