

# PHOTOCHEMISTRY

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**ELECTIVE PAPER (INORGANIC 1A)**

**FOR PG 4<sup>TH</sup> SEMESTER**

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## CHAPTER

# PHOTOCHEMISTRY : AN INTRODUCTION

**Role of Photochemistry :** Photochemistry studies the reaction of those molecules, which absorb light radiations of spectrum in the ultraviolet and visible regions and become electronically excited.

The origin of life on earth itself must have been a photochemical action. In the primitive earth conditions, light radiations were obtained from the sun; which was the only source of energy. Earth was consisting of hot gaseous molecules, such as, methane, ammonia,  $\text{CO}_2$  etc. These simple molecules reacted photochemically by absorbing solar radiations, and converted into bigger complex molecules, e.g., peptides, proteins, DNA, RNA, etc. For the initiation and propagation of life, solar radiations were used to provide food, photobiologically. Photochemistry of biological reactions helps to study and explain the phenomenon of photosynthesis, phototaxis, photoperiodism, mutagenic effects of light radiations, vision, and photodynamic action.

Photochemistry provides a phenomenon of fluorescence and phosphorescence, which is collectively known as photophysical phenomenon. It has found various applications in the field of :

- (a) Fluorescent light tubes,
- (b) Luminiscent dials for watches,
- (c) X-ray, TV screen,
- (d) Paints in advertisement hoardings which show more brilliance by utilizing fluorescence,
- (e) Microanalytical reagent;
- (f) Optical-brightness in white dress materials,
- (g) Detection of cracks in metal works, etc.

Photochemistry has provided a revolutionary advantage in the area of laser technology. The lasers are obtained from monochromatic and coherent light radiation, and are used in the following fields of science and technology :

- (a) For the surgery of eye, very small concentration of intense and powerful beam of coherent radiations is used;
- (b) In metals cutting and boring of diamonds;
- (c) In military range finders and detectors, etc.

Photopolymerization is used in photography, lithoprinting and manufacture of printed circuits for the electronic industry.

Some chemicals, such as spiropyrans, change their colour in presence of suitable radiation of light, and reverse when the irradiation source is removed.

## LAWS OF PHOTOCHEMISTRY

Two laws of photochemistry have been found :

**1. First Law of Photochemistry :** In the beginning of nineteenth century, it was realized that all the incident light was not effective in bringing about a chemical change.

It was Grotthus-Draper, who formulated First Law of Photochemistry, as :

*"Only that light which is absorbed by a system can cause chemical change".*

And, the probability or rate of absorption is given by Lambert-Beer Law, which is as follows :

**Lambert Law :** Lambert states, *"The fraction of incident light absorbed by a transparent medium is independent of the intensity of incident radiation and each successive layer of the medium absorbs an equal fraction of incident radiation".*

**Beer Law :** The Beer law states, *"the amount of radiation absorbed is proportional to the number of molecules absorbing the radiation, that is the concentration, C, of the absorbing species".*

The Lambert and Beer Laws were combined and expressed as :

$$-\frac{dl}{I} = \alpha_v C dl$$

where,

$\alpha_v$  = the proportionality constant

$dl$  = thickness of the layer

$l$  = optical path length

$I$  = Incident light intensity

$Cdl$  = amount of the solute per unit area of the layer.

Since,

$$C = \frac{\text{Mole}}{\text{Volume}} \\ = \frac{\text{Mole}}{\text{Area}} \times \text{thickness}$$

Therefore,

$$Cdl = \frac{\text{Mole}}{\text{Area}}$$

If  $l = 0$ , then  $I = I_0$  and if  $l = l$ , then  $I = I$

We have,

$$\ln \frac{I_0}{I} = \alpha_v Cl$$

$\alpha_v$  is known as absorption coefficient. It is a function of frequency or wavelength of radiation. The final form is expressed in the decadic logarithm,

$$\log \frac{I_0}{I} = \epsilon_v Cl$$

where,  $\epsilon_v = \frac{\alpha_v}{2.303}$ , and is known as molar extinction coefficient and is a function of frequency  $\nu$ .

The concentration ( $C$ ) is expressed in moles/litre. The optical path length ( $l$ ) is expressed in cm. The S.I. units of  $C = \text{mol/dm}^{-3}$ ,  $l = \text{m}$  and  $\epsilon = \text{m}^2/\text{mol}$ .

$I_0$  and  $I$  = Incident and transmitted intensity, respectively (Fig. 1).

The  $\log \frac{I_0}{I}$  is known as optical density (OD) or absorbance (A).

