Problem 3-02 Mechanism

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

$$Cl_2 + O_3 \xrightarrow{k_1} ClO^{\bullet} + ClO_2^{\bullet}$$
$$ClO_2^{\bullet} + O_3 \xrightarrow{k_2} ClO_3^{\bullet} + O_2$$
$$ClO_3^{\bullet} + O_3 \xrightarrow{k_3} ClO_2^{\bullet} + 2\,O_2$$
$$ClO_3^{\bullet} + ClO_3^{\bullet} \xrightarrow{k_4} Cl_2 + 3\,O_2$$

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.

$$\left[-\frac{d[O_3]}{d\tau} = 2\,k_3 \cdot \left(\frac{k_1}{k_4}\right)^{1/2} \cdot [Cl_2]^{1/2} \cdot [O_3]^{3/2}\right]$$

Solution:

Decrease of ozone concentration with time:

$$-\frac{d[O_3]}{d\tau} = k_1 \cdot [Cl_2] \cdot [O_3] + k_2 \cdot [ClO_2^{\bullet}] \cdot [O_3] + k_3 \cdot [ClO_3^{\bullet}] \cdot [O_3] \qquad (1)$$

Unstable intermediates:

$$\left.\begin{aligned}\frac{d[ClO_2^{\bullet}]}{d\tau} &= 0 = r_1 - r_2 + r_3\\ \frac{d[ClO_3^{\bullet}]}{d\tau} &= 0 = r_2 - r_3 - r_4\end{aligned}\right\} \quad \begin{aligned} r_1 &= r_4 \\ k_1 \cdot [Cl_2] \cdot [O_3] &= k_4 \cdot [ClO_3^{\bullet}]^2\end{aligned} \;\Rightarrow\; [ClO_3^{\bullet}] = \left(\frac{k_1}{k_4} \cdot [Cl_2] \cdot [O_3]\right)^{1/2}$$

$$-\frac{d[ClO_2^{\bullet}]}{d\tau} = 0 = k_1 \cdot [Cl_2] \cdot [O_3] - k_2 \cdot [ClO_2^{\bullet}] \cdot [O_3] + k_3 \cdot [ClO_3^{\bullet}] \cdot [O_3] =$$

$$0 = k_1 \cdot [Cl_2] \cdot [O_3] - k_2 \cdot [ClO_2^{\bullet}] \cdot [O_3] + k_3 \cdot \left(\frac{k_1}{k_4} \cdot [Cl_2] \cdot [O_3]\right)^{1/2} \cdot [O_3]$$

$$[ClO_2^{\bullet}] = \frac{k_1 \cdot [Cl_2] \cdot [O_3]}{k_2 \cdot [O_3]} + \frac{k_3}{k_2 \cdot [O_3]} \cdot \left(\frac{k_1}{k_4} \cdot [Cl_2] \cdot [O_3]\right)^{1/2} \cdot [O_3] = \frac{k_1}{k_2} \cdot [Cl_2] + \frac{k_3}{k_2} \cdot \left(\frac{k_1}{k_4} \cdot [Cl_2] \cdot [O_3]\right)^{1/2}$$

Substituting $[ClO_2^{\bullet}]$ and $[ClO_3^{\bullet}]$ into eq. (1):

$$-\frac{d[O_3]}{d\tau} = k_1 \cdot [Cl_2] \cdot [O_3] + k_2 \cdot [ClO_2^{\bullet}] \cdot [O_3] + k_3 \cdot [ClO_3^{\bullet}] \cdot [O_3] =$$

$$= k_1 \cdot [Cl_2] \cdot [O_3] + k_2 \cdot \frac{k_1}{k_2} \cdot [Cl_2] \cdot [O_3] + \frac{k_3}{k_2} \cdot \left(\frac{k_1}{k_4} \cdot [Cl_2] \cdot [O_3]\right)^{1/2} \cdot [O_3] +$$

$$+ k_3 \cdot \left(\frac{k_1}{k_4} \cdot [Cl_2] \cdot [O_3]\right)^{1/2} \cdot [O_3]$$

$$= 2\,k_1 \cdot [Cl_2] \cdot [O_3] + 2\,k_3 \cdot \left(\frac{k_1}{k_4}\right)^{1/2} \cdot [Cl_2]^{1/2} \cdot [O_3]^{3/2}$$

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

$$-\frac{d[O_3]}{d\tau} = 2\,k_3 \cdot \left(\frac{k_1}{k_4}\right)^{1/2} \cdot [Cl_2]^{1/2} \cdot [O_3]^{3/2}$$