

Photochemistry

class:- B.Sc.III

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Introduction:-

Photochemistry is the branch of chemistry which deals with the rate and mechanism of reaction taking place due to exposure of light (uv & visible). ($2000-8000 \text{ \AA}$). The reactions which can be brought about by light radiations are called photochemical reactions.

The term radiation includes radio-waves, x-rays, gamma rays and also beams of particles like α -particle, neutrons, electrons and protons. The study of photochemistry helps us to know the changes when a molecule absorbs radiations.

Difference between Photochemical and thermal Reaction:-

Photochemical Reaction	Thermal Reaction
These reactions involve absorption of light radiations.	These reactions involve absorption or evolution of heat energy.
Presence of light is the primary requirement.	These reactions can take place in light as well as in dark.
Temperature has very small effect.	Temperature has significant effect.
ΔG may be +ve or -ve.	ΔG is always -ve.
Photochemical activation is highly selective process.	Thermal activation is not selective in nature.

Absorption of light(radiation):-

When a monochromatic or heterogeneous light (I_0), is incident upon a homogeneous medium, a part of it is absorbed (I_a), a part is reflected (I_r) and remaining is transmitted (I_t).

We can write, $I_0 = I_a + I_r + I_t$.

For comparison cell I_r is very small. Hence, $I_0 = I_a + I_t$.

In photochemistry, we concerned with absorbed light.

Laws of photochemistry:

(A) Grotthus Draper Law:-

“Only those radiations which are absorbed by a reacting substance or system are responsible for producing chemical change.”

According to this law, all light radiations are not bringing the chemical reaction. Some are increase the kinetic energy of molecule while some are re-emitted. (I.e. fluorescence).

(B) Lamberts law:-

When a monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease in the intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident radiation.

$$\frac{-dI}{dx} \propto I \quad \text{ie.} \quad \frac{-dI}{dx} = k \cdot I \quad \rightarrow \quad \frac{dI}{I} = -k \cdot dx$$

On integrating above eq. between respective limits, $\int_{I_0}^I \frac{dI}{I} = k \cdot \int_0^x dx$

$$\text{ie.} \quad \ln \frac{I}{I_0} = -k \cdot x \quad \text{or} \quad 2.303 \log_{10} \frac{I}{I_0} = -k \cdot x$$

$$\log_{10} \frac{I}{I_0} = -\frac{k}{2.303} \cdot x \quad \rightarrow \quad \log_{10} \frac{I}{I_0} = -a \cdot x \quad \rightarrow \quad \frac{I}{I_0} = 10^{-a \cdot x}$$

I_0 = initial intensity before passing absorbing medium.

I = intensity after passing absorbing medium. x = thickness of absorbing medium.

a = extinction coefficient. $\frac{I}{I_0}$ = transmission or transmittance (T).

$\log \frac{I_0}{I} = a \cdot x$ = absorbance (A) or optical density (D). $\frac{I_0}{I}$ = opacity.

(C) Lamberts-Beer's law (or Beer's law):-

When a monochromatic radiation is passed through a solution of absorbing medium, the rate of decrease in the intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident radiation and concentration of the solution.

$$\frac{-dI}{dx} \propto I \cdot c \quad \text{ie.} \quad \frac{-dI}{dx} = k' \cdot I \cdot c \quad \rightarrow \quad \frac{dI}{I} = -k \cdot dx$$

On integrating above eq. between respective limits, $\int_{I_0}^I \frac{dI}{I} = k' \cdot c \int_0^x dx$

$$\text{ie.} \quad \ln \frac{I}{I_0} = -k' \cdot c \cdot x \quad \text{or} \quad 2.303 \log_{10} \frac{I}{I_0} = -k' \cdot c \cdot x$$

$$\log_{10} \frac{I}{I_0} = -\frac{k'}{2.303} \cdot c \cdot x \quad \rightarrow \quad \log_{10} \frac{I}{I_0} = -\epsilon \cdot c \cdot x$$

$$\log \frac{I_0}{I} = D = \epsilon \cdot c \cdot x$$

I_0 = initial intensity before passing absorbing medium.

I = intensity after passing absorbing medium.

x = thickness of absorbing medium. ϵ = molecular extinction coefficient.

(D) Stark-Einstein Law:- (Einstein law of photochemical equivalence)

“Each molecule of absorbing substance absorb one photon (or quantum) of the radiation in primary process.”

