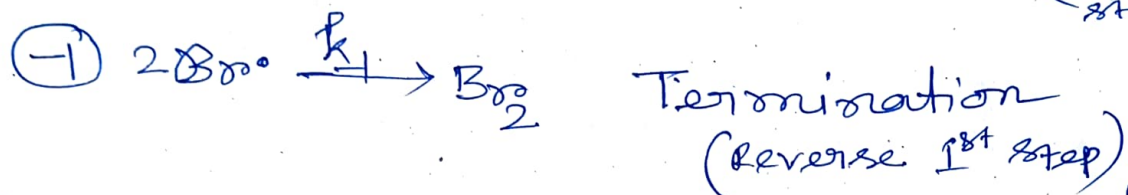
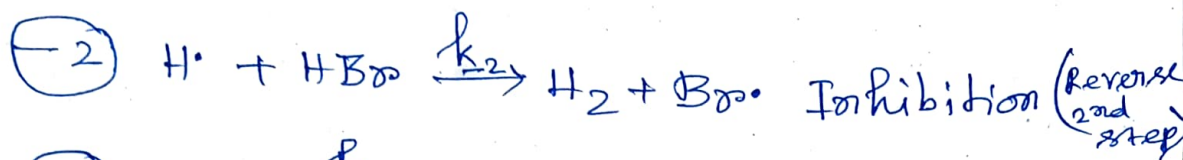
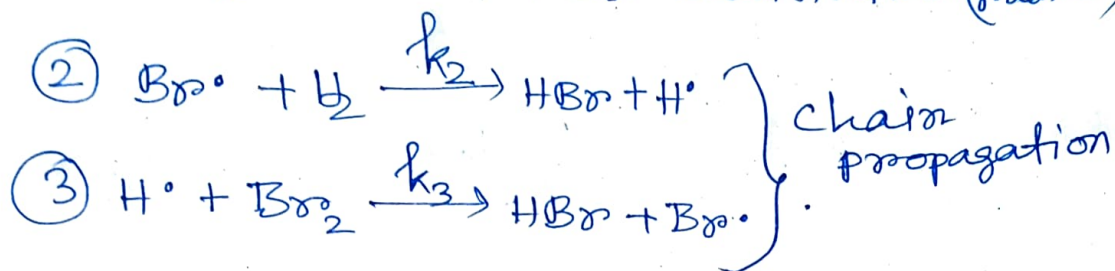
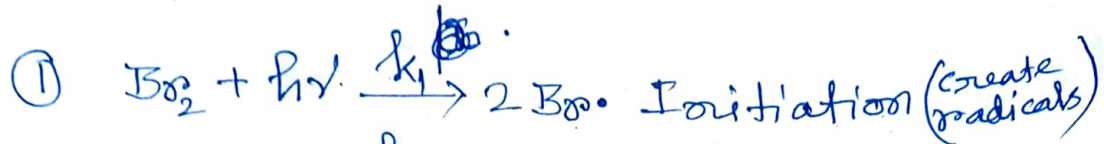


① Hydrogen - Bromine Reaction (photochemical)

The proposed mechanism is



Steady-state approximation on radicals \rightarrow very reactive, never build up

See the condition of steady state approximation

The steady-state hypothesis must be applied to the two intermediates $\text{Br}\cdot$ and $\text{H}\cdot$, both of which are present at very low concentrations.

The steady-state equation for $\text{H}\cdot$ is

$$\frac{d[\text{H}\cdot]}{dt} = k_2[\text{Br}\cdot][\text{H}_2] - k_3[\text{H}\cdot][\text{Br}_2] - k_4[\text{H}\cdot][\text{HBr}] = 0 \quad \text{--- ①}$$

That for $\text{Br}\cdot$ is

$$\frac{d[\text{Br}\cdot]}{dt} = 2I - k_2[\text{Br}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Br}_2] + k_4[\text{H}\cdot][\text{HBr}] - k_5[\text{Br}\cdot]^2 = 0 \quad \text{--- ②}$$

