# Kinetics of photochemical reaction:

A reaction which takes by absorption of the visible & UV radiation is called photochemical reaction.

The branch of chemistry which deals with the study of photochemical reaction is photochemistry.

## Absorption of light:

When light is passed through a medium a part it is absorptioned. It is this absorbed proton of light which causes photochemical reaction. Let a beam of monochromatic light pass through a thickness $dn$ of the medium. The intensity of radiation reduced from $I$ to $I dl$.

The intensity of radiation can be defined as the no. of photons that pass across in unit area in unit time
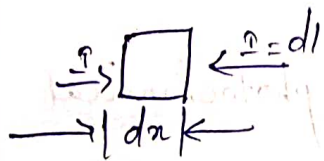
As a beam of intensity of $I$ passes through a medium of thickness $dx$, the intensity of the beam is reduced to $I\, dl$.

Let us denoted the no. of incident photons by $N$ & the no. of absorbtion in thickness $dx$ by $dN$. The fraction of photons absorbed is then $dN/N$ which is proportional to thickness.

That is $\dfrac{dn}{N} = b \cdot da$

$$= \dfrac{-dI}{I}$$

where is propotionality to const called absorption co-efficient.

Let us set $I = I_0$ at $x = 0$ & integrate. This gives.

$$I = I_0 (-bx) \quad or \quad -\ln(I/I_0) = -bx \longrightarrow ①$$

Lambert derived equ ① & it is known as Lambert law - Beer extended. This relation to Sol. of compounds is tranfered solvents The equ ① Then takes the form ②

$$\ln(I/I_0) = -E(\text{a}) \cdot C_x \longrightarrow ②$$

where $C$ = molar concentration. $E$ is a constant characteristic of the solute called the molar ~~obser~~ absorption co-efficient. The relation ② is known as Lambert - Beers law. This law forms the basis of Spectroscopy method of chemical analysis.

## Stark - Einstein law of photochemical Equation :

Stark & Einstein studied (1905) the quantitative aspects of photochemical reaction by application of quantum theory of light. They noted that each only a single quantum or photon of light. The molecules that gains one photon equivialent energy is activated & enters into reaction

Stark & Einstein. This proposed a basic law of photochemistry which is named after them The Stark-Einstein law of photochemical equivalence may be stated as.

One photon (hʋ)

Reactant          Excited          A product
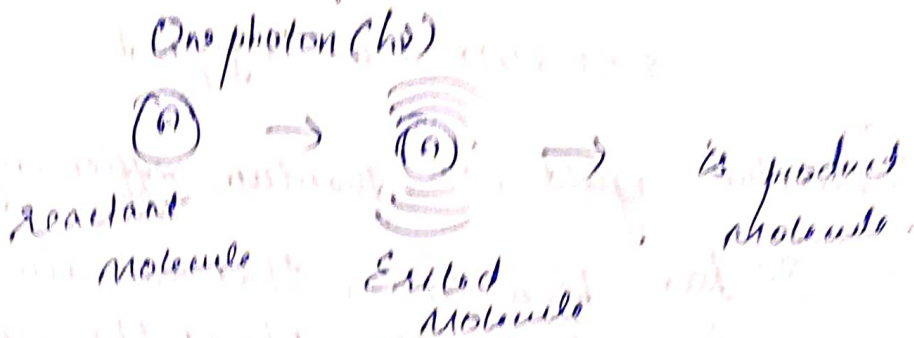Molecule          Molecule         molecule.

Illustration of law of photochemical equivalence

absorption of one photon decomposed one molecule.

In a photochemical reaction each molecule of the reacting starts absorbs a single photon of radiation causing the reaction and is activated to from the products.

The law of photochemical equivalence is illustrated in figure where a molecule 'A' absorbes a photon of radiation and gets activated. The activated molecules (A°) then decomposed to yield B. we could say the same thing in equation form as.

$$A + h\nu \longrightarrow A^{*}$$
$$A^{*} \longrightarrow B$$

Overall $A + h\nu \longrightarrow B$
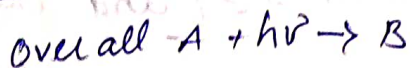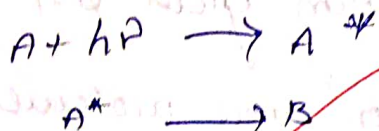
In practice we used motal quantities that is one mole of absorbs are mole of photons or one einstein of energy $E'$