Explanation:-

A molecule acquire energy by absorbing photon as, $A + h\nu \rightarrow A^*$

Thus energy of photon is, $E = h\nu$

Where ν = frequency of absorbing photon. h = plank's constant = 6.624×10^{-34} J.s

The energy of 1 mol photon (ie. Einstein) is given by, $E = N.h.\nu$

But, $\nu = C/\lambda$. $E = \frac{N.h.C}{\lambda}$

N = Avogadro's no. = 6.023×10^{23} mol⁻¹. C = velocity of light. = 3×10^8 m/s.

$$E = \frac{6.023 \times 10^{23} \times 6.624 \times 10^{-34} \times 3 \times 10^8}{\lambda \times 10^{-9}}$$

$$E = \frac{1.1962 \times 10^8}{\lambda} \text{ J/mol} = \frac{119620}{\lambda} \text{ KJ/mol}$$

A mole of photon can excite a mole of molecule. But if electromagnetic radiations are extremely intense, molecule may absorb two or more photons.



Hence this law is not valid for all condition.

Quantum yield or Quantum efficiency (Φ):-

It is defined as the ratio of number of molecules reacting in given time to the number of quanta absorbed in the same time.

$$\Phi = \frac{\text{number of molecules reacting in given time}}{\text{number of quanta absorbed in the same time.}}$$

$$\Phi = \frac{\text{Rate of chemical reaction}}{\text{number of quanta absorbed in the same time.}}$$

Determination of Quantum yield:- (Efficiency of Quantum yield):-

A). Reasons for unique Quantum yield:

According to Einstein law of photochemical equivalence law, in primary process each molecule absorbs one quanta. Hence Quantum yield is unity.

B) Reasons for high Quantum yield: $\Phi > 1$

1. The product of primary process may collide with 2nd molecule & transfer energy. 2nd to 3rd and so on. Thus chain reaction starts and no. of reacting molecule will be high.
2. Due formation of intermediate product which act as a catalyst.
3. Exothermic reaction may activate more molecules.
4. Eg. Reaction between Hydrogen and Halogen.

C) Reasons for low Quantum yield: $\Phi < 1$

1. In some reaction deactivation of activated molecule take place in primary process before transfer to product.
2. The product of primary process may react back to form reactants.
3. Eg. Decomposition of HI and HBr, Polymerization of anthracene.

Factors affecting quantum yield:-

1. All primary photochemical process is endothermic. Hence, quantum yield increases with temperature.
2. We know energy absorbed by molecule is inversely proportional to wavelength. Hence, quantum yield will be higher at the lower wavelength and vice versa.
3. As speed of photochemical reaction is proportional to intensity of light. Hence, quantum yield increases with intensity and vice versa.
4. The addition of inert gas in photochemical reaction the quantum yield.

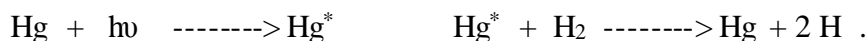
Photosensitized Reaction:-

The reactions which are take place by presence of sensitizer are called Photosensitized Reactions.

Sensitizer absorbs the radiation and transfers it to reacting molecules.

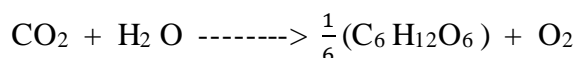
Eg. A) Dissociation of Hydrogen

UV light of wavelength 2537 \AA does not dissociate Hydrogen Because it has more energy than dissociation energy. If small amount Hg vapour is present as a sensitizer, it bring this dissociation.



B) Photosynthesis:-

Chlorophyll acts as sensitizer in process of photosynthesis. Ie interaction of CO_2 and H_2O in sunlight to form carbohydrates and oxygen. Both CO_2 and H_2O are not absorb visible light but chlorophyll can.



Examples of Photochemical Reactions:-

Photochemical equilibrium:-

“It is the state in which system has higher concentration of product earlier than it had in the equilibrium state.”

Eg. Photodimerisation of Anthracene (Polymerization of Anthracene)

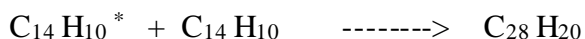
When solution of anthracene in benzene or toluene is exposed to UV light it polymerizes to dianthracene. In dark reverse reaction take place.



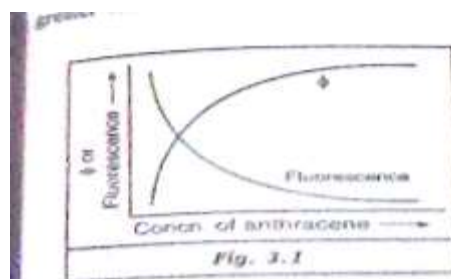
After some time a stationary state will be reached. In primary process excitation of anthracene take place as



This excited molecule collides with ordinary molecule gives dianthracene.



Quantum yield should be 2 but actually it is 0.5. Because reaction is occurs by emission of radiation & showing fluorescence. As concentration of anthracene increases, fluorescence decreases and quantum yield increases.