On adding ① and ②, we get

$$\frac{d[H^\cdot]}{dt} = k_2[H_2][Br^\cdot] - k_3[H^\cdot][Br_2] - k_{-2}[H^\cdot][HBr] = 0 \quad \text{--- ①}$$

$$\frac{d[Br^\cdot]}{dt} = 2I - k_2[H_2][Br^\cdot] + k_3[H^\cdot][Br_2] + k_{-2}[H^\cdot][HBr] - k_1[Br^\cdot]^2 = 0 \quad \text{--- ②}$$

I is the intensity of light absorbed, $2I$ is the amount of Br^\cdot produced under the same condition.

$$2I - k_1[Br^\cdot]^2 = 0$$

$$[Br^\cdot] = \sqrt{\frac{2I}{k_1}} \quad \text{--- ③}$$

Substituting the value of $[Br^\cdot]$ in equation (1), we get

$$k_2[H_2]\sqrt{\frac{2I}{k_1}} - k_3[H^\cdot][Br_2] - k_{-2}[H^\cdot][HBr] = 0$$

$$[H^\cdot](k_3[Br_2] + k_{-2}[HBr]) = k_2\sqrt{\frac{2I}{k_1}}[H_2]$$

$$[H^\cdot] = \frac{k_2\sqrt{\frac{2I}{k_1}}[H_2]}{k_3[Br_2] + k_{-2}[HBr]} \quad \text{--- ④}$$

The rate of reaction is the rate of consumption of H_2 , which is

$$v_p = -\frac{d[H_2]}{dt} = k_2[Br^\cdot][H_2] - k_{-2}[H^\cdot][HBr] \quad \text{--- ⑤}$$

from eq. (1), we obtain

$$k_2[H_2][Br^\cdot] - k_{-2}[H^\cdot][HBr] = k_3[H^\cdot][Br_2] \quad \text{--- ⑥}$$

③ Insertion of the eq. (6) into eq. (5) gives

$$v_p = -\frac{d[H_2]}{dt} = k_3[H^+][Br_2] \quad \text{--- (7)}$$

Again, substitution of eq. (4) into eq. (2) yields

$$\begin{aligned} v_p &= -\frac{d[H_2]}{dt} = k_3[Br_2] \frac{k_2 \sqrt{\frac{2I}{k_1}} [H_2]}{k_3[Br_2] + k_{-2}[HBr]} \\ &= \frac{k_2 k_3 \sqrt{\frac{2I}{k_1}} [H_2][Br_2]}{k_3[Br_2] + k_{-2}[HBr]} \\ &= \frac{k_2 (2I/k_1)^{1/2} [H_2]}{1 + \left(\frac{k_{-2}}{k_3} \right) \frac{[HBr]}{[Br_2]}} \quad \text{--- (8)} \end{aligned}$$

The rate of thermal reaction

$$\text{is } v_t = -\frac{d[H_2]}{dt} = \frac{k_2 \left(\frac{k_1}{k_{-1}} \right)^{1/2} [H_2][Br_2]^{1/2}}{1 + \left(\frac{k_{-2}}{k_3} \right) \frac{[HBr]}{[Br_2]}} \quad \text{--- (9)}$$

The ratio of the photochemical and thermal rates is

$$\frac{v_p}{v_t} = \frac{k_2 \left(\frac{2I}{k_1} \right)^{1/2} [H_2]}{1 + \left(\frac{k_{-2}}{k_3} \right) \frac{[HBr]}{[Br_2]}} \times \frac{1 + \left(\frac{k_{-2}}{k_3} \right) \frac{[HBr]}{[Br_2]}}{k_2 \left(\frac{k_1}{k_{-1}} \right)^{1/2} [H_2][Br_2]^{1/2}}$$

$$\frac{v_p}{v_t} = \sqrt{\frac{2I}{k_1}} \frac{\sqrt{k_1}}{\sqrt{k_1}} \frac{1}{[Br_2]^{\frac{1}{2}}} = \sqrt{\frac{2}{k_1}} \frac{I^{\frac{1}{2}}}{[Br_2]^{\frac{1}{2}}}$$

at the same concentrations of H_2 and Br_2 . Therefore, if v_p/v_t is measured at known values of I and $[Br_2]$, the rate constant k_1 can be obtained.