The value of E can be calculated by using the expression given below

$$E = \frac{2.85}{v} \cdot g \times 10^5 \; kcal/mol \quad (eq)$$

$$8.59 \times 4187 \times 10^{-5} kJ/mol$$

## Quantum yield (or quantum efficiency)

(It has been shown that not always a photochemical reaction obey the einstein law.) The no of molecules reacted or decompose is often found to be marked different form the no. of quanta or photons of radiation absorbed in a given them

the no. of molecules reacted or formed photon of light absorbed is termed quantum yield it is denoted by ϕ. So that

$$\phi = \frac{No. \text{ of molecules reacted or formed}}{No. \text{ of protons absorbed}}$$

For O se uon that obey strictly the Einstein law, one molecule decomposes for proton, the quantum yield ϕ = 1

when two or more molecules are decomposed per photon ϕ ≥ 1 and the reaction has high quantum yield if the no. of molecules decomposed is less then One per photon. The reaction has law quantum yield

## Calculation of quantum yield:

By definition quantum yield $\phi$ of a photochemical reaction is expressed as

$\phi = \dfrac{\text{No. of molecules decomposed or formed}}{\text{No. of photon r radiation energy absorbed}}$

(or)

$\phi = \dfrac{\text{No. of moles decomposed or formed}}{\text{No. of moles of radiation energy absorbed}}$

Thus we can calculated quantum yield from

a) Amount of reactant decomposed in a given time.

b) Amount of of radiation energy absorbed in same time.

## Comparision of thermal and photochemical reaction.

| Thermal reaction | photochemical reaction. |
|---|---|
| * There reaction involves absorbtion on or evalution of heat. | * There involves lights absorption and radiation. |
| * The reaction can take place in dark as well as in light | * The presence of light is the primary requir for the reaction to takes place. |
| * Temperature has significant effect on the rate of the thermochemi reaction | * Temperature has a very little effect on the rate of photochemical reabn |
| * Structure for Thermochemical reactins is always -ve. | * free energy $\Delta G$ for photochemical spontaneo may be +ve or -ve. |

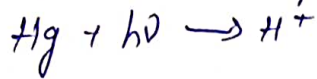| | |
|---|---|
| * Thermochemical action is not selective in nature | * Photochemical activated is highly selective. The absorbed photon excites particular atom or group of atoms which determines rate for the reaction |
| * Due to the thermodynamic atoms are formed | * Free radical are formed $Br_2$, $NO_2$, $H_2O$ |
| * Atoms are chain carries | * Free radicals are chain carries |

photosensitized reaction

A special which can both absorbed & transferred radiant energy for activation of the reactant molecules is called as photosensitized reactions.

The rate of mercury vapour is that of a zo k/w. The mercury atom absorbed the incidence radiation is it called. The excited atom collides with reactant molecules (A) & transferred to it the excitation energy. This energy is enough to it the activate the molecule (A). The mercury atom returns to the original constitutived state.

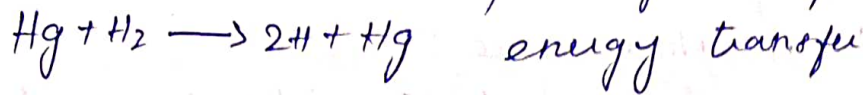$$Hg + h\nu \longrightarrow Hg^*$$

$$Hg^* + A \longrightarrow A^* + Hg$$

Ex

Reaction b/w $H_2$, $CO_2$

This reaction is photosensitized by Hg vapour. The product is hydrogen peroxide.

$$Hg + h\nu \longrightarrow H^+ \qquad \text{primary absorption}$$

$$Hg + H_2 \longrightarrow 2H + Hg \qquad \text{energy transfer}$$

$$H + O_2 \longrightarrow HO_2$$
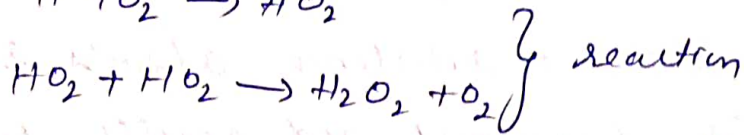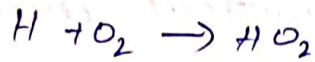
$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \Big\} \text{ reaction}$$

Hydrogen peroxide may decomposed to form water water.

## Fluorescence:

certain molecules (or atom) when expressed to light radiation of short wavelength (high free) emit light of larger wavelength. the process is called fluorescence or the subs that exhibits fluorescence it is called fluorescent rules. Fluorescence stops as soon as the incident radiation is cut off.

Ex a) A solution of quinine sulfate or exposure to visible light, exhibits blue fluorescence.

b) A solution of chlorophyl in ether shais blood red fluorescence.