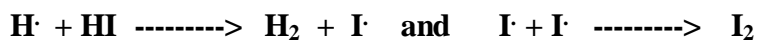


Decomposition of HI and HBr:-

The electronic spectrum of HI found in uv region. Hence, primary process is decomposition of HI. $\Phi = 2$.



The H and HI reacts in secondary process as,



Overall reaction is $2 \text{HI} + h\nu \longrightarrow \text{H}_2 + \text{I}_2$

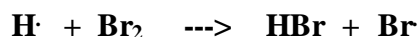
As reaction precedes quantum yield decreases because of thermal reaction. $\text{H}\cdot + \text{I}_2 \longrightarrow \text{HI} + \text{I}\cdot$

Decomposition of HBr:-

Primary process: $\text{HBr} + h\nu \longrightarrow \text{H}\cdot + \text{Br}\cdot$

Secondary process: $\text{H}\cdot + \text{HBr} \longrightarrow \text{H}_2 + \text{Br}\cdot$ and $\text{Br}\cdot + \text{Br}\cdot \longrightarrow \text{Br}_2$

As reaction precedes quantum yield decreases because of thermal reaction.



Photophysical Processes:-

By absorbing radiations, electrons are excited. During de-excitations, (1) excited electron returns to normal state instantaneously called fluorescence. (2) Excited electron returns to normal state after some time called phosphorescence. These two phenomena are called Photophysical Processes.

Photochemical Processes:-

By absorbing radiations, electrons are excited. During de-excitations, excited electron returns to normal state after producing some chemical change is called Photochemical Processes. These processes take place directly or indirectly under the influence of light radiation.

Jablonski Diagram:-

It is pictorial illustration of different energy states which absorb by molecule.

To understand Jablonski diagram we know spin multiplicity ($S = 2s + 1$) of state.

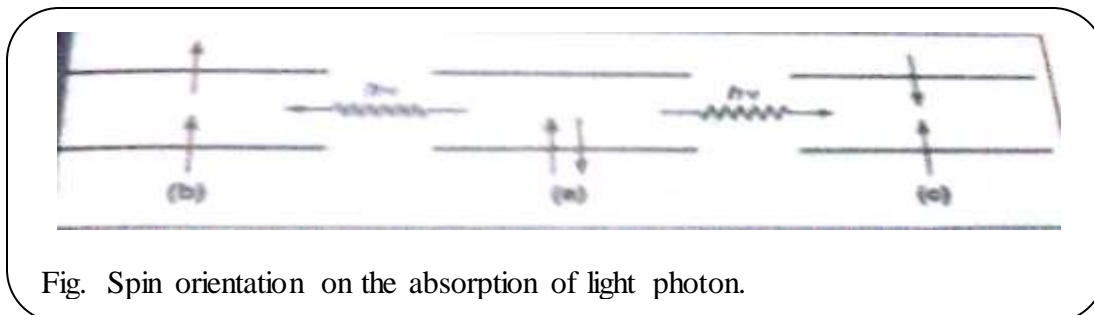


Fig. Spin orientation on the absorption of light photon.

fig. (a) at ground state $s = \frac{1}{2} - \frac{1}{2} = 0 \rightarrow S = 2 \times 0 + 1 = 1$. Molecule in Singlet ground state.

When the molecule absorbs energy & gets excited in higher energy level. There are two possibilities.

Fig. (b) $s = \frac{1}{2} + \frac{1}{2} = 1 \rightarrow S = 2 \times 1 + 1 = 3$. Molecule in Triplet excited state. (T).

fig. (c) $s = \frac{1}{2} - \frac{1}{2} = 0 \rightarrow S = 2 \times 0 + 1 = 1$. Molecule in Singlet excited state. (S)

Thus, depending upon energy we get series of singlet excited state $S_1, S_2, S_3 \dots$ And triplet excited state $T_1, T_2, T_3 \dots$

