Phosgene rate expression derivation

⇒ reaction: $CO + Cl_2 \rightarrow COCl_2$

mechanism: ① $\boxed{Cl_2 \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} 2Cl}$. (fast)

② $Cl + CO \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} COCl$. (fast)

③ $COCl + Cl_2 \underset{}{\overset{k_{f3}}{\rightleftharpoons}} COCl_2 + Cl$ (slow)

Assumption

Phosgene.

As highlighted above Cl & $COCl$ are intermediates therefore PSA can be valid on both.

$$r_{COCl_2} = \frac{d[COCl_2]}{dt} =$$

⇒ Rate expression is:

$$r_{COCl_2} = k_{f3}[COCl][Cl_2] - k_{b3}[COCl_2][Cl]$$

Assuming that $k_{f3} \gg k_{b3}$

$$\therefore \boxed{r = k_{f3}[COCl][Cl_2]} \rightarrow \text{eq 1}$$

we find an expression for each of the terms above and substitute to get the desired form.

For $[CoCl]$, Applying PSA:

$$\frac{d[CoCl]}{dt} = 0 = k_{f_2}[Co][Cl] - k_{b2}[CoCl] - k_{f3}[CoCl][Cl_2] \quad \text{eq 2}$$

$$k_{f_2}[Co][Cl] = \{k_{b_2} + k_{f3}[Cl_2]\}[CoCl]$$

$$\therefore \quad [CoCl] = \frac{k_{f_2}[Co][Cl]}{k_{b_2} + k_{f3}[Cl_2]} \quad \text{eq 3}$$

unknown

Now for $[Cl]$, Applying PSA:

cost

$$\frac{d[Cl]}{dt} = 0 = k_{f1}[Cl_2] - k_{b1}[Cl]^2 + k_{f2}[Co][Cl] - k_{b2}[CoCl] - k_{f3}[CoCl][Cl_2] \quad \text{eq 4}$$

The underlined term is equal to zero as per eq 2

$$\therefore \quad k_{f_1}[Cl_2] = k_{b_1}[Cl]^2$$

$$\therefore \quad [Cl] = \left(\frac{k_{f_1}}{k_{b_1}}\right)^{1/2} [Cl_2]^{1/2}$$

Substituting $[Cl]$ in eq 3 :

$$[CoCl] = \frac{k_{f_2} \quad [Co]}{k_{b_2} + k_{f_3}[Cl_2]} \times \left(\frac{k_{f_1}}{k_{b_1}}\right)^{1/2} [Cl_2]^{1/2}$$

Substituting $[CoCl]$ in eq ① :

$$r = \frac{k_{f_3} \; k_{f_2} \quad [Co]}{k_{b_2} + k_{f_3}[Cl_2]} \times \left(\frac{k_{f_1}}{k_{b_1}}\right)^{1/2} [Cl_2]^{3/2}$$

Since $k_{f_3}, k_{f_2}, k_{b_2} \gg k_{f_3}$

$$\therefore \quad \boxed{r = k_{eff} \, [Co] \, [Cl_2]^{3/2}}$$

where $\left\{ k_{eff} = \dfrac{k_{f3} \cdot k_{f2}}{k_{b2} + k_{f3}[Cl_2]} \times \left(\dfrac{k_{f1}}{k_{b1}}\right)^{1/2} \right.$

$$Cl_2 \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} 2Cl \quad \text{fast.}$$

ESA

$$\frac{d[Cl]}{dt} = k_{f1}[Cl] - k_{b1}[Cl]^2 = 0$$

$$[Cl] = \frac{k_b}{k_{f1}}[Cl]^2$$