① Hydrogen – Bromine Reaction (Photochemical)

The proposed mechanism is

① $Br_2 + h\nu \xrightarrow{k_1} 2\,Br\cdot$ Initiation (Create radicals)

② $Br\cdot + H_2 \xrightarrow{k_2} HBr + H\cdot$

③ $H\cdot + Br_2 \xrightarrow{k_3} HBr + Br\cdot$

② + ③ : chain propagation

−② $H\cdot + HBr \xrightarrow{k_{-2}} H_2 + Br\cdot$ Inhibition (Reverse 2nd step)

−① $2\,Br\cdot \xrightarrow{k_{-1}} Br_2$ Termination (Reverse 1st step)

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

See the condition of steady state approximation

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

The steady-state equation for $H\cdot$ is

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

$$= 0 \qquad \text{——— ①}$$

That for $Br\cdot$ is

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

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

$$k_2[H_2]\sqrt{\frac{2I}{k_{-1}}} - k_3[H^\cdot][Br_2] - k_{-2}[H^\cdot][HBr] = 0$$

$$[H^\cdot]\left(k_3[Br_2] + k_{-2}[HBr]\right) = k_2\sqrt{\frac{2I}{k_{-1}}}[H_2]$$

$$[H^\cdot] = \frac{k_2\sqrt{\frac{2I}{k_{-1}}}[H_2]}{k_3[Br_2] + k_{-2}[HBr]} \quad \text{—— ④}$$

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

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

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

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

Again, substitution of eq. ④ into eq ② yields

$$v_p = -\frac{d[H_2]}{dt} = k_3[Br_2]\frac{k_2\sqrt{\frac{2I}{k_1}}[H_2]}{k_3[Br_2]+k_{-2}[HBr]}$$

$$= \frac{k_2k_3\sqrt{\frac{2I}{k_1}}[H_2][Br_2]}{k_3[Br_2]+k_{-2}[HBr]}$$

$$= \frac{k_2\left(2I/k_1\right)^{1/2}[H_2]}{1+\left(\frac{k_{-2}}{k_3}\right)\frac{[HBr]}{[Br_2]}} \quad \text{—— 8}$$

The rate of thermal reaction is

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

The ratio of the photochemical and thermal rates is —— ⑨

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

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

at the same concentrations of I_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.