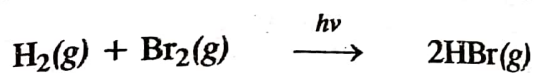
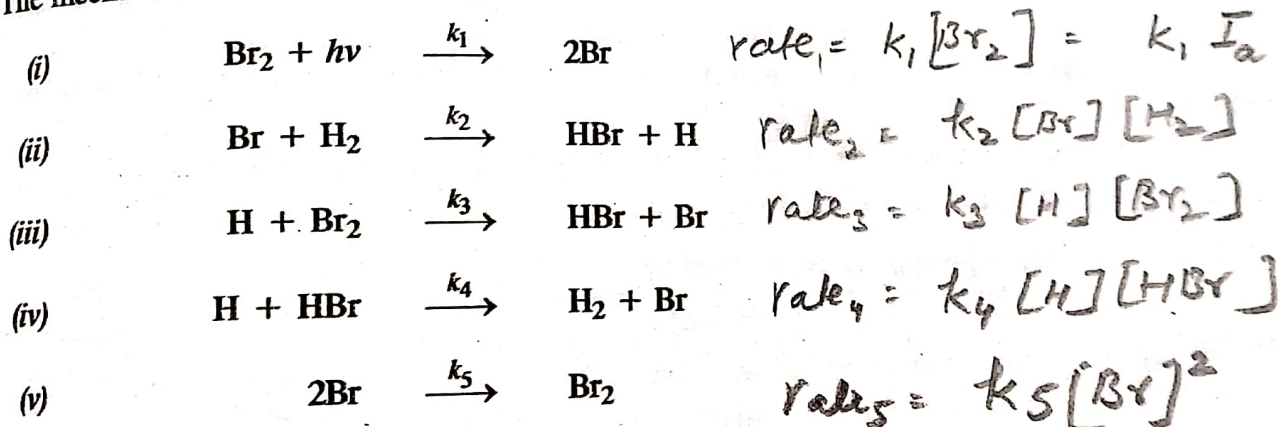


2. Kinetics of the Hydrogen-Bromine Reaction :



The mechanism of this reaction is given below :



The rate of formation of HBr is given by

$$r = \frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \quad \dots(20)$$

Applying steady state approximation to [Br], we have

$$d[\text{Br}]/dt = k_1 I_a - k_2 [\text{Br}][\text{H}_2] + k_3 [\text{H}][\text{Br}_2] + k_4 [\text{H}][\text{HBr}] - k_5 [\text{Br}]^2 = 0 \quad \dots(21)$$

Applying s.s.a. to [H], we have

$$d[\text{H}]/dt = k_2 [\text{Br}][\text{H}_2] - k_3 [\text{H}][\text{Br}_2] - k_4 [\text{H}][\text{HBr}] = 0 \quad \dots(22)$$

Adding Eqs. 21 and 22,

$$k_1 I_a - k_5 [\text{Br}]^2 = 0 \text{ whence}$$

$$[\text{Br}] = \left(\frac{k_1 I_a}{k_5} \right)^{1/2} \quad \dots(23)$$

From Eq. 22,

$$[\text{H}] = \frac{k_2 [\text{H}_2] [\text{Br}]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \quad \dots(24)$$

Substituting Eq. 23 into Eq. 24, we have

$$[\text{H}] = \frac{k_2 (k_1 I_a / k_5)^{1/2} [\text{H}_2]}{k_3 [\text{Br}_2] + k_4 [\text{HBr}]} \quad \dots(25)$$

Substituting Eqs. 23 and 25 into Eq. 20 and simplifying, we get

$$r = \frac{d[\text{HBr}]}{dt} = \frac{2k_2 (k_1 / k_5)^{1/2} I_a^{1/2} [\text{H}_2]}{1 + \frac{k_4 [\text{HBr}]}{k_3 [\text{Br}_2]}} \quad \dots(26)$$

We see that the *reaction rate varies as the square root of the intensity I_a of the absorbed radiation*. The rate law given by Eq. 26 agrees with the experimentally observed rate law. The quantum yield for this reaction is 0.01.