## Explanation:

when a molecule absorb high energy radiation it is excited to higher energies state. Then it emits excess energy through several transitions to the ground state. Thus the excited molecule emits

light of longer frequency the colour of fluoroscence depends on wavelength of light emitted.

## phosphoroscence:

Emitted light without incident light when a substence absorbs radiation of high frequency and emitts light even after the incident radiation is cut off the process is called phosphorexence. The sub. which shows phosphoroscence is called phosphoroscence substance.

phosphoroscence is chiefly caused by $UV$ & visible light. It is generally shown by solids.

E.g : a) Sulfates of calcium, Barium & Strontim exhibit phosphorescence.

b) Fluoroscein is Boric acid shows phosphoroscence in the blue region $5.7 \times 10^7$ in wavelength.

## Explanation:

As in fluoroscence in molecule absorbs light radiation & gets excited while returning to the grand state. It emitts light energy of longer wavelength. In doing so the excited molecules passes from one sesies of electronic state to another and gets trapped.

This shows the emission of light which persists even after the removal of light source. Thus phosphorescence could be designed as delayed fluoroscence.

$$A + h\nu \longrightarrow A^* \xrightarrow{\text{Slow}} h\nu.$$
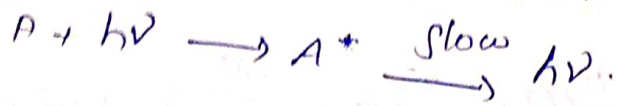
## Chemiluminescence :

Some chemical reaction are accompained by the emission of visible light at ordinary temp. The emission of light as a result of chemical action is called Chemiluminescence. Such a reaction is the reverse of a photochemical reaction. which proceed by absorption of light. The light emitted is a chemiluminescence reaction is called "cold light" because it is produced at ordinary temperature.

### E.g:

a) The glow of fireflies den to actual oxidation of luciferin (a protein) in the presence of enzyme luciferase.

b) The oxidiation of E-amino phthalic cyclic hydrazide (luminol) by hydrogen peroxide in alkaline cohn producing bright green light.

### Explanation :

In a chemiluminescent reaction the energy released in the reaction make the product molecule electronically.

excited. The excited molecule then give up its excess energy as visible light while reverting to ground state.

## Kinetic of photo chemical chain reaction

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

The mechanism of this reaction is the same as that of the thermal reaction. The only difference being that the first step in the photochemical reaction is the decomposition of $HBr_2$ into $Br$ atom, the absorption of a quantum of energy.

Reaction b/w $H_2$ & $Br_2$

step (1)

i) $Br_2 + h\nu \xrightarrow{k_1} 2Br$ [chain initiation]

ii) $Br + H_2 \xrightarrow{k_2} HBr + H^+$ [chain propagation]

iii) $H^+ + Br_2 \xrightarrow{k_3} HBr + Br^+$ [ " ]

iv) $H^+ + HBr \xrightarrow{k_4} H_2 + Br$ [chain perturbation]

v) $Br^+ + Br^+ \xrightarrow{k_5} Br_2$ [Termination]

$H_2$ & $Br_2$ to formation to HBr $500 - 1500\,k$

$$H_2 + Br_2 \xrightarrow{500-1500k} 2HBr$$

Rate

$$\frac{dHBr}{dt} = k_a [H_2][Br_2]$$

Rate formation

$$\frac{d[HBr]}{dt} = k_2 [Br][H] + k_3 [H^+][Br_2] \quad — ①$$

Rate of disappearance.

$$-\frac{d[HBr]}{dt} = k_4 [H^+][HBr] \longrightarrow ②$$

overall reaction

$$\frac{d[HBr]}{dt} = k_2 [Br^*][H_2] + k_3 [H^+][Br_2] -$$
$$k_4 [H^+][HBr] \longrightarrow ③$$

According to the steady state approximation
for Br.

$$\frac{d[Br]}{dt} = 2k_1 [Br_2] - k_2 [Br^*][H_2] + k_4 [H^+][HBr]$$
$$+ K_3 [H^+][Br_2] - 2k_3 [Br^2] \longrightarrow ④$$

According to the SSA for H

$$\frac{d[H]}{dt} = k_2 [Br^T][H_2] - k_3 [H^+][Br_2] - *$$
$$k_4 [H][HBr] \longrightarrow ⑤$$

