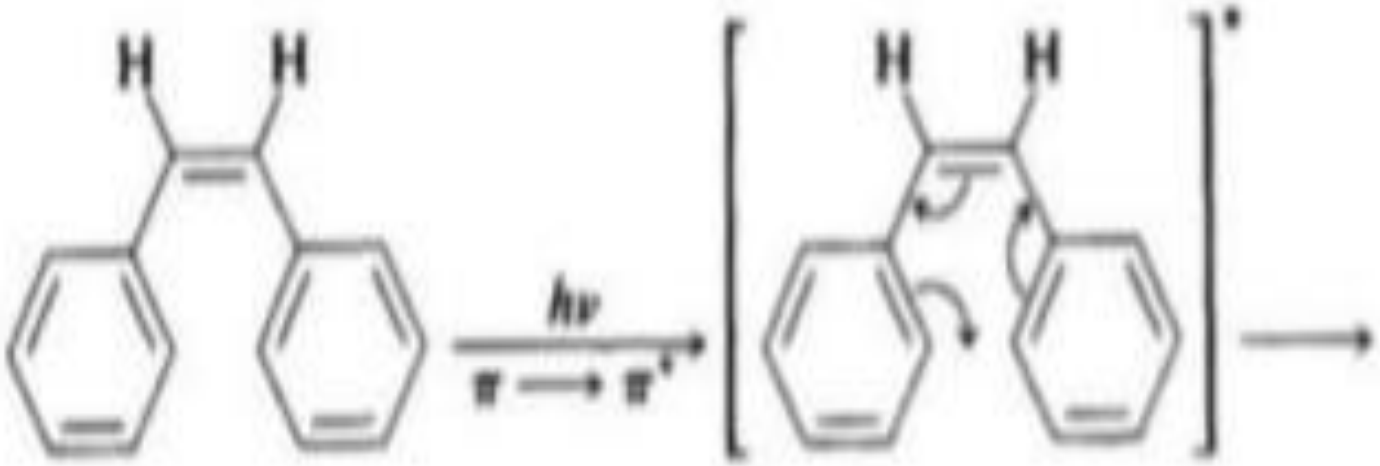
GOVT. DR. SHAYAMA PRASHAD MUKHARJEE SCIENCE & COMMERCE PG COLLEGE (OLD BENAZEER BHOPAL

