Photochemical reaction: A lightning phenomena

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Abstract

The chemical reaction which is occur by the absorption of the light or photon is called as Photochemical reaction. And the branch of the chemistry which is dealing with the study of these types of reactions is called as photochemistry. Photochemical reaction are also called as light reaction, because they have got the activation energy from the light.

In this article we have covered the important aspects of photochemistry. Like the various rules of photochemistry which are the base of photochemical reaction and the important phenomena Jablonski Diagram which states about the mechanism of photochemical reaction and various light radiation process which are happened by the electronic transitions. We have also discussed the Quantum Yield by which we can determine about the number of molecules activated or decomposed by absorption of single photon. Including the Quantum Efficiency which gives the description about the efficiency of the Photosensitive Devices and also with the types of photochemical reaction with examples, which gives the idea about the various chemical reaction which are types of photochemical reactions.

Keywords: Photochemical Reaction, Photochemistry, Light Reaction, Jablonski, Diagram, Quantum Yield, Quantum Efficiency

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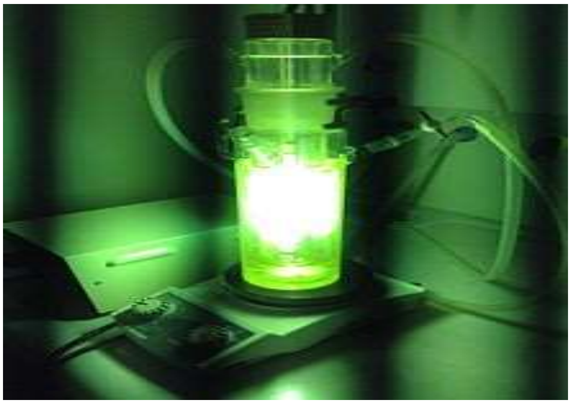
Introduction

The study of chemical Reactions, Isomerization & Physical behavior that may occur under the influence of visible/ultraviolet light is called photochemistry. It is the branch of chemistry concerned with chemical effects of light. Photochemistry is used to describe a chemical reaction caused by absorption of UV (wavelength 100-400 nm), visible light (400-750 nm), or infrared (750-2500 nm) radiation. Photochemical reaction are valuable in organic & inorganic chemistry because they proceed differently than thermal reaction. Many thermal reaction have photochemical part in them.

Thermodynamically disfavored products can be formed through photochemical reactions.



Basics of Photochemistry

1. **Rules of Photochemistry**

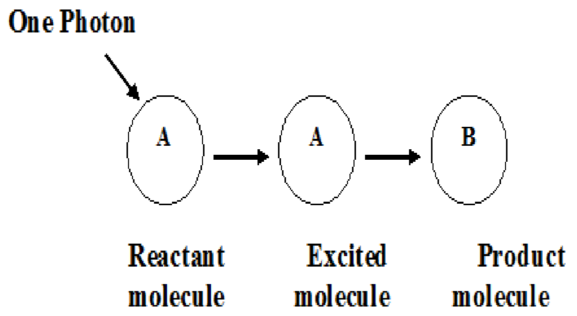
a. **Grothus Draper Law** (1st Law of Photochemistry): This law was developed by Theodor Grotthus & John W Draper.

The very 1st step in a photochemical reaction is the photo excitation where the reactant is elevated to a state of higher energy that in excited state.

If light of particular wavelength is not absorbed by system, no photochemistry will occur & no photo biological effects will be observed no matter how long one irradiates with that wavelength of light.

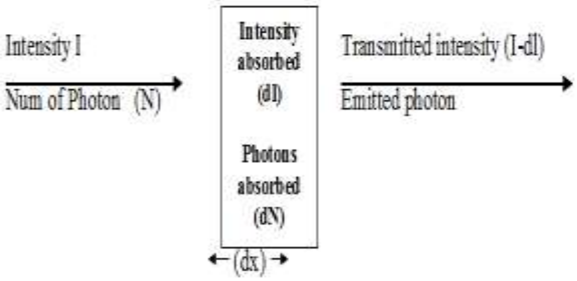
b. **Stark- Einstein Law:** This law was derived by Albert Einstein, during his development of quantum theory of light.

This law is also called "Photo equivalence Law". "For each photon of light absorbed by chemical system, only 1 molecule is activated for a photochemical reaction."



c. **Bunsen Roscoe Law of Reciprocity:** "Photochemical effect is directly proportional to the total energy dose, irrespective of the time required to deliver the dose."

d. **Beer Lambert Law:** This law states that:
"As the thickness and concentration of medium increases the intensity of transmitted light from medium decreases."



