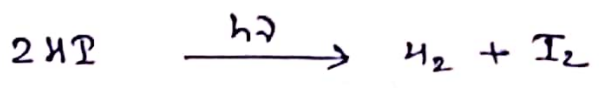


* Photolytic decomposition of HI.



The proposed mechanism for this reaction are:

- (i) $HI + h\nu \xrightarrow{P_{abs}} H + I$
- (ii) $H + HI \xrightarrow{k_2} H_2 + I$
- (iii) $I + I \xrightarrow{k_3} I_2$

The rate of decomposition of HI is given by -

$$-\frac{d[HI]}{dt} = P_{abs} + k_2 [H][HI] \quad \text{--- (1)}$$

The rate of formation of H is given by -

$$\frac{d[H]}{dt} = P_{abs} - k_2 [H][HI] \quad \text{--- (2)}$$

Using S.S.A

$$\frac{d[H]}{dt} = 0.$$

Hence, eqn (2) becomes -

$$0 = P_{abs} - k_2 [H][HI]$$

$$\Rightarrow P_{abs} = k_2 [H][HI]$$

$$\Rightarrow [H] = \frac{P_{abs}}{k_2 [HI]}$$

Putting the value of [H] in eqn (1) we get -

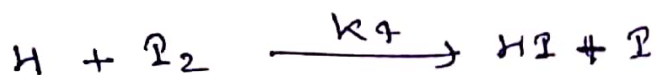
$$-\frac{d[HI]}{dt} = P_{abs} + \cancel{k_2} \frac{P_{abs}}{\cancel{k_2} [HI]} [HI]$$

$$-\frac{d[HI]}{dt} = 2 P_{abs}.$$

The quantum yield for such reaction is ϕ .

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When the reaction proceeds, the quantum yield (ϕ) decreases. This is due to the fact that as iodine accumulates, the thermal reaction -



Now, the rate of formation of H is given as -

$$\frac{d[H]}{dt} = I_{abs} - k_2 [H] [CHI] - k_4 [H] [I_2]$$

using SSA -

$$0 = I_{abs} - k_2 [H] [CHI] - k_4 [H] [I_2]$$

$$[H] = \frac{I_{abs}}{k_2 [CHI] + k_4 [I_2]}$$

putting the value of $[H]$ in eqn (1) we get,

$$-\frac{d[CHI]}{dt} = I_{abs} + k_2 [CHI] \frac{I_{abs}}{k_2 [CHI] + k_4 [I_2]}$$

$$-\frac{d[CHI]}{dt} = I_{abs} \left(1 + \frac{1}{1 + \{k_4 [I_2] / k_2 [CHI]\}} \right)$$

~~As the reaction proceeds,~~
As the reaction proceeds, $[I_2]$ increases and hence the quantum yield decreases.

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