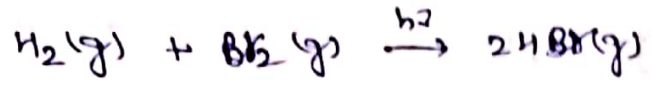
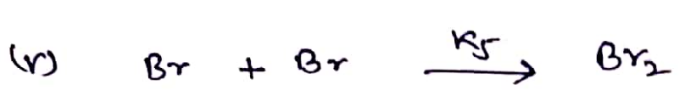
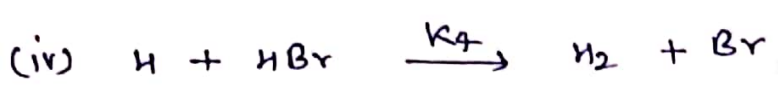
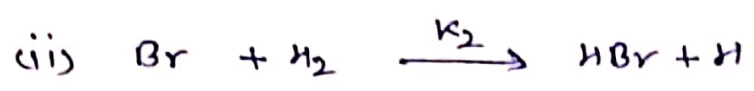
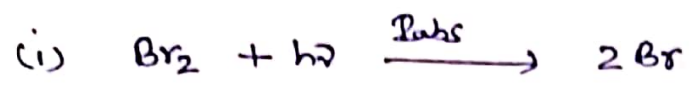


(2). Photochemical Reaction between —



The proposed mechanisms for this reaction are —



The rate of formation of HBr is given by —

$$r = \frac{d(HBr)}{dt} = k_2 [Br] [H_2] + k_3 [H] [Br_2] - k_4 [H] [HBr] \quad \text{--- (1)}$$

The rate of formation of 'Br' is given by —

$$\frac{d[Br]}{dt} = I_{abs} - k_2 [Br] [H_2] + k_3 [H] [Br_2] + k_4 [H] [HBr] - k_5 [Br]^2$$

on using SSA —

$$0 = I_{abs} - k_2 [Br] [H_2] + k_3 [H] [Br_2] + k_4 [H] [HBr] - k_5 [Br]^2 \quad \text{--- (2)}$$

Similarly, the rate of formation of 'H' is given by —

$$\frac{d[H]}{dt} = k_2 [Br] [H_2] - k_3 [H] [Br_2] - k_4 [H] [HBr]$$

using SSA —

$$0 = k_2 [Br] [H_2] - k_3 [H] [Br_2] - k_4 [H] [HBr] \quad \text{--- (3)}$$

Now adding eqs - (2) & (3) -

$$0 = r_{\text{obs}} - k_2 [\text{Br}] [\text{H}_2] + k_3 [\text{H}] [\text{Br}_2] + k_4 [\text{H}] [\text{HBr}] - k_5 [\text{Br}]^2 + k_2 [\text{Br}] [\text{H}_2] - k_3 [\text{H}] [\text{Br}_2] - k_4 [\text{H}] [\text{HBr}]$$

$$\therefore r_{\text{obs}} - k_5 [\text{Br}]^2 = 0$$

$$[\text{Br}]^2 = \frac{r_{\text{obs}}}{k_5}$$

$$\therefore [\text{Br}] = \left(\frac{r_{\text{obs}}}{k_5} \right)^{1/2}$$

from eqs - (3)

$$0 = k_2 \left(\frac{r_{\text{obs}}}{k_5} \right)^{1/2} [\text{H}_2] - k_3 [\text{H}] [\text{Br}_2] - k_4 [\text{H}] [\text{HBr}]$$

$$\therefore 0 = k_2 \left(\frac{r_{\text{obs}}}{k_5} \right)^{1/2} [\text{H}_2] - \left\{ k_3 [\text{Br}_2] + k_4 [\text{HBr}] \right\} [\text{H}]$$

$$\therefore [\text{H}] = \frac{k_2 \left(\frac{r_{\text{obs}}}{k_5} \right)^{1/2} [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \quad \text{--- (4)}$$

Now putting the value of [H] in eqs - (1) we get-

$$r = \frac{d[\text{HBr}]}{dt} = \frac{k_2 [\text{Br}] [\text{H}_2] + k_3 k_2 \left(\frac{r_{\text{obs}}}{k_5} \right)^{1/2} [\text{H}_2] [\text{Br}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]}$$

$$- k_4 k_2 \left(\frac{r_{\text{obs}}}{k_5} \right)^{1/2} [\text{H}_2] [\text{HBr}] \quad \text{--- (5)}$$

$$\frac{\quad}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]}$$

Now, putting the value of [Br] in eqs - (5) and solving

We get,

$$r = \frac{d[\text{HBr}]}{dt} = \frac{2k_2 \left(\frac{r_{\text{obs}}}{k_5} \right)^{1/2} [\text{H}_2]}{1 + \frac{k_4 [\text{HBr}]}{k_3 [\text{Br}_2]}} \quad \text{--- (6)}$$

10

From eqⁿ - (6) we see that the rate varies as the square root of the intensity I_{abs} of the absorbed radiation. The rate law given in eqⁿ - (6) agree with the observed rate law.

The quantum yield for this reaction is very low i.e. 0.01.

form
Dr. A.R. Gupta.
chemistry (L.S. College).