- When light is passed through a medium, some amount of it is absorbed. This absorbed amount of light causes photo chemical reaction.
- Let a medium of thickness dx is placed such that light of Intensity I is incident on it. Let dl be the amount of absorbed intensity of light.
- The Intensity of Transmitted light will be I-dl.
- The intensity of radiation can be defined as the number of photons that pass across a unit area in the unit time.
- Let N be the number of incident photons, & the number of absorbed photons in dx thickness be dN.
- The fraction of photons absorbed will be $\frac{dN}{N}$

$$\frac{dN}{N} = bdx = -\frac{dI}{I}$$

b = proportionality constant (Absorption coefficient)
Let us set $I=I_0$ at x=o & integrate
This gives,

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

This equation is known as Lambert law.

Beer extended this relation to solution of compounds in transparent solvents.

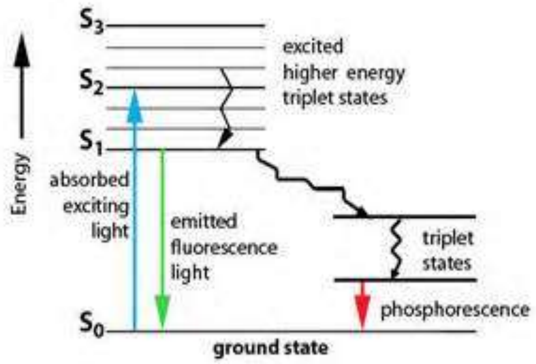
$$\ln(I/Io) = -\epsilon Cx \longrightarrow (2)$$

C= molar concentration
ϵ =molar absorption co-efficient
Equation 2 is called Beer – Lambert Law
Beer-Lambert law forms the basis of specctrophotometric methods of chemical analysis.

2. **Jablonski Diagram:** Jablonski diagram was developed by Alexander Jablonski.

He developed a written representation that generally shows a portion of the possible consequences of applying photons from visible spectrum of light to particular molecule.

These schematics are referred to as Jablonski Diagram.



When a molecule is at rest or ground state it has 3 energy level.
1. Rotational energy
2. Vibrational energy
3. Electronic energy

When electromagnetic radiation fall on molecule, it absorbs the radiation & changes are seen in its energy level.
In Jablonski Diagram,
Energy is indicated on X –axis
Vibrational energy is indicated on Y- axis.

At each electronic level of ground state, there is large number of vibrational energy levels (S_0, S_1, S_2, S_3…..)

Electrons of a molecule prefer to remain at lowest vibration level of the electronic ground state.

When the molecules absorb ultraviolet or visible light the molecul moves into its excited electronic state.

Excited electronic state has many different vibrational energy levels (S_0', S_1', S_2',S_3'……)

The electrons absorb hv1 radiation and move to one of the vibrational levels of excited state.

It is singlet state in which all electrons are paired and electrons spin in opposite dierection to each other.

The electrons remain in this vibrational energy of excited state for 10-8 to 10-6 seconds

The molecules in excited state lose energy by emitting photons or by collisions of molecules.

The molecules emit the same amount of light that is absorbed.

Due to intercollisions between molecules, the atoms move to lowest vibrational energy of excited state.

From the lowest vibrational energy of excited state, molecules return to ground state by photoemission of energy.

- **Fluorescence:** When the molecules falls from lower vibrational energy of excited state to ground state it emits energy hv2 that is lower than the energy absorbed.

  Also this emitted radiation ha longer wavelength

Flourescence is a radiation emitted in Transition of a molecule from lowest level of singlet excited state to singlet ground state

In some cases,

Electrons travel from excited vibrational singlet state to excited vibrational triplet state.

Electrons can remiainin excited vibrational triplet state for fraction of seonds to seconds.