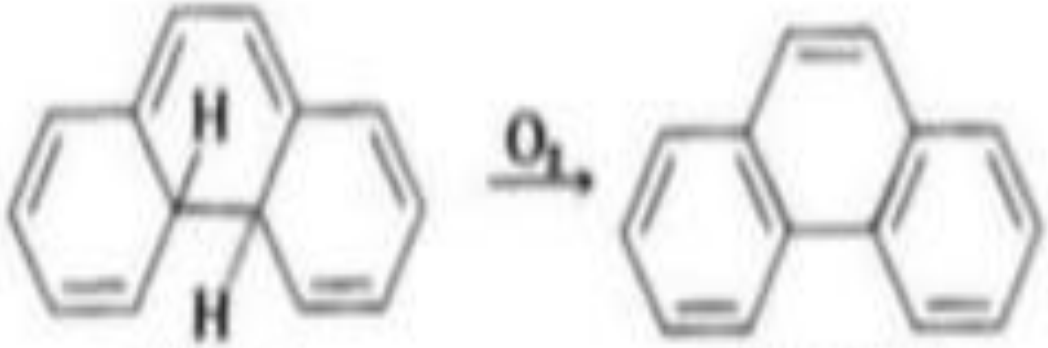
SUBJECT- PHOTOCHEMISTRY

- TOPIC-PHOTOCHEMICAL CYCLISATION OF ALKENE
- CLASS-MSC 3rd SEMESTER
- PRESENTED By-AARTI KUSHWAHA

PHOTOCHEMICAL CYCLISATION REACTION OF ALKENE

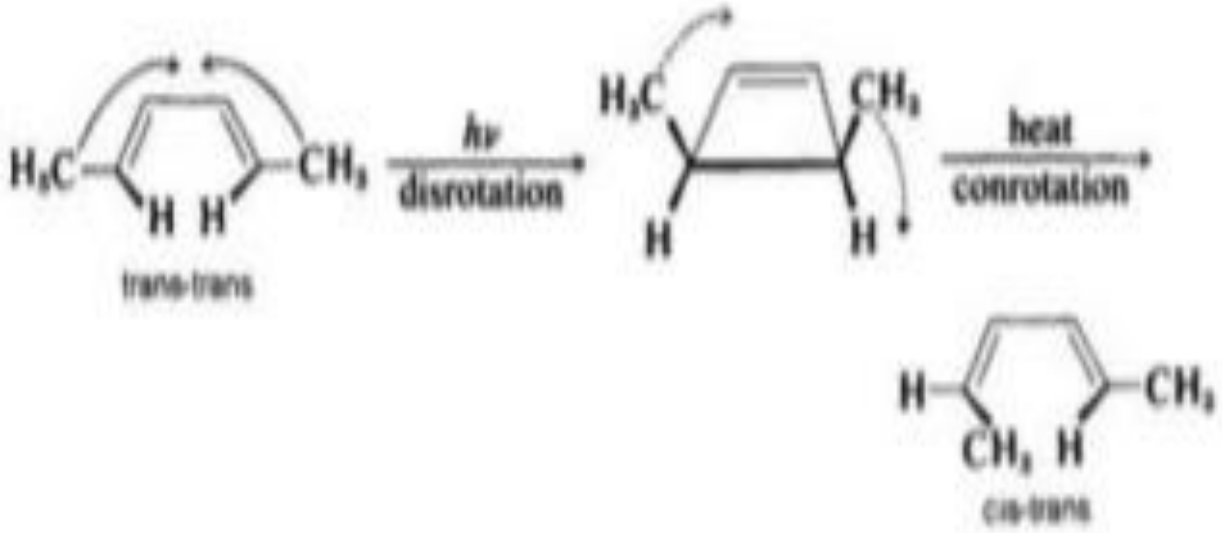
One may well ask why the isomerization of alkenes discussed in the preceding section requires a sensitizer. Why cannot the same result be achieved by direct irradiation? One reason is that a singlet excited state (5_1) produced by direct irradiation of an alkene or arene crosses over to the triplet state (7) inefficiently compared to a excitation of ketones). Also, the S, state leads to other reactions beside isomerization which, in the case of 1.2-diphenyl ethene and other conjugated hydrocarbons, produce cyclic products. For example, cir-1.2-diphenylethene irradiated in the presence of oxygen gives phenanthrene by the sequence of Equation 28-8. The primary photoreaction is cyclization to a dihydrophenanthrene intermediate, & which, in the presence of oxygen, is converted to phenanthrene:





6 (trans) phenanthrene (28-8)

- The cyclization step of Equation 28-8 is a photochemical counterpart of the electrocyclic reactions discussed in Section 21-10D. Many similar photochemical reactions of conjugated dienes and trienes are known, and they are of great interest because, like their thermal relatives, they often are stereo specific but tend to exhibit stereochemistry opposite so what is observed for formally similar thermal reactions. For example.


H3C
CH3
H H
trans-trans
hν
disrotation
H3C
CH3
H
H
heat
conrotation
H
CH3
CH3 H
cis-trans

- These reactions are 4n-electron concerted processes controlled by the symmetry of the reacting orbitals. The thermal reaction is most favorable with a Mobius transition state (achieved by conrotation), whereas the photochemical reaction is most favorable with a Hückel transition state.

GOVT. DR. SHYAMA PRASAD MUKHERJEE SCIENCE AND COMMERCE COLLEGE BHOPAL (M.P.)

- TOPIC – PHOTOCHEMICAL CYCLIZATION OF ALKENE
- CLASS – MSC 3rd SEMESTER
- SUBJECT – PHOTOCHEMISTRY
- PRESENTED BY – ABHISHEK SINGH RAJPOOT

PHOTOCHEMICAL CYCLIZATION REACTION OF ALKENE

(2) CYCLISATION REACTIONS

In the olefinic bonds, there is found two types of cyclisation reactions :

(1) Concerted cycloaddition Reactions

(2) Non-concerted cycloaddition Reactions

Cyclisation reactions of alkenes can be carried out by triplet sensitizer and are often accompanied by cis-trans isomerisation.

