Marks 2

- It has been proposed that the reaction $Cl_2(g) + CHCl_3(g) \rightarrow HCl(g) + CCl_4(g)$ proceeds by the following mechanism:

$$Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl(g) \qquad \text{(fast equilibrium)}$$

$$Cl(g) + CHCl_3(g) \xrightarrow{k_2} HCl(g) + CCl_3(g) \qquad \text{(slow)}$$

$$CCl_3(g) + Cl(g) \xrightarrow{k_3} CCl_4(g) \qquad \text{(fast)}$$

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:

$$\text{rate} = k_2[Cl(g)][CHCl_3(g)]$$

As Cl is a highly reactive intermediate, its concentration cannot be included in the rate equation which is to be experimental tested. As the first step is fast, the equilibrium between $Cl_2(g)$ and Cl(g) will be set up rapidly and maintained for most of the reaction. For an equilibrium,

rate forward reaction = rate backward reaction

$$k_1[Cl_2(g)] = k_{-1}[Cl(g)]^2$$

$$\text{or } [Cl(g)]^2 = \frac{k_1}{k_{-1}}[Cl_2(g)]$$

Hence,

$$\text{rate} = k_2[Cl(g)][CHCl_3(g)] = k_2 \times \sqrt{\frac{k_1}{k_{-1}}[Cl_2(g)]} \times [CHCl_3(g)$$

$$= k_2\sqrt{\frac{k_1}{k_{-1}}}[CHCl_3(g)][Cl(g)]^{1/2} = k[CHCl_3(g)][Cl(g)]^{1/2}$$

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

Answer: rate = $k[CHCl_3(g)][Cl(g)]^{1/2}$

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.