A plot of  $\epsilon_{\nu}$  against wavelength or wave number gives rise to familiar absorption bands.

Since,

$$I = I_0 10^{-\epsilon_{\nu} Cl}$$

The amount of light absorbed  $I_a$ , by the system is :

$$\begin{aligned} I_a &= I_0 - I \\ &= I_0 - I_0 10^{-\epsilon_{\nu} Cl} \\ &= I_0 (1 - 10^{-\epsilon_{\nu} Cl}) \end{aligned}$$

For more than one absorbing components :

$$\text{Optical Density} = \sum \epsilon_{\nu i} C_i l,$$

where  $\epsilon_{\nu i}$  = molar absorptivity at frequency  $\nu_i$  for the  $i^{\text{th}}$  component, and

$C_i$  = concentration, assuming path length to be unity.

Hence,

$$\text{Measured OD} = OD_1 + OD_2 + OD_3 + \dots$$

**2. Second Law of Photochemistry:** The second law of photochemistry was given by Stark (1908) and later by Einstein (1912). The Stark-Einstein law states that, "one quantum of light is absorbed per molecule of absorbing and reacting substance that disappears."

It were Warburg and Bodenstein (1912-1925) who clarified earlier confusion between photon particle absorption and observed chemical change.

Molecules, which absorb photons become physically excited, and this must be identified from becoming chemically active. Excited molecules may lose their energy in non-chemical path ways, or may trigger off thermal reaction of large chemical yield. The so called 'law', therefore, rarely holds in its strict sense, but rather provides essential information about the primary photochemical action.

To express the efficiency of a photochemical reaction, the quantity of quantum efficiency,  $\phi$ , is defined as :

$$\phi_{\text{reaction}} = \frac{\text{Number of molecules decomposed or formed}}{\text{Number of quanta absorbed}}$$

Einstein provided the concept of quantum yield or quantum efficiency  $\phi$ . Quantum yield as absorbed may change from a million to a very small fraction of unity due to the frequent complexity of photoreactions.

When high intensity light sources are used as lasers or flash lamp, 'biphotonic' photochemical effects may produce which modify the application of Einstein law.

At very high intensity of light, a molecule can absorb two photon particles simultaneously, a more common effect, is for a second photon of longer wavelength to be absorbed by a metastable (triplet or radical) species generated by the action of the first photon particle. The nature of the photo-products and the quantum yields are

"biphotonic", photochemical reaction, which occur by the interaction of two excited molecules. Here, the rate of reaction is directly proportional to square of light intensity i.e.,  $I^2$ . Because of their long life, triplet states are involved in the second of these processes, and provide a mechanism by which cleavage of high energy bonds takes place, and this may be affected by lower energy of photon particles.

### TYPES OF PHOTOCHEMICAL REACTIONS

The chemical nature of a molecule depends on the electrons which are more weakly bound. The energy and electron wave function of a ground state molecule differs from the molecule in the excited state; and hence differs in its chemical behaviour. Irradiation of light photons on a molecule produce an excited electronic state, which alters the reactivity of molecules in a number of ways, which decide the nature of any photochemical reaction.

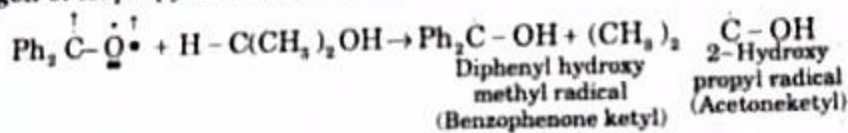
The important photoreactions are as follows :

- (1) Photoreduction
- (2) Photoaddition
- (3) Photoisomerisation
- (4) Photooxidation
- (5) Photodissociation

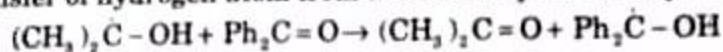
**(1) Photoreduction Reaction :** To explain the photoreduction reaction, benzophenone and isopropyl alcohol are taken as an example. The solution of above reactants is irradiated with ultraviolet light with a wavelength of 300-350 nm. In this region, isopropyl alcohol does not absorb light radiations, whereas benzophenone undergoes as  $n \rightarrow \pi^*$  singlet transition near wavelength 350 nm.

In benzophenone, the state with one of the oxygen  $n$  electrons in a  $\pi^*$  orbital,  $S_1$ , undergoes very rapid intersystem crossing to  $T_1$  (the lifetime of  $S_1$  is  $10^{-10}$  seconds), and the triplet is actually species which reacts with isopropyl alcohol.