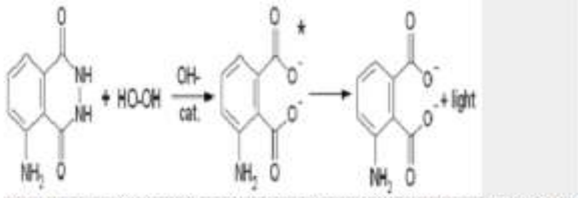
- **Phosphorescence:** When electron moves from triplet excited state to ground level if emits energy hv_2, this light emitted is called phosphorescence

- **Chemiluminescence:** When some chemicals react with each other, then in that reaction the bond of reactants getting broken down and the new bonds of the products has been formed, so for this process some amount of energy have been required by these reacting chemicals or in some case they release the energy. In the reaction, if the chemicals required the energy or absorb the energy in the form of heat, then these types of chemicals reactions are called as Endothermic Reaction. And if the energy is release in the form of heat then these types of reactions are called as Exothermic Reactions. More unusually, the energy release from the reaction is in the form of light and in this case it is called a Chemiluminescence**.**

In photochemistry, we are usually concerned with providing molecules with light to activate a reaction. But with the chemiluminescence, it's the other way around, it is a chemical reaction results in the emission of light.

The example of Chemiluminescence is as below:

When hydrogen peroxide (e.g. from household bleach) is added to luminol, in the presence of base and a catalyst (such as iron(III) which gets involved in the oxidation, 3-aminophthalate is formed. But the energy involved in the oxidation of luminol by the peroxide results in the phthalate having an electronically excited state. The releases this excess energy by emission of light, giving the blue colour observed.



Luminol reacts with hydrogen peroxide to produce an electronically excited 3-aminophthalate, which emits in the blue (450 nm)

3. **Quantum Yield:** "The number of molecules reacyed or formed per photon of light absorbed is termed as quantum yield"

$$\text{Quantum yield} = \frac{\text{No. of molecules reacted or formed}}{\text{No. of photons absorbed}}$$

When photochemical reaction strictly obeys Einstein's law, quantum yield =1. Many a times photochemical reactions obey Einstein's law but sometimes not.

The number of molecules reacted or decomposed is often found to be markedly different from the number of photons of radiation absorbed in given time.

a. **High Quantum Yield:** When two or more molecules are decomposed per photon, the Quantum Yield > 1, so the reaction has a high quantum yield.

- **Causes of High Quantum Yield:**

a. Reaction subsequent to primary reaction: One photon absorbed in primary reaction dissociates one molecule of reactant.

But excited atoms that were formed in primary reaction may result in start of primary reaction in which a next molecule is decomposed.

b. Formation of Chain Reaction: When there are two or more reactants one of their molecules absorbs a photon and dissociates (primary reaction). The excited atom that is produced starts a secondary reaction chain

- **Examples of High Quantum Yield**
  - Decomposition of HI
  - Hydrogen-Chloride Reaction

b. **Low Quantum Yield:** When two or more photons are reuire to decomposed a single molecule.

The Quantum Yield < 1, so the reaction has a low quantum yield.

- **Causes of Low Quantum Yield**

(i) Deactivation of Reacting Molecules: Excited molecules in primary reaction may be activated before they get opportunity to react.

This occurs due to collisions with some inert molecules or by fluorescence

(ii) Occurrence of Reverse of Primary Reaction: Primary reaction generally yields a plymer.

The product then undergo a thermal reaction giving back the reactant molecules.

The reverse thermal reaction proceeds till the equilibrium state is reactant.

(iii) Recombination of Dissociation Fragments: In a primary process, reactant molecules may dissociates to give smaller fragments

These fragments recombine to give back reactant

This will create greatly lower yield.

- **Examples of Low Quantum Yield**

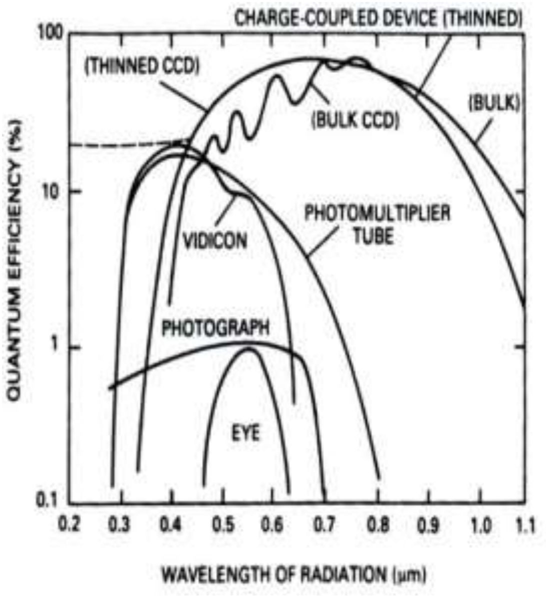
1. Dimeration of Anthracene
2. Combination of H2 and Br2

4. **Quantum Efficiency:** Quantum efficiency is the ratio of incident photon to converted electron of the photosensitive device.

