(2). Photochemical Reaction between —

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

The proposed mechanism for this reaction are —

(i) $Br_2 + h\nu \xrightarrow{I_{abs}} 2Br$

(ii) $Br + H_2 \xrightarrow{K_2} HBr + H$

(iii) $H + Br_2 \xrightarrow{K_3} HBr + Br$

(iv) $H + HBr \xrightarrow{K_4} H_2 + Br$

(v) $Br + Br \xrightarrow{K_5} Br_2$

The rate of formation of HBr is given by —

$$r = \frac{d[HBr]}{dt} = K_2[Br][H_2] + K_3[H][Br_2] - K_4[H][HBr] \quad —(1)$$

The rate of formation of 'Br' is given by —

$$\frac{d[Br]}{dt} = I_{abs} - K_2[Br][H_2] + K_3[H][Br_2] + K_4[H][HBr] - K_5[Br]^2$$

on using SSA —

$$0 = I_{abs} - K_2[Br][H_2] + K_3[H][Br_2] + K_4[H][HBr] - K_5[Br]^2 \quad —(2)$$

Similarly, the rate of formation of 'H' is given by —

$$\frac{d[H]}{dt} = K_2[Br][H_2] - K_3[H][Br_2] - K_4[H][HBr]$$

using SSA —

$$0 = K_2[Br][H_2] - K_3[H][Br_2] - K_4[H][HBr] \quad —(3)$$

Now adding eqs – (2) & (3) –

$$0 = I_{abs} - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - k_5[Br]^2 + k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr]$$

or $$I_{abs} - k_5[Br]^2 = 0$$

$$[Br]^2 = \frac{I_{abs}}{k_5}$$

or $$[Br] = \left(\frac{I_{abs}}{k_5}\right)^{1/2}$$

from eqs – (3)

$$0 = k_2\left(\frac{I_{abs}}{k_5}\right)^{1/2}[H_2] - k_3[H][Br_2] - k_4[H][HBr]$$

or $$0 = k_2\left(\frac{I_{abs}}{k_5}\right)^{1/2}[H_2] - \{k_3[Br_2] + k_4[HBr]\}[H]$$

or $$[H] = \frac{k_2\left(\frac{I_{abs}}{k_5}\right)^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]} \quad \text{—— (4)}$$

Now putting the value of [H] in eqs – (1) we get –

$$r = \frac{d[HBr]}{dt} = k_2[Br][H_2] + \frac{k_3 k_2\left(\frac{I_{abs}}{k_5}\right)^{1/2}[H_2][Br_2]}{k_3[Br_2] + k_4[HBr]} - \frac{k_4 k_2\left(\frac{I_{abs}}{k_5}\right)^{1/2}[H_2][HBr]}{k_3[Br_2] + k_4[HBr]} \quad \text{— (5)}$$

Now, putting the value of [Br] in eqs – (5) and solving we get,

$$r = \frac{d[HBr]}{dt} = \frac{2k_2\left(\frac{I_{abs}}{k_5}\right)^{1/2}[H_2]}{1 + \frac{k_4[HBr]}{k_3[Br_2]}} \quad \text{— (6)}$$

From eqn - (6) we see that the rate varies as the square root of the intensity Iabs of the absorbed radiation. The rate law given in eqn (6) agree with the observed rate law.

The quantum yield for this reaction is very low i.e. 0.01.

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