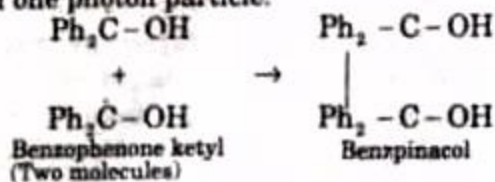
$n \rightarrow \pi^*$  triplet has an odd electron in an oxygen  $n$  orbital which makes it resemble an oxygen free radical like other oxygen radicals it can remove the  $\alpha$ -hydrogen of isopropyl alcohol leading to two stabilised radicals.



The transfer of hydrogen atom from acetone ketyl to benzophenone occurs :



This reaction occurs because benzophenone ketyl is more resonance stabilized than acetone ketyl. Thus two benzophenone ketyl molecules are formed by the absorption of one photon particle.

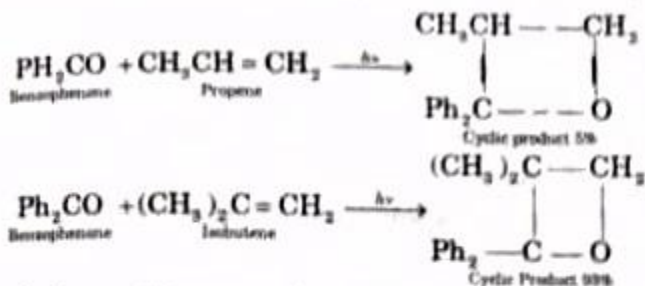


**(2) Photoaddition Reaction :** Photoaddition is the reaction between the ground state of an olefin molecule and the excited state of another molecule which

may be a carbonyl compound, quinone, aromatic compound or second molecule of the same olefin, thus formed a 1 : 1 adduct (generally cyclic).

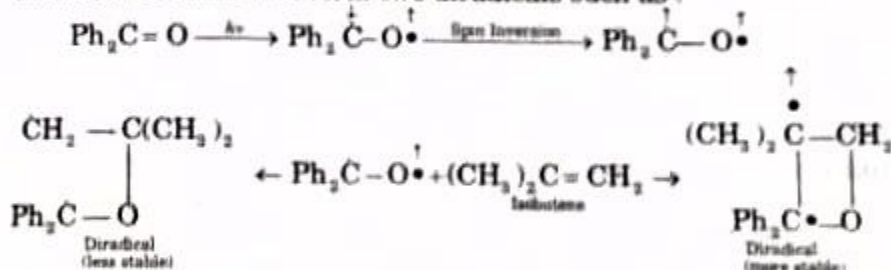
**Example :** The most important example of photoaddition reaction is Paterno Buchi reaction where triplet state of carbonyl compound reacts with the ground state of olefin.

Photoaddition is more efficient when the triplet is of  $n \rightarrow \pi^*$  rather than  $\pi \rightarrow \pi^*$  type.



The whole reaction occurs in two steps :

- (a) The excited carbonyl compound (in triplet state) add through its oxygen atom to the olefin and form two diradicals such as :

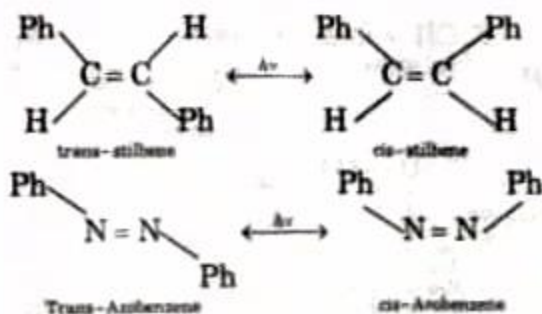


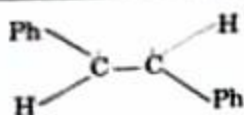
- (b) In the second step, a spin-inversion takes place and the second bond is formed.



(3) **Photoisomerization Reaction :** Photoisomerization can occur due to the  $\pi$ -bond which normally prevent it, is lost in the passage of excited state. The excited state of many organic compounds decay to isomers of the starting structures.

**Examples :** The important examples of the photoisomerization are given below:





Here (above structure) the two sets of substituents tend to occupy mutually perpendicular planes, so as to minimise the repulsive forces between them. When the molecule returns to the ground state, it can twist in two directions to give both cis- and trans-isomers.

