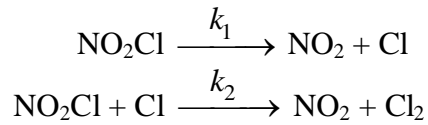


Problem 3-01 Reaction mechanisms

The decomposition $\text{NO}_2\text{Cl} = \text{NO}_2 + 1/2 \text{Cl}_2$ is a first-order reaction for which the following mechanism was proposed:



Assume that atomic chlorine is so reactive that it cannot be proved in the reaction mixture. Show that the proposed mechanism corresponds to experimental reaction order.

$$\left[-\frac{dc_{\text{NO}_2\text{Cl}}}{d\tau} = 2 k_1 \cdot c_{\text{NO}_2\text{Cl}} \right]$$

Solution:

Reaction rate = rate of NO_2Cl decrease:

$$-\frac{dc_{\text{NO}_2\text{Cl}}}{d\tau} = k_1 \cdot c_{\text{NO}_2\text{Cl}} + k_2 \cdot c_{\text{NO}_2\text{Cl}} \cdot c_{\text{Cl}}$$

Cl is unstable intermediate:

$$\frac{dc_{\text{Cl}}}{d\tau} = 0 = k_1 \cdot c_{\text{NO}_2\text{Cl}} - k_2 \cdot c_{\text{NO}_2\text{Cl}} \cdot c_{\text{Cl}} \quad \Rightarrow \quad c_{\text{Cl}} = \frac{k_1}{k_2}$$

$$-\frac{dc_{\text{NO}_2\text{Cl}}}{d\tau} = k_1 \cdot c_{\text{NO}_2\text{Cl}} + k_2 \cdot c_{\text{NO}_2\text{Cl}} \cdot \frac{k_1}{k_2}$$

$$-\frac{dc_{\text{NO}_2\text{Cl}}}{d\tau} = 2 k_1 \cdot c_{\text{NO}_2\text{Cl}}$$