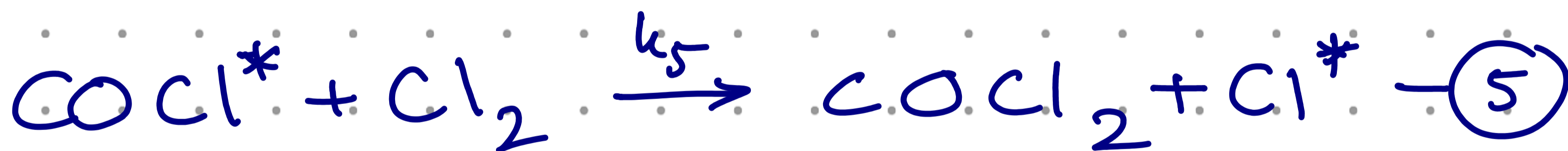
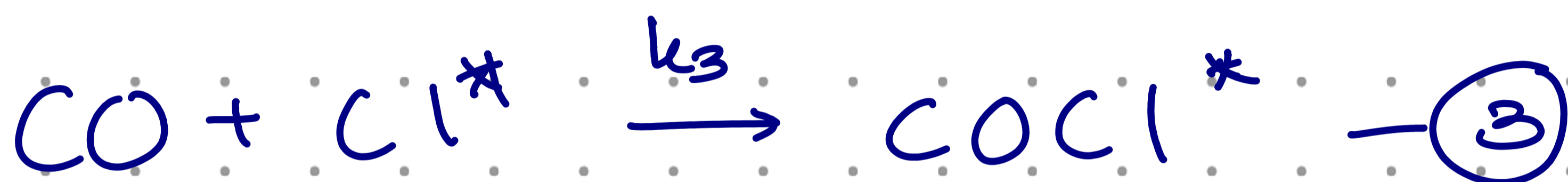
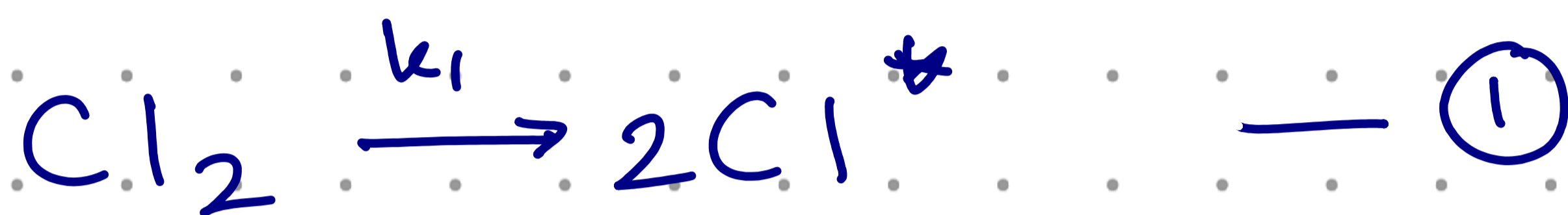


Active intermediates : Cl^* , COCl^*

Reactions:



Rates:

$$r_1 = k_1 [\text{Cl}_2]$$

$$r_2 = k_2 [\text{Cl}^*]^2$$

$$r_3 = k_3 [\text{CO}][\text{Cl}^*]$$

$$r_4 = k_4 [\text{COCl}^*]$$

$$r_5 = k_5 [\text{COCl}^*][\text{Cl}_2]$$

Rate of product formation

$$r_{\text{COCl}_2} = r_5 = k_5 [\text{COCl}^*] [\text{Cl}^*]$$

Net rate of formation of active intermediates

$$r_{\text{COCl}^*} = r_3 - r_4 - r_5$$

$$r_{\text{Cl}^*} = \frac{r_1}{2} - r_2 - r_3 + r_4 + r_5$$

PSSH:

$$r_{\text{COCl}^*} = 0 = k_3 [\text{CO}] [\text{Cl}^*] - k_4 [\text{COCl}^*] - k_5 [\text{COCl}^*] [\text{Cl}_2]$$

$$\Rightarrow [\text{COCl}^*] = \frac{k_3 [\text{CO}] [\text{Cl}^*]}{k_4 + k_5 [\text{Cl}_2]}$$

$$r_{\text{Cl}^*} = 0 \Rightarrow r_{\text{Cl}^*} + r_{\text{COCl}^*} = 0$$

$$\Rightarrow \cancel{r_3} - \cancel{r_4} - \cancel{r_5} + \frac{r_1}{2} - r_2 - \cancel{r_3} + \cancel{r_4} + \cancel{r_5} = 0$$

$$\Rightarrow \frac{r_1}{2} - r_2 = 0 \quad \frac{k_1}{2} [\text{Cl}_2] - k_2 [\text{Cl}^*]^2 = 0$$

$$[\text{Cl}^*] = \sqrt{\frac{k_1}{2k_2} [\text{Cl}_2]}$$

$$r_{\text{COCl}_2} = k_5 \left[\frac{k_3 [\text{CO}] \sqrt{\frac{k_1}{2k_2}} [\text{Cl}_2]^{1/2}}{k_4 + k_5 [\text{Cl}_2]} \right] [\text{Cl}_2]$$

$$r_{\text{COCl}_2} = \frac{k' [\text{CO}] [\text{Cl}_2]^{3/2}}{k_4 + k_5 [\text{Cl}_2]}$$

$$k' = k_3 k_5 \sqrt{\frac{k_1}{2k_2}}$$

IF $k_4 \gg k_5 [\text{Cl}_2]$

$$r_{\text{COCl}_2} = k [\text{CO}] [\text{Cl}_2]^{3/2}$$

$$k = \frac{k'}{k_4}$$