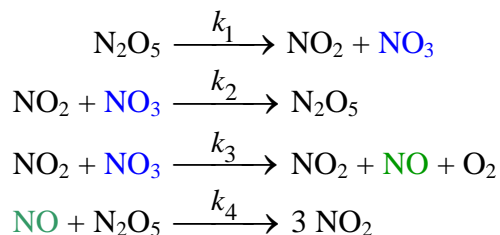


Problem 3-03 Reaction mechanism

The decomposition of nitric oxide, $\text{N}_2\text{O}_5 = 2 \text{NO}_2 + \frac{1}{2} \text{O}_2$, proceeds probably according to the following scheme



NO and NO₃ are unstable intermediates. Write the rate equation of the decomposition.

$$\left[-\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} = \frac{2 k_1 \cdot k_3}{(k_2 + k_3)} \cdot [\text{N}_2\text{O}_5] \right]$$

Solution:

$$\begin{aligned}\frac{dc_{\text{NO}_3}}{d\tau} = 0 = r_1 - r_2 - r_3 &\quad \Rightarrow \quad r_1 = r_2 + r_3 : \\ k_1 \cdot [\text{N}_2\text{O}_5] = k_2 \cdot [\text{NO}_2] \cdot [\text{NO}_3] + k_3 \cdot [\text{NO}_2] \cdot [\text{NO}_3] \\ [\text{NO}_3] = \frac{k_1 \cdot [\text{N}_2\text{O}_5]}{[\text{NO}_2] \cdot (k_2 + k_3)}\end{aligned}$$

$$\begin{aligned}\frac{dc_{\text{NO}}}{d\tau} = 0 = r_3 - r_4 &\quad \Rightarrow \quad r_3 = r_4 : \\ k_3 \cdot [\text{NO}_2] \cdot [\text{NO}_3] = k_4 \cdot [\text{NO}] \cdot [\text{N}_2\text{O}_5] \\ k_3 \cdot [\text{NO}_2] \cdot \frac{k_1 \cdot [\text{N}_2\text{O}_5]}{[\text{NO}_2] \cdot (k_2 + k_3)} = k_4 \cdot [\text{NO}] \cdot [\text{N}_2\text{O}_5] \Rightarrow [\text{NO}] = \frac{k_1 \cdot k_3}{k_4 \cdot (k_2 + k_3)}\end{aligned}$$

Reaction rate:

$$\begin{aligned}-\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} = r_1 - r_2 + r_4 &= k_1 \cdot [\text{N}_2\text{O}_5] - k_2 \cdot [\text{NO}_2] \cdot [\text{NO}_3] + k_4 \cdot [\text{NO}] \cdot [\text{N}_2\text{O}_5] \\ &= k_1 \cdot [\text{N}_2\text{O}_5] - k_2 \cdot [\text{NO}_2] \cdot \frac{k_1 \cdot [\text{N}_2\text{O}_5]}{[\text{NO}_2] \cdot (k_2 + k_3)} + k_4 \cdot \frac{k_1 \cdot k_3}{k_4 \cdot (k_2 + k_3)} \cdot [\text{N}_2\text{O}_5] \\ &= k_1 \cdot [\text{N}_2\text{O}_5] - \frac{k_1 \cdot k_2}{(k_2 + k_3)} \cdot [\text{N}_2\text{O}_5] + \frac{k_1 \cdot k_3}{(k_2 + k_3)} \cdot [\text{N}_2\text{O}_5] \\ &= \frac{k_1(k_2 + k_3) - k_1 \cdot k_2 + k_1 \cdot k_3}{(k_2 + k_3)} \cdot [\text{N}_2\text{O}_5] \\ -\frac{dc_{\text{N}_2\text{O}_5}}{d\tau} &= \frac{2 k_1 \cdot k_3}{(k_2 + k_3)} \cdot [\text{N}_2\text{O}_5]\end{aligned}$$