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UNIT-III: Photochemical Reactions

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Photochemical Reactions: Basic principles of photochemical reactions. Photo-oxidation, photo-addition and photo-fragmentation.

- Photochemistry is the branch of chemistry concerned with the chemical effects of light. Generally, this term is used to describe a chemical reaction caused by absorption of ultraviolet (wavelength from 100 to 400 nm), visible light (400 – 750 nm) or infrared radiation (750 – 2500 nm).

- **The Basic Laws of Photochemistry**

- **The First Law of Photochemistry** states that light must be absorbed for photochemistry to occur. This is a simple concept, but it is the basis for performing photochemical and photobiological experiments correctly. If light of a particular wavelength is not absorbed by a system, no photochemistry will occur, and no photobiological effects will be observed, no matter how long one irradiates with that wavelength of light.
- **The Second Law of Photochemistry** states that for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction. This law is true for ordinary light intensities, however, with high-powered lasers, two-photon reactions can occur, i.e., the molecule is raised to a higher energy state than produced by single-photon absorption.
- **The Bunsen-Roscoe Law of Reciprocity** states that a photochemical effect is directly proportional to the total energy dose, irrespective of the time required to deliver the dose. This law is true for chemicals in a test tube, but the response of cells to radiation usually involves a sequence of interacting biological reactions, making a linear "dose x time" relationship highly unlikely. There is no reciprocity when damage is produced, e.g., DNA damage, but there can be reciprocity over a narrow range of doses for photoreceptors that trigger a response, such as phytochrome
- **Grotthus-Draper Law (or) The Principle of Photochemical Activation:** Grotthus-Draper law states that only the light which is absorbed by a substance can bring about a photochemical change. However, the absorbed radiation does not necessarily cause a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy may be reemitted as heat or light or it remains unused.

Some important relations:

Photons	≡	quanta
One molecule absorbs	≡	one photon
One mole of a substance		one mole of quanta (or)
Containing 6.023×10^{23}	≡	6.023×10^{23} quanta of
(Avogadro number)		light (or) one Einstein
Molecules absorbs		

$$\begin{aligned} \text{One Einstein} &= N h \nu \\ &= N h c / \lambda \quad [\because \nu = c / \lambda] \end{aligned}$$

The energy of photons and Einstein: The energy of a photon (or quantum) E, is given by the equation $E = h \nu = h c / \lambda$, where, h – Planck's constant (6.625×10^{-34} Js; c – velocity of light = 3.0×10^8 ms⁻¹; λ – wavelength of light.

The energy of an Einstein E, is an Avogadro number (N) of photons. It is given as $E = N h c / \lambda$

On substituting the values in the above equation it becomes

$$\begin{aligned} E &= (6.023 \times 10^{23}) \times (6.625 \times 10^{-34}) \times (3 \times 10^8) / \lambda \text{ J mol}^{-1} \\ &= 0.1196 / \lambda \text{ J mol}^{-1} \text{ in SI units} \end{aligned}$$

In CGS units: $c = 3 \times 10^{10} \text{ cm s}^{-1}$; $h = 6.625 \times 10^{-27} \text{ erg s}^{-1}$

$$\begin{aligned} \therefore E &= (6.023 \times 10^{23}) \times (6.625 \times 10^{-27}) \times (3 \times 10^{10})/\lambda \text{ erg mol}^{-1} \\ &= 1.196 \times 10^{16}/\lambda \text{ (in } \text{Å}) \text{ erg mol}^{-1} \end{aligned}$$

1 cal = 4.184×10^7 ergs

$$\begin{aligned} \therefore E &= 1.196 \times 10^8/4.184 \times 10^7/\lambda \text{ cal mol}^{-1} \\ &= 2.859/\lambda \text{ cal mol}^{-1} \end{aligned}$$

If l is expressed in Å, then $E = 2.859 \times 10^8/\lambda \text{ (in } \text{Å}) \text{ cal mol}^{-1}$
 $= 2.859 \times 10^5/\lambda \text{ (in } \text{Å}) \text{ kcal mol}^{-1}$

• LAMBERT'S LAW:

