SUBJECT - CHEMISTRY
CLASS - B.Sc (Hons) PART - III
PAPER - V
TOPIC - Kinetics of Decomposition of HI
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Kinetics of Decomposition of HI The following mechanism has been suggested for the photochemical decomposition of HI

(i) $HI \xrightarrow{h\nu, K_1} H + I$

(ii) $H + HI \xrightarrow{K_2} H_2 + I$

(iii) $I + I \xrightarrow{K_3} I_2$

The rate law for the decomposition of HI is

$$-\frac{d[H]}{dt} = K_1 I_a + K_2 [H][HI] \quad —— (1)$$

Applying steady state approximation to [H], we have

$$\frac{d[H]}{dt} = K_1 I_a - K_2 [H][HI] = 0 \quad -- (2)$$

$$\therefore K_2 [H][HI] = K_1 I_a \quad --- (3)$$

Substituting Eq (3) In Eq (1), we obtain

$$-\frac{d[HI]}{dt} = 2K_1 I_a \quad —— (4)$$

The quantum yield of the reaction is given by

$$\phi = \frac{\text{Rate of disappearance of HI}}{\text{Rate of absorption of light}} = \frac{-d[HI]/dt}{K_1 I_a}$$

$$= \frac{2K_1 I_a}{K_1 I_a} = 2$$

The reason why ϕ decreases as the reaction proceeds is that as iodine accumulates, the thermal reaction

$$H + I_2 \xrightarrow{K_4} HI + I$$

becomes significant. If this reaction is also included. Then the steady state approximation for [H] gives

$$\frac{d[H]}{dt} = K_1 I_a - K_2 [H][HI] - K_4 [H][I_2] = 0 \quad --(5)$$

$$\therefore [H] = \frac{K_1 I_a}{K_2 [HI] + K_4 [I_2]} \quad --(6)$$

Substituting for [H] from Eq-(6) in Eq(1), we obtain.

$$-\frac{d[HI]}{dt} = K_1 I_a + K_2 [HI] \frac{K_1 I_a}{K_2 [HI] + K_4 [I_2]}$$

$$= K_1 I_a \left(1 + \frac{1}{1 + \{K_4 [I_2] / K_2 [HI]\}}\right) \quad --(7)$$

$$\therefore \frac{-d[HI]/dt}{I_a} = K_1 + \frac{K_1}{1 + \{K_4 [I_2] / K_2 [HI]\}} \quad --(8)$$

As the reaction proceeds, $[I_2]$ increases whereas [HI] decreases; hence, the quantum yield decreases from the original value of 2.