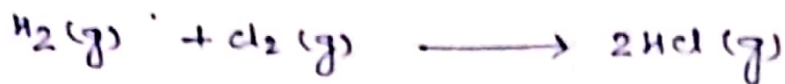


(11)

\* Kinetics of

\* Photochemical Reaction between  $H_2$  &  $Cl_2$



The proposed mechanisms are:

- (i)  $Cl_2 + h\nu \xrightarrow{I_{abs}} 2Cl$
- (ii)  $Cl + H_2 \xrightarrow{k_2} HCl + H$
- (iii)  $H + Cl_2 \xrightarrow{k_3} HCl + Cl$
- (iv)  $Cl \xrightarrow{k_4} \frac{1}{2} Cl_2$

Now,

the rate of formation of  $HCl$  is given by -

$$r = \frac{d[HCl]}{dt} = k_2 [Cl] [H_2] + k_3 [H] [Cl_2] \quad \text{--- (1)}$$

the rate of formation of  $Cl$  is given by -

$$r = \frac{d[Cl]}{dt} = I_{abs} - k_2 [Cl] [H_2] + k_3 [H] [Cl_2] - k_4 [Cl]$$

Using steady state approximation (s.s.A) -

$$\frac{d[Cl]}{dt} = 0.$$

$$\therefore 0 = I_{abs} - k_2 [Cl] [H_2] + k_3 [H] [Cl_2] - k_4 [Cl] \quad \text{--- (2)}$$

Similarly, the rate of formation of  $H$  is given by -

$$r = \frac{d[H]}{dt} = k_2 [Cl] [H_2] - k_3 [H] [Cl_2]$$

Using s.s.A -

$$\frac{d[H]}{dt} = 0$$

$$\therefore 0 = k_2 [Cl] [O_2] - k_3 [H] [Cl_2] \quad \text{--- (3)} \quad (12)$$

on adding eqs (2) & (3) we get -

$$0 = I_{abs} - k_2 [Cl] [O_2] + k_3 [H] [Cl_2] - k_4 [Cl] + k_2 [Cl] [O_2] - k_3 [H] [Cl_2]$$

$$0 = I_{abs} - k_4 [Cl]$$

$$[Cl] = \frac{I_{abs}}{k_4} \quad \text{--- (4)}$$

putting the value of  $[Cl]$  in eq (3) we get -

$$0 = k_2 \frac{I_{abs}}{k_4} [H_2] - k_3 [H] [Cl_2]$$

$$\therefore k_3 [H] [Cl_2] = k_2 \frac{I_{abs}}{k_4} [H_2]$$

$$\therefore [H] = \frac{k_2 I_{abs} [H_2]}{k_3 k_4 [Cl_2]} \quad \text{--- (5)}$$

Now putting the value of  $[Cl]$  &  $[H]$  from eqs (4) & (5) in eq (1) we get -

$$r = \frac{d[HO_2]}{dt} = k_2 \frac{I_{abs}}{k_4} [H_2] + k_3 \frac{k_2 I_{abs}}{k_3} \frac{[H_2]}{k_4} \frac{[Cl_2]}{[Cl_2]}$$

$$= 2 \left( k_2 \frac{I_{abs}}{k_4} [H_2] \right)$$

$$\boxed{\frac{d[HO_2]}{dt} = R' I_{abs} [H_2]}$$

$$\left( \text{Where, } R' = 2 \frac{k_2}{k_4} \right)$$

\* The quantum yield for this reaction varies between  $10^4 - 10^6$ .

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## \* Law of photochemical Equivalence Process

(13)

M. Bodenstein proposed that photochemical reactions involve two distinct processes—

### (1). Primary process :-

In this process, the light quantum  $h\nu$  is absorbed by a molecule 'A' resulting in the formation of an excited molecule  $A^*$ . Thus,



The molecule which absorbed light may get excited atoms or free radicals. The primary process may also involve loss of vibrational energy of excited molecule by collision with other molecules as well as fluorescence and phosphorescence.

### (2). Secondary Process :-

In this process, the excited atoms or free radicals produced in the primary process react further giving rise to high quantum yields. Some times, the atoms or free radicals initiate a series of chain reactions.

If the secondary reaction is exothermic, the heat of the reaction may activate other molecules thereby causing them to react. This is another reason for high quantum yields.

\* Reason for low quantum yields :-

There are following reasons for low quantum yields.

These are:-

- (1). Excited molecules may get deactivated before they form products.
- (2). Collisions of excited molecules with non-excited molecules may cause the ~~former~~ former to lose energy.
- (3). The primary photochemical process may get reversed.
- (4). The dissociated fragments may recombine to form the original molecule.