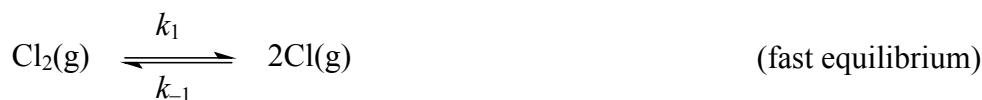


- It has been proposed that the reaction $\text{Cl}_2(\text{g}) + \text{CHCl}_3(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{CCl}_4(\text{g})$ proceeds by the following mechanism:

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Derive the rate expression for this mechanism.

As the second reaction is slow, it is rate determining. From the mechanism, the rate of this step is given by:

$$\text{rate} = k_2[\text{Cl}(\text{g})][\text{CHCl}_3(\text{g})]$$

As Cl is a highly reactive intermediate, its concentration cannot be included in the rate equation which is to be experimentally tested. As the first step is fast, the equilibrium between $\text{Cl}_2(\text{g})$ and $\text{Cl}(\text{g})$ will be set up rapidly and maintained for most of the reaction. For an equilibrium,

rate forward reaction = rate backward reaction

$$k_1[\text{Cl}_2(\text{g})] = k_{-1}[\text{Cl}(\text{g})]^2$$

$$\text{or } [\text{Cl}(\text{g})]^2 = \frac{k_1}{k_{-1}}[\text{Cl}_2(\text{g})]$$

Hence,

$$\text{rate} = k_2[\text{Cl}(\text{g})][\text{CHCl}_3(\text{g})] = k_2 \times \sqrt{\frac{k_1}{k_{-1}}[\text{Cl}_2(\text{g})]} \times [\text{CHCl}_3(\text{g})]$$

$$= k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{CHCl}_3(\text{g})][\text{Cl}_2(\text{g})]^{1/2} = k[\text{CHCl}_3(\text{g})][\text{Cl}_2(\text{g})]^{1/2}$$

$$\text{where } k = k_2 \sqrt{\frac{k_1}{k_{-1}}}$$

$$\text{Answer: rate} = k[\text{CHCl}_3(\text{g})][\text{Cl}_2(\text{g})]^{1/2}$$

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.