

SUBJECT - CHEMISTRY

CLASS - B.Sc (Hons) PART - III

PAPER - V

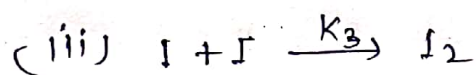
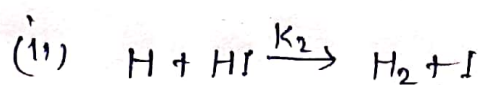
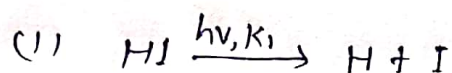
TOPIC - Kinetics of Decomposition of HI

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Kinetics of Decomposition of HI The following mechanism has been suggested for the photochemical decomposition of HI



The rate law for the decomposition of HI is

$$-\frac{d[HI]}{dt} = k_1 I_a + k_2 [H][HI] \quad \text{--- (1)}$$

Applying steady state approximation to [H], we have

$$\frac{d[H]}{dt} = k_1 I_a - k_2 [H][HI] = 0 \quad \text{--- (2)}$$

$$\therefore k_2 [H][HI] = k_1 I_a \quad \text{--- (3)}$$

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

$$-\frac{d[HI]}{dt} = 2k_1 I_a \quad \text{--- (4)}$$

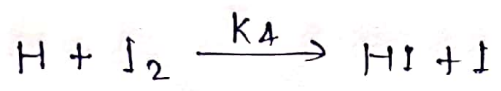
The quantum yield of the reaction is given by

$$\phi = \frac{\text{Rate of disappearance of HI}}{\text{Rate of absorption of light}} = \frac{-d[HI]/dt}{k_1 I_a}$$

$$= \frac{2k_1 I_a}{k_1 I_a} = 2$$

The reason why  $\phi$  decreases as the reaction proceeds is

That as iodine accumulates, the thermal reaction



becomes significant. If this reaction is also included,

Then the Steady State approximation for  $[H]$  gives

$$\frac{d[H]}{dt} = k_1 I_a - k_2 [H] [HI] - k_4 [H] [I_2] = 0 \dots (5)$$

$$\therefore [H] = \frac{k_1 I_a}{k_2 [HI] + k_4 [I_2]} \dots (6)$$

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

$$-\frac{d[HI]}{dt} = k_1 I_a + k_2 [HI] \frac{k_1 I_a}{k_2 [HI] + k_4 [I_2]}$$

$$= k_1 I_a \left( 1 + \frac{1}{1 + \{k_4 [I_2] / k_2 [HI]\}} \right) \dots (7)$$

$$\therefore \frac{-d[HI]/dt}{I_a} = k_1 + \frac{k_1}{1 + \{k_4 [I_2] / k_2 [HI]\}} \dots (8)$$

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