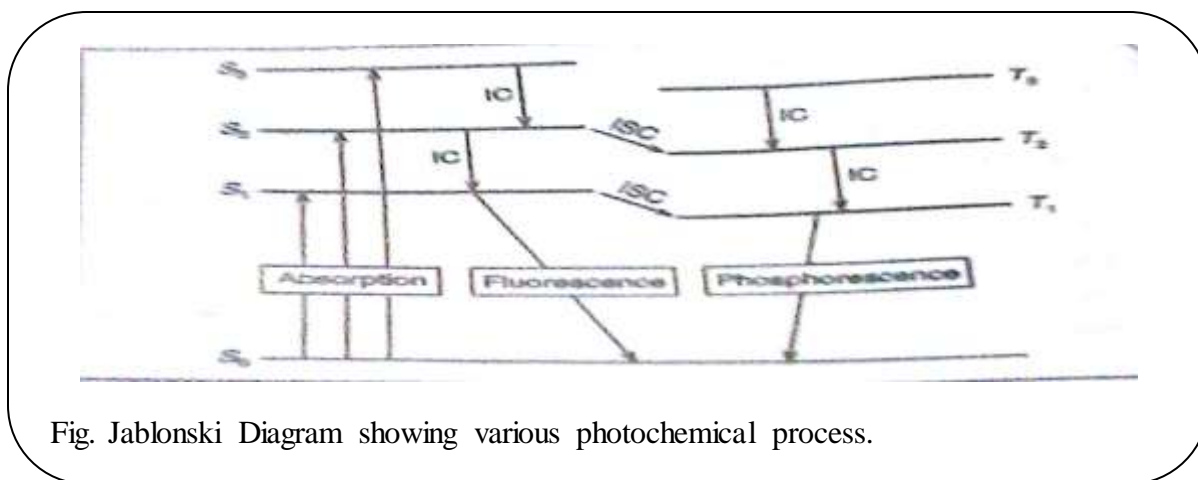


Fig. Jablonski Diagram showing various photochemical process.

The activated molecule returns to ground state by loss of energy through the following process

(A) Non-radiative transition:-

It involves transition from $S_2 \rightarrow S_1$ or $S_3 \rightarrow S_1$ Or $T_2 \rightarrow T_1$ or $T_3 \rightarrow T_1$. It does not involve emission of any radiation hence called Non-radiative transition. It only involves emission of heat.

1. Internal Conversion (IC):-

In this process energy loss in the form of heat. It involves transition from, $S_3 \rightarrow S_2$ or $S_2 \rightarrow S_1$ Or $T_3 \rightarrow T_2$ or $T_2 \rightarrow T_1$. It occurs in less than 10^{-11} second.

2. Intersystem Crossing (ISC):-

It involves transition from $S_3 \rightarrow T_3$, $S_2 \rightarrow T_2$ Or $S_1 \rightarrow T_1$. Both these transitions are forbidden.

(B) Radiative transition:-

It involves transition from $S_1 \rightarrow S_0$ or $T_1 \rightarrow T_0$. It involves emission of transition.

Fluorescence :- The emission of transition from $S_1 \rightarrow S_0$ is called Fluorescence. It is allowed transition and occurs in 10^{-8} second.

Phosphorescence:- The emission of transition from $T_1 \rightarrow S_0$ is called Phosphorescence. It is forbidden transition.

* Luminescence:-

The production of visible radiation due to some cause other than temperature is called Luminescence. It is also called as cold-light. There are 2 types of Luminescence.

A) Fluorescence B) Phosphorescence.

Fluorescence:-

(1) Atom or molecule returns from excited state to ground state with emission of radiation is called Fluorescence.

(2) The electronic transition of electron is depends on wavelength of radiation. In case of atom, wave length of Fluorescence is same as absorbed radiation is called **resonance Fluorescence**. While in case of molecule it longer than absorbed radiation.

(3) When photochemically excited atom collides with another atom, intensity of Fluorescence radiation is decreased is called quenching of Fluorescence.

(4) Eg. Fluorite (CaF_2), Uranium glass, fluorescein, eosin, chlorophyll etc.

Phosphorescence:-

1. Even after incident light radiation is cut off there is emission of light for some time is called Phosphorescence. It is also called slow Fluorescence.
 2. The substance which shows Phosphorescence is called fluorescent substance.
 3. The name Phosphorescence is derived from phosphorous which glows in dark.
- Eg. Organic dye, certain fungi sulphides of alkali metal etc.

Chemiluminescence:-

1. The emission of light as a result of chemical reactions at ordinary temperature is called Chemiluminescence.
2. Chemiluminescence is reverse of photochemical reaction because light is given out instead of being absorbed.
3. In Chemiluminescence excited product emits radiations of appropriate wavelength which is lie in visible region of spectrum.
4. a) $4 P + 5 O_2 \rightarrow 2P_2 O_5^*$ (excited state)
 $2P_2 O_5^*$ (excited state) $\rightarrow 2P_2 O_5$ (ground state) + Radiation (Greenish glow).
- b) Oxidation of decaying wood containing certain forms of bacteria.
- c) The light emitted from fire-fly is very spectacular.

Electroluminescence (EL):-

1. **Electroluminescence** is a characteristic of a material that enables it to emits light in response to an electric current.
2. It involves radiative recombination of electron and hole to form exciton which undergoes spontaneous emission.
3. EL is non-thermal conversion of electrical energy into light energy.
4. This phenomena used in EL-lamps, LEDs and OLEDs.
5. It is used in manufacture of Night signal light, decorative luminescent clothing, watch illumination, computer monitors.