**(4) Photo Oxidation Reaction :** There are two types of photooxidation reactions :

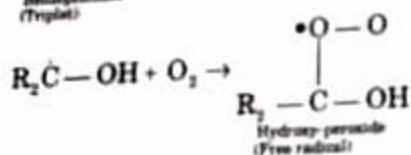
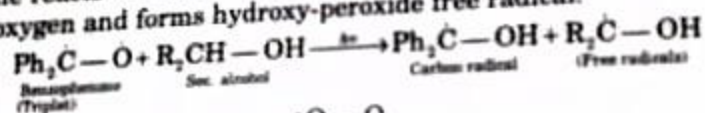
- (A) Formation of Peroxy compounds
- (B) Oxidative coupling of Aromatic compounds.

**(A) Formation of Peroxy compounds :** In the formation of peroxy compounds, sensitizers are used. Some examples of sensitizers are benzophenone, Rose Bengal, fluorescein etc.

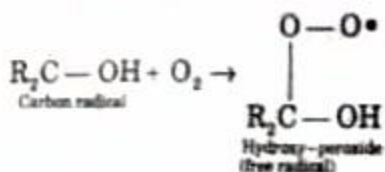
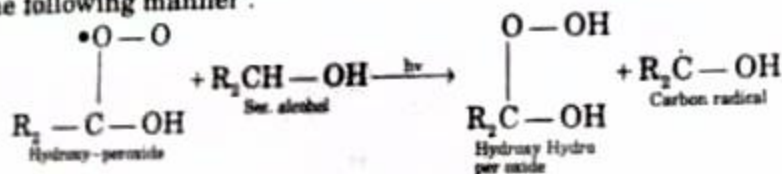
Certain compounds when irradiated with sensitizer in presence of oxygen, forms peroxy compounds. This reaction occurs in two stages.

- (a) In the first step, the sensitizer is oxidised to its triplet state.
- (b) (i) In the second step, the triplet abstracts a hydrogen atom from the substrate to form a radical, which then reacts with oxygen to form hydroxy peroxy compound.

**Example :** The oxidation of secondary alcohol to hydroxy-hydroperoxide with benzophenone (sensitizer) is the best example of such type reaction. The triplet benzophenone reacts with secondary alcohol to a free radical. This carbon radical reacts with oxygen and forms hydroxy-peroxide free radical.

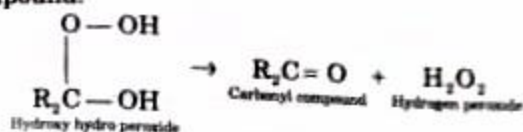


The hydroxy-peroxide free radical now abstracts a hydrogen atom from the fresh molecule of secondary alcohol and gives hydroxy-hydroperoxide and a carbon radical. Again it reacts with oxygen to give hydroxy-peroxide radical, the reaction goes on in the following manner :



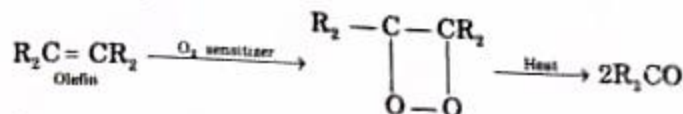


The hydroxy-hydroperoxide readily eliminate hydrogen peroxide and forms carbonyl compound.

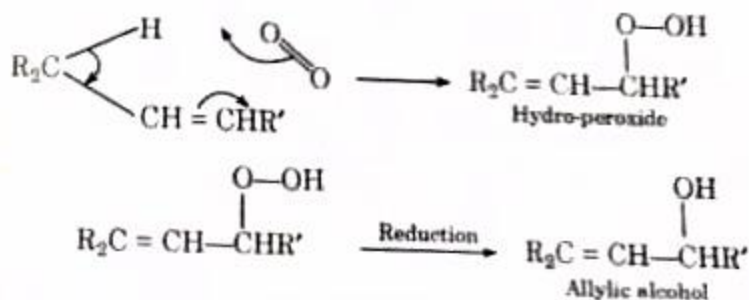


(b) (ii) In the alternative path, the excited sensitizer (triplet state) interacts with the ground state of oxygen (triplet oxygen molecule) to give the excited oxygen molecule (singlet oxygen), while the sensitizers return to its ground state ( $S_0$ ). The excited oxygen molecule (singlet oxygen) now interacts directly with the organic substrate to form peroxide. In this way, the peroxide formation is explained in the following examples :

(a) Olefins (without allylic hydrogen atom) form dioxetans, which on heating forms carbonyl compounds.



(b) Olefins (with an allylic hydrogen atom) form hydroperoxide, which can be reduced to give allylic alcohol.



(c) Cyclohexa 1, 3-diene, phenanthrene etc. (conjugated diene) react with singlet oxygen to form the respective peroxide, which can be reduced easily to diols.

