2. Kinetics of the Hydrogen–Bromine Reaction :

$$H_2(g) + Br_2(g) \xrightarrow{h\nu} 2HBr(g)$$

The mechanism of this reaction is given below :

(i) $$Br_2 + h\nu \xrightarrow{k_1} 2Br$$ $rate_1 = k_1[Br_2] = k_1 I_a$

(ii) $$Br + H_2 \xrightarrow{k_2} HBr + H$$ $rate_2 = k_2[Br][H_2]$

(iii) $$H + Br_2 \xrightarrow{k_3} HBr + Br$$ $rate_3 = k_3[H][Br_2]$

(iv) $$H + HBr \xrightarrow{k_4} H_2 + Br$$ $rate_4 = k_4[H][HBr]$

(v) $$2Br \xrightarrow{k_5} Br_2$$ $rate_5 = k_5[Br]^2$

The rate of formation of HBr is given by

$$r = \frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad ...(20)$$

Applying steady state approximation to [Br], we have

$$d[\mathrm{Br}]/dt = k_1 I_a - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{H}][\mathrm{HBr}] - k_5[\mathrm{Br}]^2 = 0 \quad ...(21)$$

Applying *s.s.a.* to [H], we have

$$d[\mathrm{H}]/dt = k_2[\mathrm{Br}][\mathrm{H_2}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] = 0 \quad ...(22)$$

Adding Eqs. 21 and 22,

$$k_1 I_a - k_5[\mathrm{Br}]^2 = 0 \text{ whence}$$

$$[\mathrm{Br}] = \left(\frac{k_1 I_a}{k_5}\right)^{1/2} \quad ...(23)$$

From Eq. 22,

$$[\mathrm{H}] = \frac{k_2[\mathrm{H_2}][\mathrm{Br}]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \quad ...(24)$$

Substituting Eq. 23 into Eq. 24, we have

$$[\mathrm{H}] = \frac{k_2(k_1 I_a/k_5)^{1/2}[\mathrm{H_2}]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \quad ...(25)$$

Sustituting Eqs. 23 and 25 into Eq. 20 and simplifying, we get

$$r = \frac{d[\mathrm{HBr}]}{dt} = \frac{2k_2(k_1/k_5)^{1/2} I_a^{1/2}[\mathrm{H_2}]}{1 + \dfrac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}} \quad ...(26)$$

We see that the *reaction rate varies as the square root of the intensity I_a of the absorbed radiation.* The rate law given by Eq. 26 agrees with the experimentally observed rate law. The quantum yield for this reaction is 0·01.