- When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of the light.
- Mathematically, it may be stated as follows

$$-dI/dl \propto I \quad \text{(or)} \quad -dI/dl = kI \quad \text{----- (1)}$$

Where I = the intensity of incident light of wavelength λ

l = the thickness of the medium

k = the proportionality factor

on integrating **equation 1** and putting $I = I_0$ when $l = 0$, we get

$$\ln I_0/I = kl \quad \text{(or)} \quad I = I_0 e^{-kl} \quad \text{----- (2)}$$

• BEER'S LAW:

- The intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically.

$$I = I_0 e^{-kc} \quad \text{----- (3)}$$

- On combining both laws: $\log I_0/I = \epsilon cl$ ----- (4)

- The equation 4 is termed as mathematical statement of Beer-Lambert's law.

- In the above equation ϵ = the molar absorption coefficient.

A = $\log I_0/I$ is the absorbance (or) optical density (OD)

❖ Limitations of Beer-Lambert's law :

- The law is not valid
 - (i) When non-monochromatic radiation is used,
 - (ii) If temperature changes during measurements,
 - (iii) The law is applicable only to dilute solutions.

❖ **Quantum Yield (or) Quantum Efficiency (ϕ):**

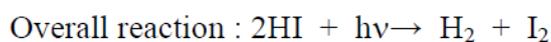
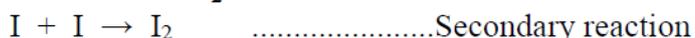
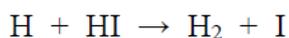
- To express the relationship between the numbers of molecules reacting with the number of photons absorbed, the concept of quantum yield or quantum efficiency “ ϕ ” is introduced.
- Quantum yield is defined as “the number of molecules of the substance undergoing photochemical change per quantum of radiation absorbed. Thus,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

- In certain photochemical reaction,
 λ = wavelength of light in Å;
 q = amount of radiation absorbed in certain interval of t s.
 n = number of moles of substance reacted in the same time interval (t), then

❖ **High (or) Low Quantum Yield:**

- The **quantum efficiency** varies from **zero** to **10^6** . If a reaction obeys the Einstein law, one molecule is decomposed per photon, the quantum yield $\phi = 1$.
- **High Quantum Yield:** When two or more molecules are decomposed per photon, the quantum yield $\phi > 1$ and the reaction has a high quantum yield.
- **Low Quantum Yield:** When the number of molecules decomposed is less than one per photon, the quantum yield $\phi < 1$ and the reaction has a low quantum yield.
- **Conditions for high and low quantum yield:** The reacting molecules should fulfil the following conditions:
 - 1) All the reactant molecules should be initially in the same energy state and hence equally reactive.
 - 2) The reactivity of the molecules should be temperature independent.
 - 3) The molecules in the activated state should be largely unstable and decompose to form the products.
- **Causes (or) Reasons for high quantum yield:**
 - 1) Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions.
 - 2) Formation of intermediate products will act as a catalyst.
 - 3) If the reactions are exothermic, the heat evolved may activate other molecules without absorbing the additional quanta of radiation.
 - 4) The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules
- **Examples:**
 - 1) **Decomposition of HI:**
 - In the primary reaction, one HI molecule absorbs a photon and dissociated to produce **one H** and **one I**. This is followed by the second reaction as shown below:



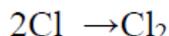
- The overall reaction shows that the two HI are decomposed for one photon ($h\nu$). Thus, the quantum yield (ϕ) = 2

2) **Formation of HCl:**

- In the primary step, one Cl_2 molecule absorbs a photon and dissociates into **two Cl** atoms.
- This is followed by the secondary reaction:



- The **Cl atom** consumed in **step 2** is regenerated in **step 3**, this will propagate the chain reaction. The chain reaction gets terminated when the **Cl atoms** recombine at the walls of the vessel, where they lose their excess energy.



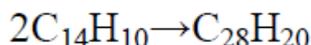
- Thus the quantum yield varies from 10^4 to 10^6 .

