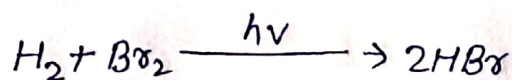
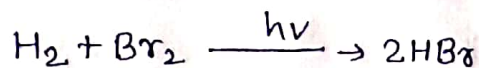


Q Discuss briefly the kinetic of the following photochemical reaction

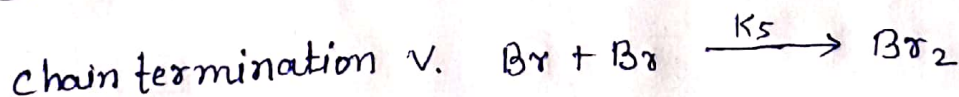
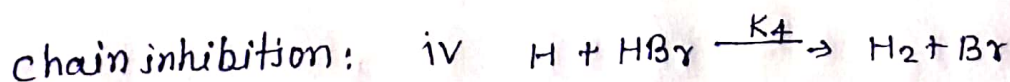
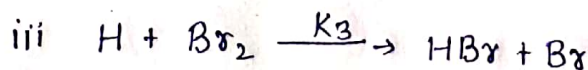
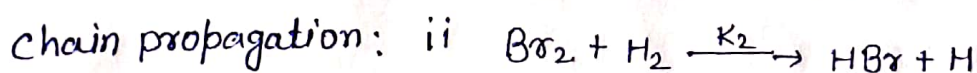
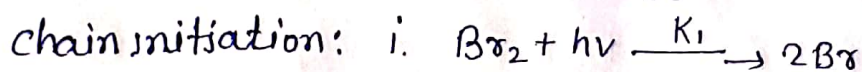


Ans. Kinetic of the formation of HBr:

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



The following mechanism is suggested:



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

$$\frac{d[\text{HBr}]}{dt} = K_2[\text{H}_2][\text{Br}] + K_3[\text{H}][\text{Br}_2] - K_4[\text{H}][\text{HBr}] \dots (1)$$

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

$$\frac{d[\text{H}]}{dt} = K_2[\text{Br}][\text{H}_2] - K_3[\text{H}][\text{Br}_2] - K_4[\text{H}][\text{HBr}]$$

Applying steady state approximation, one can get,

$$0 = k_2 [\text{Br}] [\text{H}_2] - k_3 [\text{H}] [\text{Br}_2] - k_4 [\text{H}] [\text{HBr}]$$

$$\text{or } k_2 [\text{Br}] [\text{H}_2] = k_3 [\text{H}] [\text{Br}_2] + k_4 [\text{H}] [\text{HBr}] \dots (2)$$

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

$$\frac{d[\text{Br}]}{dt} = k_1 \text{Iabs} - k_2 [\text{Br}] [\text{H}_2] + k_3 [\text{H}] [\text{Br}_2] + k_4 [\text{H}] [\text{HBr}] - k_5 [\text{Br}]^2$$

Applying steady state approximation, we get -

$$k_1 \text{Iabs} + k_3 [\text{H}] [\text{Br}_2] + k_4 [\text{H}] [\text{HBr}] = k_2 [\text{H}_2] [\text{Br}] + k_5 [\text{Br}]^2 \dots (3)$$

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

$$k_1 \text{Iabs} = k_5 [\text{Br}]^2$$

$$[\text{Br}] = (k_1 \text{Iabs} / k_5)^{1/2}$$

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

$$k_2 (k_1 \text{Iabs} / k_5)^{1/2} [\text{H}_2] = k_3 [\text{H}] [\text{Br}_2] + k_4 [\text{H}] [\text{HBr}]$$

$$\text{or } [\text{H}] = \frac{k_2 [\text{H}_2] (k_1 \text{Iabs} / k_5)^{1/2}}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]}$$

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

$$\frac{d[\text{HBr}]}{dt} = k_2 [\text{H}_2] (k_1 \text{Iabs} / k_5)^{1/2} + k_3 \frac{k_2 [\text{H}_2] (k_1 \text{Iabs} / k_5)^{1/2}}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} [\text{Br}_2]$$

$$- k_4 \frac{k_2 [\text{H}_2] (k_1 \text{Iabs})^{1/2}}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} [\text{HBr}]$$

$$= k_2 (k_1 \text{Iabs} / k_5)^{1/2} [\text{H}_2] \left[1 + \frac{k_3 [\text{Br}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} - \frac{k_4 [\text{HBr}]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \right]$$

$$= k_2 (k_1 \text{Iabs} / k_5)^{1/2} [\text{H}_2] \left[\frac{k_3 [\text{Br}_2] + k_4 [\text{HBr}] + k_3 [\text{Br}_2] - k_4 [\text{HBr}]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \right]$$

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

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

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

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

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}).