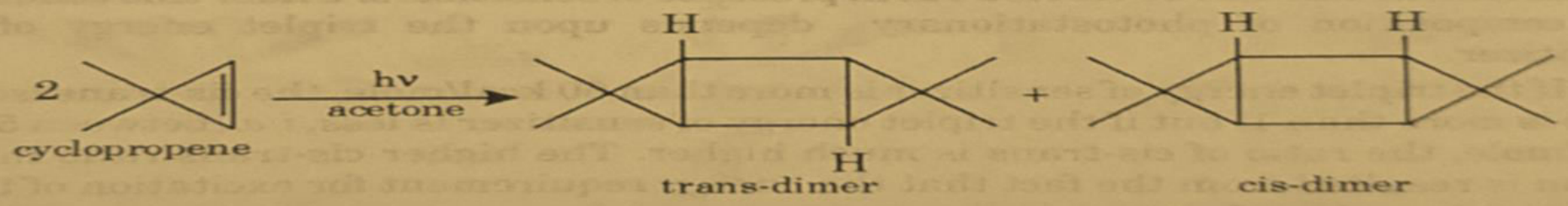
Most of the simple alkenes have high triplet energy to be sensitized efficiently by organic sensitizer.

The cyclisation of cyclic alkenes with three, four or five membered ring can be sensitized with high energy organic sensitizer such as acetone rather than benzophenone (which gives oxetane).

The cyclisation process involves the formation of an excited state triplet molecule which subsequently reacts with a ground state olefin molecule.

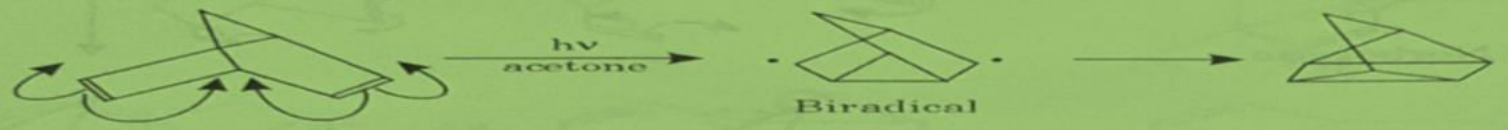
The non-concerted cyclisation reactions consist of two steps, first is the formation of a biradical intermediate and the second is, non-stereospecific or partially stereospecific cyclic product.

Some characteristic cyclisation reactions of alkenes are given below :



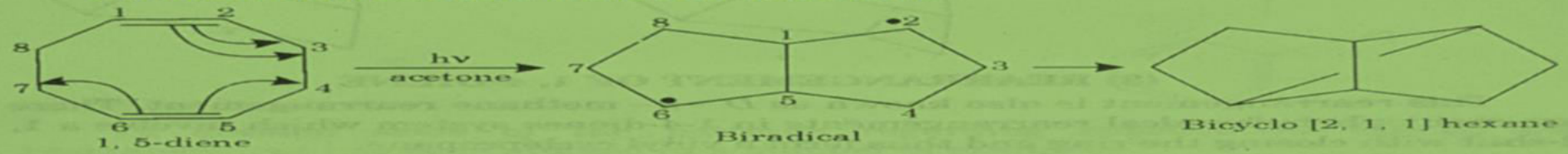
PHOTOCHEMICAL CYCLIZATION REACTION OF ALKENE

Intra molecular cyclisation between Two Double Bonds :

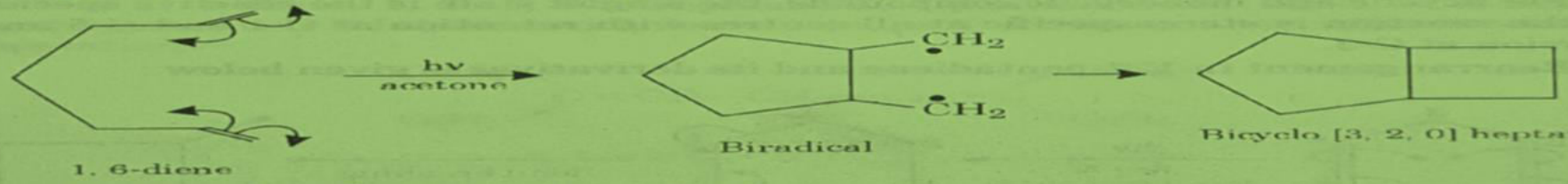


Here, cyclisation reaction occurs between two properly situated double bonds in a molecule, which yields an isomeric product.