By adding equ ④ & ⑤

$$2k_1 [Br_2] - 2k_5 [Br_2]^2 = 0$$
$$k_1 [Br_2] - k_5 [Br]^2 = 0$$

$$\frac{k_1}{k_5} [Br_2] = [Br]^2 \qquad \sqrt{2} \ or \ \frac{1}{2}$$

$$[Br] = \left[\frac{k_1}{k_5}\right]^{1/2} (Br_2)^{1/2} . \qquad Br_2 = 6$$

From equ ①

$$\frac{dH}{dt} = k_2 [Br][H_2] - k_3 [H][Br_2] - k_4 [H][HBr]$$
$$\Rightarrow k_2 [Br][H_2] = k_3 [H][Br_2] + k_4 [H][HBr]$$
$$k_2 [Br][H_2] = [H](k_3 [Br_2] + k_4 [HBr])$$

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

Sub [Br] in above

$$[H] = k_2 \left(\frac{k_1}{k_5}\right)^{1/2} \frac{I_a^{1/2} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \quad \text{——⑦}$$

sub ⑥ ⑦ in ①

$$r = \frac{d[HBr]}{dt} = \frac{2 k_2 \left(\frac{k_1}{k_5}\right)^{1/2} I_a^{1/2} [H_2]}{1 + \frac{k_4 [HBr]}{k_3 [Br_2]}}$$

## Thermal chain reaction of $H_2 - Br_2$

$$H_2 (g) + Br_2(g) \xrightarrow{\Delta} 2HBr(g)$$

$$Br_2 + h\nu \xrightarrow{k_1} 2Br$$

$$Br + H_2 \xrightarrow{k_2} HBr + Br$$

$$Br_2 + H \xrightarrow{k_3} HBr + Br$$

$$HBr + H \xrightarrow{k_4} H_2 + Br$$

$$Br + Br \xrightarrow{k_5} Br_2$$

Rate formation

$$\frac{d[HBr]}{dt} = k_2 [Br][H_2] + k_3 [Br_2][H] \quad \text{——①}$$

Rate disappearence.

$$-\frac{d[HBr]}{dt} = k_4 [HBr][H] \quad \text{——②}$$

Overall reaction

$$\frac{d[HBr]}{dt} = k_2 [Br][H_2] + k_3 [Br_2][H]$$
$$- k_4 [HBr][H] \quad \text{——③}$$

According to steady state approximation of

Br:

$$\frac{d[Br]}{dt} = 2k_1[Br_2] - k_2[Br][H_2] + k_3[Br_2][H]$$

$$+ k_4[HBr][H] - 2k_5[Br]^2 \quad \text{④}$$

According to the SSA for H

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

$$k_4[HBr][H] - \text{⑤}$$

By adding 4 & 5

$$2k_1[Br_2] - 2k_5[Br]^2 = 0$$

$$k_1[Br_2] - k_5[Br]^2 = \cancel{0} \frac{0}{2} = 0$$

$$k_1[Br_2] = \cancel{[Br]^2} k_5[Br]^2$$

$$\frac{k_1}{k_5}[Br_2] = [Br]^2$$

$$[Br] = \left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}$$

$$[Br] = \left(\left(\frac{k_1}{k_5}\right)[Br_2]\right)^{1/2}$$

from equ ⑤ we get

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

$$k_2[Br][H_2] = k_3 \cdot [H][Br_2] + k_4[H][HBr]$$

$$= [H]\left[k_3[Br_2] + k_4[HBr]\right]$$

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

Sub [Br] value in [H]

$$[H] = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]}$$

Sub [Br] & [H] value in equ ③ we get

$$\frac{d[HBr]}{dt} = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}$$

# photochemistry

| Thermal reaction | photochemical reaction |
|---|---|
| 1. Can takes place in light as well as in dark | 1. presence of light is the primary requirement |
| 2. $\Delta G$ is always -ve | 2) $\Delta G$ may be -ve or +ve |
| 3. Involves absorption or eveluation of heat energy | 3. Involves absorption of light radiation. |
| 4. Initiate when reactants get heat energy | 4. Initiate when the reactant get energy from photons. |
| 5. Rate of thermal reaction depends on the temperature | 5. Rate of photochemical reaction is independent of temperature |
| 6. Temperature has significant effect on the thermal reaction | 6. Temperature has even very little effect an photochemical reaction. |
| 7. They are accelearted by catalyst | 7. They involve photosensitizes instead of catalyst |
| 8. EX: production of NH3 in blacher process | 8. EX: Reaction of H & Br |
| 9. They are slow reaction. | 9. They are fast reaction |
| 10. non zero order reaction. | 10. Zero order reaction |