- **Causes (or) Reasons for low quantum yield:**

- 1) Excited molecules may get deactivated before they form products.
- 2) Excited molecules may lose their energy by collisions with non-excited molecules.
- 3) Molecules may not receive sufficient energy to enable them to react.
- 4) The primary photochemical reaction may be reversed.
- 5) Recombination of dissociated fragments will give low quantum yield.

- **Example:**

- The **quantum yield = 2**, but actually it is found to be = **0.5** ; the reason is the above reaction is reversible.

❖ **Processes of Photochemical Reactions**

- The overall photochemical reaction consists of Primary reaction and Secondary reaction.

(i) **In the primary reaction**, the quantum of light is absorbed by a molecule „A“ resulting in the formation of an excited molecule A^* . $\text{A} + h\nu \rightarrow \text{A}^*$

(ii) **In the secondary reaction**, the excited molecules react further to give the product of higher quantum yield. $\text{A}^* \rightarrow \text{B}$

❖ **Energy Transfer in Photochemical Reactions:**

- Photosensitizations and Quenching: In some photochemical reactions, the reactant molecules do not absorb radiation and no chemical reaction occurs. However, if a suitable foreign substance (called sensitizer), which absorbs radiation, is added to the reactant, the reaction takes place. The sensitizer gets excited during absorption of radiation and transfers its energy to the reactants and initiates the reaction.

1) **Photosensitization:** The foreign substance absorbs the radiation and transfers the absorbed energy to the reactants is called a photosensitizer. This process is called photosensitized reaction (or) photosensitization. Examples,

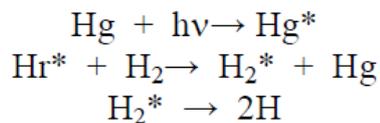
(a) Atomic photosensitizers: mercury, cadmium, zinc

(b) Molecular photosensitizers: benzophenone, sulphur dioxide.

2) **Quenching:** When the excited foreign substance collides with another substance it gets converted into some other product due to the transfer of its energy to the colliding substance. This process is known as quenching.

- **Examples for photosensitized reactions:**

- 1) **Dissociation of hydrogen molecule:** UV light does not dissociate H₂ molecule, because the molecule is unable to absorb the radiation. But, if a small amount of mercury vapour is added, dissociation of hydrogen takes place. Here Hg acts as photosensitizer.



- 2) **Photosynthesis in plants:**

- During photosynthesis of carbohydrates in plants from CO₂ and H₂O, chlorophyll of plants acts as a photosensitizer. The energy of the light absorbed by the chlorophyll (due to the presence of conjugation in chlorophyll) is transformed to CO₂ and H₂O molecules, which then react to form glucose.
- In the presence of light and chlorophyll ΔG^0 becomes negative; thereby the reaction proceeds and produces glucose. But in the absence of chlorophyll, the ΔG^0 for this reaction is +2875 kJ. Since ΔG^0 is positive, the above reaction is not possible.

- **Types of photophysical process:**

(i) **FLUORESCENCE**

- ✓ When a molecule or atom absorbs radiation of higher frequency (shorter wavelength), it gets excited. Then the excited atom or molecule re-emits the radiation of the same frequency or lower frequency within short time (about 10⁻⁸ sec.). This process is called fluorescence, stops as soon as the incident radiation is cut off. The substance which exhibits fluorescence is called fluorescent substance.
- ✓ Examples: CaF₂, uranium, petroleum, organic dyes like eosin, fluorescein, chlorophyll, quinine sulphate solution, vapours of sodium, iodine, mercury, etc.
- ✓ *Types of fluorescence:*
 - (a) **Resonance fluorescence:**
 - If the excited atom emits the radiation of the same frequency, the process is known as resonance fluorescence.
 - Example, when mercury vapour at low pressure is exposed to radiation of wavelength 253.7 nm, it gets excited.
 - Subsequently, when it returns to its ground state, it emits radiation of the same frequency, which it absorbed.
 - (b) **Sensitized fluorescence:**
 - If the molecule is excited, due to the transfer of part of excitation energy from the foreign substance, it emits the radiation of lower frequency, the process is known as sensitized fluorescence.
 - Example, if the mercury vapour is mixed with the vapours of silver, thallium, lead or zinc, which do not absorb radiation at 253.7 nm and then exposed to the radiation, a part of the excitation energy from mercury is transferred and gets excited to higher energy state.
 - When it returns to its ground state, it emits radiation of lower frequency.

