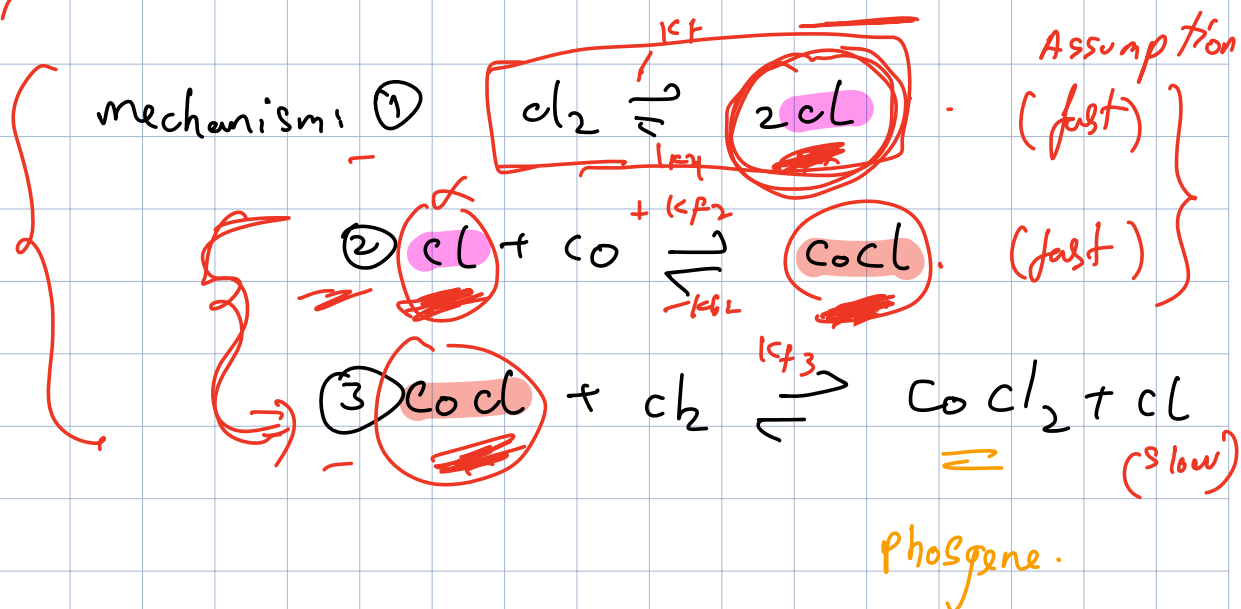
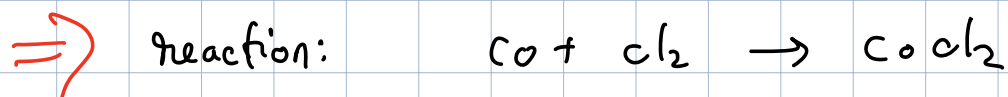


Phosgene rate expression derivation



As highlighted above $\text{Cl} \cdot$ & $\text{COCl} \cdot$ are intermediates therefore PSA can be valid on both.

⇒ Rate expression is:

$$r_{\text{COCl}_2} = \frac{d[\text{COCl}_2]}{dt}$$

$$\left\{ \begin{aligned} r_{\text{COCl}_2} &= k_{f3} [\text{COCl} \cdot] [\text{Cl}_2] \\ &\quad - k_{b3} [\text{COCl}_2] [\text{Cl} \cdot] \end{aligned} \right.$$

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

∴ $r = k_{f3} [\text{COCl} \cdot] [\text{Cl}_2]$ (eq 1)

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

in

the desired form.

For $[CoCl]$, Applying PSA:

$$\left\{ \frac{d[CoCl]}{dt} = 0 = k_{f2}[Co][Cl] - k_{b2}[CoCl] - k_{f3}[CoCl][Cl_2] \right.$$

eq 2

$$k_{f2}[Co][Cl] = \{k_{b2} + k_{f3}[Cl_2]\}[CoCl]$$

$$\therefore [CoCl] = \frac{k_{f2}[Co][Cl]}{k_{b2} + k_{f3}[Cl_2]}$$

eq 3

Now for $[Cl]$, Applying PSA:

lost

$$\left\{ \frac{d[Cl]}{dt} = 0 = k_{f1}[Cl_2] - k_{b1}[Cl]^2 + k_{f2}[Co][Cl] - k_{b2}[CoCl] - k_{f3}[CoCl][Cl_2] \right.$$

eq 4

The underlined term is equal to zero
as per eq 2

$$\therefore k_{f1} [Cl_2] = k_{b1} [Cl]^2$$

$$\therefore [Cl] = \left(\frac{k_{f1}}{k_{b1}} \right)^{1/2} [Cl_2]^{1/2}$$

Substituting $[Cl]$ in eq 3 :

$$[CoCl] = \frac{k_{f2} [Co]}{k_{b2} + k_{f3} [Cl_2]} \times \left(\frac{k_{f1}}{k_{b1}} \right)^{1/2} [Cl_2]^{1/2}$$

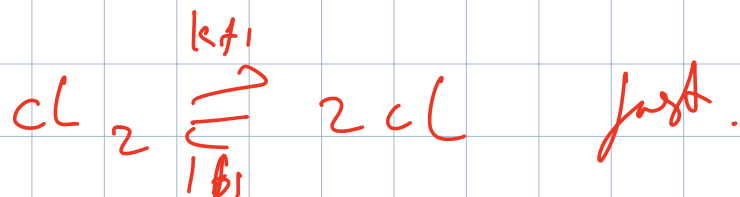
Substituting $[CoCl]$ in eq ① :

$$r = \frac{k_{f3} k_{f2} [Co]}{k_{b2} + k_{f3} [Cl_2]} \times \left(\frac{k_{f1}}{k_{b1}} \right)^{1/2} [Cl_2]^{3/2}$$

Since $k_{f3}, k_{f2}, k_{b2} \gg k_{f3}$

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

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



ESA $\Rightarrow \left[\frac{d[CC]}{dt} = k_{f1}[Cl] - k_{b1}[CC]^2 = 0 \right]$
 ~~$[CC]$~~ \Rightarrow

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