$$H_2 + Br_2 \longrightarrow 2HBr$$

Active intermediates : Br^*, H^*

Mechanism :

$$Br_2 \xrightarrow{k_1} 2Br^* \quad -(1)$$

$$2Br^* \xrightarrow{k_2} Br_2 \quad -(2)$$

$$Br^* + H_2 \xrightarrow{k_3} HBr + H^* \quad -(3)$$

$$HBr + H^* \xrightarrow{k_4} Br^* + H_2 \quad -(4)$$

$$H^* + Br_2 \xrightarrow{k_5} HBr + Br^* \quad -(5)$$

Rates :

$$r_1 = k_1 [Br_2]$$

$$r_2 = k_2 [Br^*]^2$$

$$r_3 = k_3 [Br^*][H_2]$$

$$r_4 = k_4 [HBr][H^*]$$

$$r_5 = k_5 [H^*][Br_2]$$

Rate of production of HBr

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

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

PSSH:

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

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

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

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

$$\frac{k_1}{2}[Br_2] - k_2[Br^*]^2 = 0$$

$$[Br^*] = \left(\frac{k_1}{2k_2}[Br_2]\right)^{1/2}$$

$$r_{H^*} \Rightarrow k_3 [Br^*][H_2] - k_4 [HBr][H^*] - k_5 [H^*][Br_2] = 0$$

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

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

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

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

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

$$\frac{}{k_4\left([HBr] + \frac{k_5}{k_4}[Br_2]\right)} + k_5 k'[Br_2]^{3/2}[H_2]$$

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

$$= \frac{k'[Br]^{1/2}[H_2][HBr] - k'[Br]^{1/2}[H_2][HBr] + \left(\frac{k_5 k'}{k_4}\right)[Br]^{3/2}[H_2]}{[HBr] + \frac{k_5}{k_4}[Br_2]}$$

$$r_{HBr} = \frac{\left(\frac{k_5 k'}{k_4}\right)[Br]^{3/2}[H_2]}{[HBr] + \frac{k_5}{k_4}[Br_2]}$$

$$r_{HBr} = \frac{k'_1 [Br]^{3/2}[H_2]}{[HBr] + k'_2 [Br_2]}$$

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