SUBJECT - CHEMISTRY

CLASS - B.Sc (Hons) PART - III

PAPER - V

TOPIC · kinetics of photochemical reaction

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Q Discuss briefly the Kinetic of the following photochemical reaction

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

Ans. Kinetic of the formation of HBr :

The photochemical Combination of moist H_2 and Br_2 vapour in visible light (< 510.7 nm) is a chain reaction. It occurs at 433-491 K.

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

The following mechanism is Suggested:

Chain initiation: i. $Br_2 + h\nu \xrightarrow{K_1} 2Br$

Chain propagation: ii $Br_2 + H_2 \xrightarrow{K_2} HBr + H$

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

Chain inhibition: iv $H + HBr \xrightarrow{K_4} H_2 + Br$

Chain termination v. $Br + Br \xrightarrow{K_5} Br_2$

where K_1, K_2, K_3, K_4 & K_5 are rate Constants. Since HBr is formed in steps (ii) and (iii) and removed in step (iv), hence the net rate of formation of HBr

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

The H atoms are formed in step (ii) and removed in steps (iii) and (iv), hence -

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

Applying Steady state approximation, one can get,

$$0 = K_2[Br][H_2] - K_3[H][Br_2] - K_4[H][HBr]$$

or $$K_2[Br][H_2] = K_3[H][Br_2] + K_4[H][HBr] \quad \ldots (2)$$

The Br-atoms are formed in steps (i), (iii) and (IV) and removed by steps (ii) and (V), hence

$$\frac{d[Br]}{dt} = K_1 I_{abs} - K_2[Br][H_2] + K_3[H][Br_2] + K_4[H][HBr] - K_5[Br]^2$$

Applying steady state approximation, we get-

$$K_1 I_{abs} + K_3[H][Br_2] + K_4[H][HBr] = K_2[H_2][Br] + K_5[Br]^2 \quad \ldots (3)$$

Substracting equation (2) from equation (3) we get-

$$K_1 I_{abs} = K_5[Br]^2$$

$$[Br] = (K_1 I_{abs}/K_5)^{1/2}$$

putting [Br] value in equation (2), we get-

$$K_2(K_1 I_{abs}/K_5)^{1/2}[H_2] = K_3[H][Br_2] + K_4[H][HBr]$$

or $$[H] = \frac{K_2[H_2](K_1 I_{abs}/K_5)^{1/2}}{K_3[Br_2] + K_4[HBr]}$$

Now putting [H] and [Br] in equation (1), we get

$$\frac{d[HBr]}{dt} = K_2[H_2](K_1 I_{abs}/K_5)^{1/2} + K_3\frac{K_2[H_2](K_1 I_{abs}/K_5)^{1/2}}{K_3[Br_2] + K_4[HBr]}[Br_2]$$

$$- K_4\frac{K_2[H_2](K_1 I_{abs})^{1/2}}{K_3[Br_2] + K_4[HBr]}[HBr]$$

$$= K_2(K_1 I_{abs}/K_5)^{1/2}[H_2]\left[1 + \frac{K_3[Br_2]}{K_3[Br_2] + K_4[HBr]} - \frac{K_4[HBr]}{K_3[Br_2] + K_4[HBr]}\right]$$

$$= K_2(K_1 I_{abs}/K_5)^{1/2}[H_2]\left[\frac{K_3[Br_2] + K_4[HBr] + K_3[Br_2] - K_4[HBr]}{K_3[Br_2] + K_4[HBr]}\right]$$

$$= K_2 (K_1 I_{abs}/K_5)^{1/2} [H_2] \left[\frac{2K_3 [Br_2]}{K_3[Br_2] + K_4 [HBr]} \right]$$

$$= \frac{2K_2 (K_1 I_{abs}/K_5)^{1/2} [H_2]}{K_3 [Br_2]/K_3 [Br_2] + K_4 [HBr]/K_3 [Br_2]}$$

$$= \frac{2K_2 (K_1/K_5)^{1/2} [H_2] (I_{abs})^{1/2}}{1 + K_4 [HBr]/K_3 [Br_2]}$$

or $$\frac{d[HBr]}{dt} \propto (I_{abs})^{1/2}$$

This equation agrees with the experimental value. Therefore The rate of the reaction varies with the square root of the intensity of light (I_{abs}).