Quantum efficiency is the measurement of electrical sensitivity of the device to light. In a charged Coupled Device, Quantum Efficiency is the percentage of photons hitting the device's photoreactive surface that produce charge carriers.

It is measured in electrons/photon or Amp/watt The energy of a photon is inversely proportional to its wavelength, quantum efficiency is often measured over a range of different wavelength.

When the photons have energy below the band gap their Quantum Efficiency is zero.



Quantum Efficiency of solar cells

A Quantum Efficiency value pf solar cell indicates the amount of current that the cell will produce when photons are incident of particular wavelength.

If the Quantum Efficiency of cell is integrated over whole solar electromagnetic spectrum we can evaluate the amount of current that the cell will produce when exposed to sunlight Ratio of Energy-Production valve and the highest possible energy production value of cell gives the over all energy conversion efficiency value of the cell

Types of Quantum Efficiency

(i) **External Quantum Efficiency:** It is the ratio of the number of charge carriers collected by solar cell to the number of photon of given energy shining on the solar cell from outside.

External Quantum Efficiency =

$$\frac{\text{No. of electrons produced}}{\text{No. of incident photons}}$$

(ii) **Internal Quantum Efficiency:** It is the ratio of number of charge carriers collected by the solar cell to the number of photons of photons of a particular energy that shines on the surface of solar cell from outer side and are absorbed by the cell

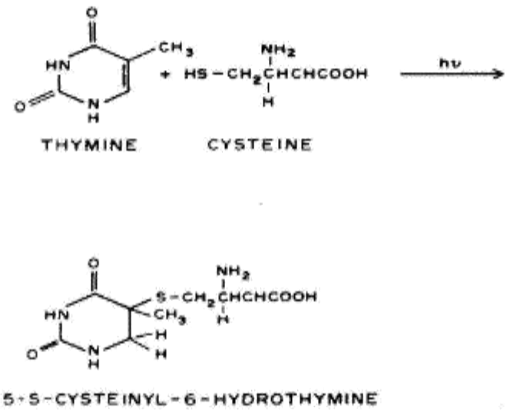
Internal Quantum Efficiency =

$$\frac{\text{No. of electrons produced}}{\text{No. of absorbed photons}}$$

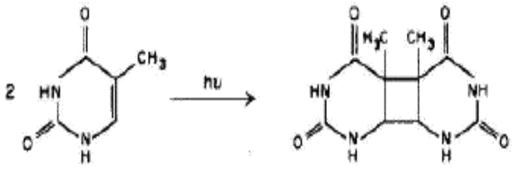
Photochemical Reactions

(a) **Linear Addition to an Unsaturated Molecule**

Example: The pyrimidine base, thymine in DNA can combine with the Amino acid residue, cysteine in proteins. This proves to be a model for the photochemical cross linkage of the proteins and DNA by ultraviolet Radiation.



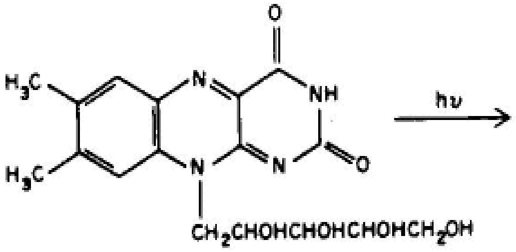
(b) **Cycloaddition of Unsaturated Molecule:** When there occurs a reaction between two thymines a ring product is formed and also an important class of products thymine dimmer is formed in DNA by Ultraviolet radiation.



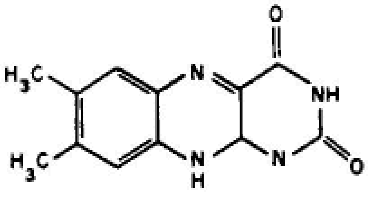
THYMINE THYMINE DIMER

(c) **Photo Fragmentation**

Example: The side chain of Riboflavin can split off to form Lumiflavin.



