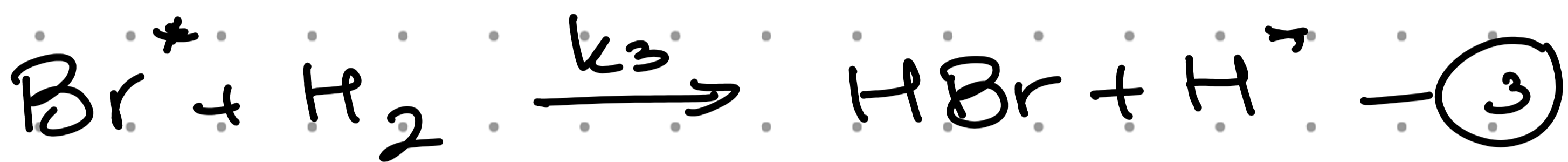
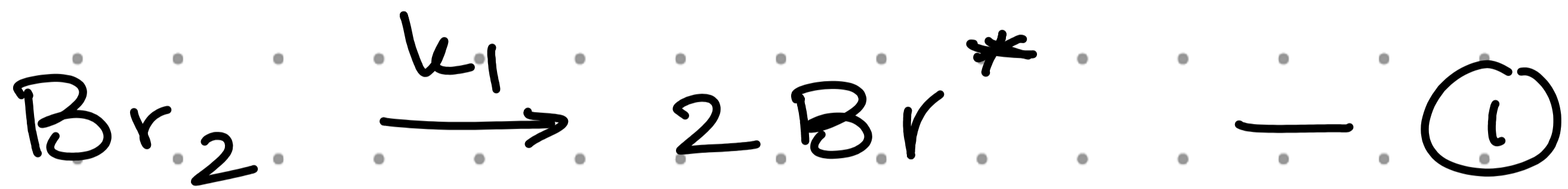


Active intermediates : Br^* , H^*

Mechanism :



Rates:

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

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

$$r_3 = k_3 [\text{Br}^*] [\text{H}_2]$$

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

$$r_5 = k_5 [\text{H}^*] [\text{Br}_2]$$

Rate of production of HBr

$$r_{\text{HBr}} = r_3 - r_4 + r_5$$

$$r_{\text{HBr}} = k_3 [\text{Br}^*] [\text{H}_2] - k_4 [\text{HBr}] [\text{H}^*] + k_5 [\text{H}^*] [\text{Br}_2]$$

PSSH:

$$r_{\text{Br}^*} = \frac{r_1}{2} - r_2 - r_3 + r_4 + r_5 = 0$$

$$r_{\text{H}^*} = r_3 - r_4 - r_5 = 0$$

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

$$0 = \frac{r_1}{2} - r_2$$

$$\frac{k_1}{2} [\text{Br}_2] - k_2 [\text{Br}^*]^2 = 0$$

$$[\text{Br}^*] = \left(\frac{k_1}{2k_2} [\text{Br}_2] \right)^{1/2}$$

$$r_{\text{H}^*} \Rightarrow k_3 [\text{Br}^*] [\text{H}_2] - k_4 [\text{HBr}] [\text{H}^*] - k_5 [\text{H}^*] [\text{Br}_2] = 0$$

$$[\text{H}^*] = \frac{k_3 [\text{H}_2] [\text{Br}^*]}{k_4 [\text{HBr}] + k_5 [\text{Br}_2]}$$

$$[H^*] = \frac{k_3 \left(\frac{k_1}{2k_2} \right)^{1/2} [H_2] [Br_2]^{1/2}}{k_4 [HBr] + k_5 [Br_2]}$$

$$\text{Let } k' = k_3 \left(\frac{k_1}{2k_2} \right)^{1/2}$$

$$r_{HBr} = k_3 [Br^*] [H_2] - k_4 [HBr] [H^*] + k_5 [H^*] [Br_2]$$

$$= k' [Br_2]^{1/2} [H_2]$$

$$- \cancel{k_4} k' [Br_2]^{1/2} [H_2] [HBr]$$

$$\cancel{k_4} \left([HBr] + \frac{k_5 [Br_2]}{k_4} \right)$$

$$+ k_5 k' [Br_2]^{3/2} [H_2]$$

$$k_4 \left([HBr] + \frac{k_5 [Br_2]}{k_4} \right)$$

~~$$= k' [Br]^{1/2} [H_2] [HBr] - k' [Br]^{1/2} [H_2] [HBr]$$~~

~~$$+ \left(\frac{k_5 k'}{k_4} \right) [Br]^{3/2} [H_2]$$~~

$$[HBr] + \frac{k_5}{k_4} [Br_2]$$

$$r_{\text{HBr}} = \frac{\left(\frac{k_5 k'}{k_4}\right) [\text{Br}]^{3/2} [\text{H}_2]}{[\text{HBr}] + \frac{k_5}{k_4} [\text{Br}_2]}$$

$$r_{\text{HBr}} = \frac{k'_1 [\text{Br}]^{3/2} [\text{H}_2]}{[\text{HBr}] + k'_2 [\text{Br}_2]}$$

$$k'_1 = \frac{k_5 k'}{k_4} k' \quad ; \quad k'_2 = \frac{k_5}{k_4}$$