* Photolytic decomposition of HI.

$$2HI \xrightarrow{h\nu} H_2 + I_2$$

The proposed mechanism for this reaction are:

(i) $HI + h\nu \xrightarrow{I_{abs}} H + I$

(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 –

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

The rate of formation of H is given by –

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

Using S.S.A

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

Hence, eqn (2) becomes –

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

$$\text{or} \quad I_{abs} = k_2 [H][HI]$$

$$\text{or} \quad [H] = \frac{I_{abs}}{k_2 [HI]}$$

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

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

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

The quantum yield for such reaction is 2.

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

$$H + I_2 \xrightarrow{k_4} HI + I$$

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

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

Using SSA -

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

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

putting the value of [H] in eq^n (1) we get,

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

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

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

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