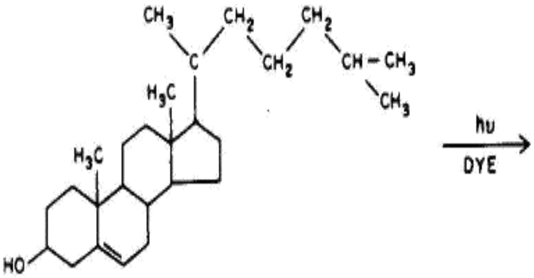
RIBOFLAVIN



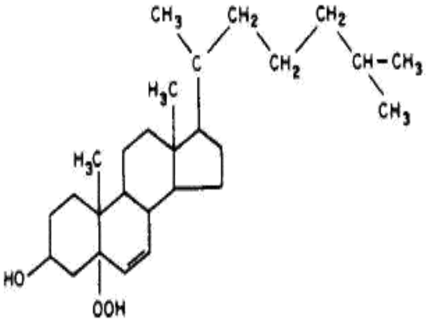
LUMIFLAVIN

(d) **Photo Oxidation**

Example: The ring structure of cholesterol can add a peroxy group.



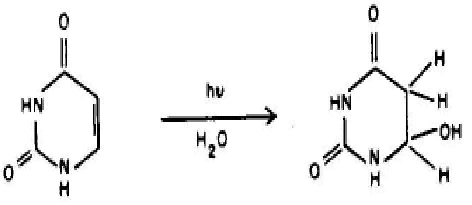
CHOLESTEROL



3β-HYDROXY-5α-HYDROPEROXY-Δ⁶-CHOLESTENE

(e) **Photo Hydration**

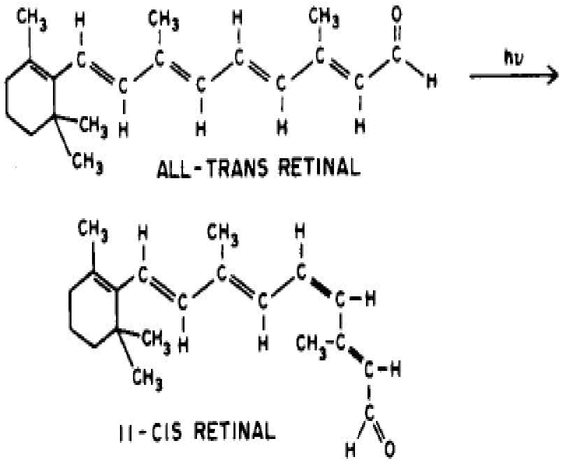
Example: Uracil can add a molecule of water to its 5-6 double bond when UV irradiated.



URACIL 6-HYDROXY-5-HYDROURACIL

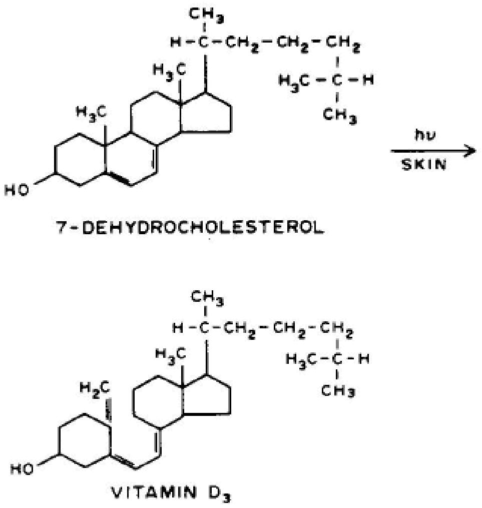
(f) **Cis-Trans Isomerization**

Example: All trans retina can be converted to 11-cis retinal



(g) **Photo Rearrangement**

Example: 7- dehydrocholesterol can be converted to Vit D3



(h) **Energy Transfer**

Example: All photosensitized reactions.

- **Examples of Photochemical Reactions**

(i) **Photo Synthesis:** Plants use solar energy for conversion of carbon dioxide of atmosphere and water into glucose and oxygen.

(ii) **Formation of Vitamin D:** Humans form vitamin D by exposure to sunlight.

(iii) **Bioluminescence:** In fireflies, an enzyme in abdomen catalyzes a reaction that produces light

(iv) **Photodegradation:** Polyvinylchloride and Fp.

Medicine bottles are prepared from darkened glass to prevent drugs from photodegradation.

(v) **Photodynamic Therapy:** Light is used for destruction of Tumors by action of Singlet oxygen generated by photochemical reaction of Triplet oxygen.

(vi) **Vision:** Vision is initiated by photochemical reaction of Rhodopsin.

Conclusion

The Photochemistry or Photochemicals Reactions covers the wide range of the organic reaction. Many of the organic reactions are the type of photochemical reaction, because they absorb the light and getting their activation energy from the absorb light of photon.

Thought light is the eternal source of the energy, we yet not able to utilize it fully. Still the photochemistry and photochemical Reaction requires some works and developments so we can driven our many of reactions more efficiently and easily.

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