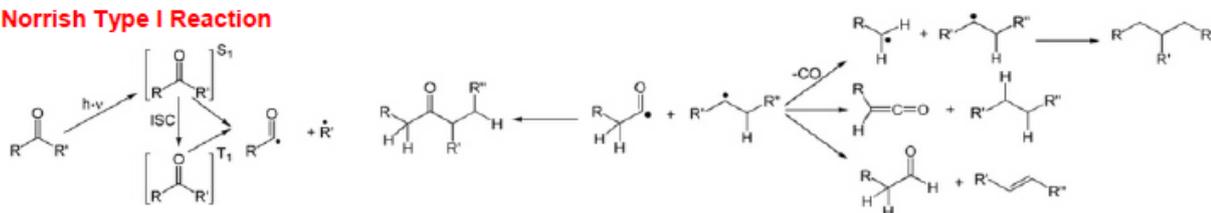
(ii) **PHOSPHORESCENCE**

- ✓ When a substance absorbs radiation of higher frequency, the emission of radiation is continuous for some time even after the incident light is cut off. This process is called phosphorescence (or) delayed fluorescence. The substance which shows phosphorescence is called phosphorescent substance.
- ✓ Examples: Zinc sulphide, alkaline-earth sulphides (eg. CaS, BaS and SrS).

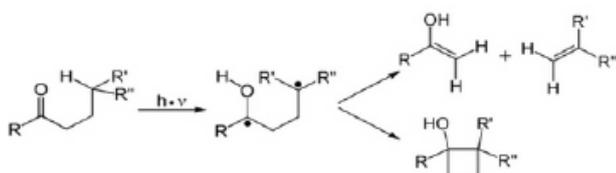
• Differences between fluorescence and phosphorescence

Fluorescence	Phosphorescence
1. Its decay period is much longer, $10^{-4} - 100$ s.	Its decay period is very short, $10^{-9} - 10^{-4}$ sec.
2. It is the radiation emitted in a transition between states of different multiplicity.	It is the radiation emitted in a transition between states of same multiplicity.
3. It is not observed in solution at room temperature.	It can be observed in solution at room temperature.
4. Its spectrum is mirror image of the absorption spectrum.	Its spectrum is not mirror image of the absorption spectrum.
5. It is exhibited by some elements in vapour state.	It is rarely observed in gaseous or vapours.
6. Examples: uranium, petroleum, organic dyes, chlorophyll, CaF_2 , etc.	Examples: ZnS, sulphides of alkaline earth metals.

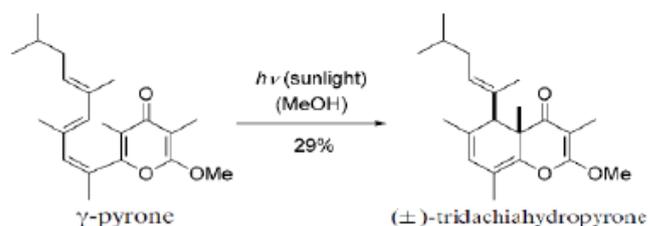
1. Norrish Type I Reaction



2. Norrish Type II Reaction

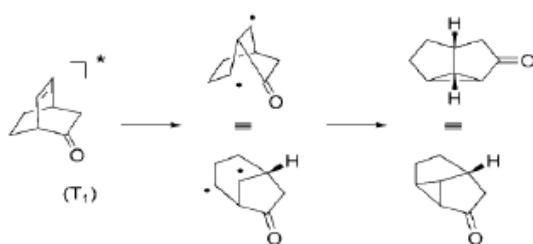


3. Photocyclisation



Conrotatory 6π ring closure – Recent work by Moses and co-workers
Disrotary 4π ring closure by Woodward Hoffmann rules

4. Photochemical Rearrangements



Oxa-di- π -Methane Rearrangement