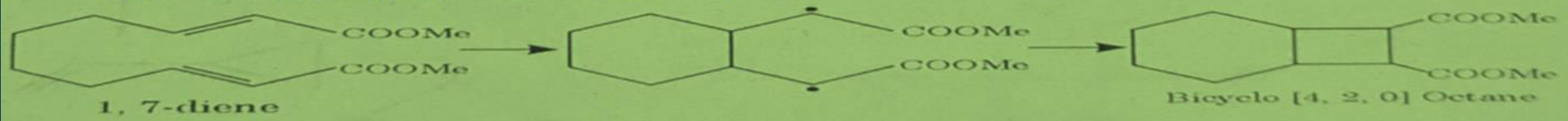
Cyclisation Reaction between 1, 5-diene



Cyclisation Reaction in 1, 6-diene : 1, 6-diene undergoes the expected straight cyclo addition in the triplet state to give bicyclo [3, 2, 0] heptane.



Cyclisation Reaction in 1, 7-diene



GOVT. SHYAMA PRASAD MUKHARJI SCIENCE & COMMERCE COLLEGE BHOPAL

SUBJECT - PHOTOCHEMISTRY

TOPIC

EQUATION DETERMINATION OF RATE CONSTANT OF PHOTOCHEMICAL REACTION

M.Sc. 3RD SEMESTER

PRESENTED BY - ANANT GOURAV

प्रकाश रासायनिक अभिक्रिया का दर स्थिरांक का निर्धारण करना -

पूर्व में हम क्रियाशील माध्यक की दर एवं जीवन काल के बीच सम्बन्ध का अध्ययन कर चुके हैं अब किसी द्वि आण्विक अभिक्रिया का उदाहरण लेकर उसके दर स्थिरांक का निर्धारण निम्नानुसार करेगे -

$$A^{*} + B \xrightarrow{k} p$$

माना कि यह अभिक्रिया त्रिक उत्तेजित अवस्था से प्राप्त हुई है।

प्रतिदीप्ति उत्सर्जन पद लेने पर

		दर
$A + h\nu \longrightarrow A^{*}$		I_a
$1\ A^{*} \longrightarrow A$		$k\ I_c\ [1\ A^{\circ}]$
$1\ A^{*} \longrightarrow 3\ A^{*}$		$1\ k_R\ [1\ A^{*}]$
$1\ A^{*} \longrightarrow 3\ A^{*}$		$k\ 1\ SC\ [1\ A^{*}]$
$1\ A^{*} + B \longrightarrow$	उत्पाद	$1\ k_R\ [1\ A^{*}]\ [B]$

स्फुरदीप्ति उत्सर्जन

$3\ A^{*} \longrightarrow A$		$k\ 1\ Isc\ [3\ A^{*}]$
$3\ A^{*} + B \longrightarrow$	उत्पाद	$3\ k\ B\ [3\ A^{*}]\ [B]$

अभिक्रिया की दर क्वाण्टम लब्धि ϕ के रूप में अभिकारक के अदृश्य उत्पाद की उपस्थिति को व्यक्त करता है।

$$\phi_R^{0} = \frac{I}{I_a}\frac{d\,(x)}{dt} = \frac{KIsc}{k1c + K1SC + kf}\ \frac{K_R\,[B]}{k^{T}{}_{1SC} + k_R[B]}$$

$$= \phi_{1SC}\ \frac{K_R\,[B]}{k^{T}{}_{1SC} + k_R[B]}$$

$$\frac{1}{\phi_R^0} = \frac{1}{\phi\, 1SC} + \frac{1}{\phi\, 1SC}\,\frac{K^T\, 1SC}{K_R\,[B]}$$

उपरोक्त समीकरण में एक आरेख 1/ΦR बनाम 1/[B] के बीच खीचे तो रेखीय प्राप्त होता है ।

इस प्रकार अभिक्रिया kR के लिए Z2 स्थीरांक तुलनात्मक विधि से गणना कर लिया जाता है ।
अभिक्रिया तृतीय पदार्थ की उपस्थिति में की जाती है जो अभिक्रिया का शमन रासायनिक भौतिक रूप से करती हैं।

THANK YOU

FOR WATCHING

GOVT. SHYAMA PRASAD MUKHARJI SCIENCE & COMMERCE COLLEGE BHOPAL

SUBJECT - PHOTOCHEMISTRY

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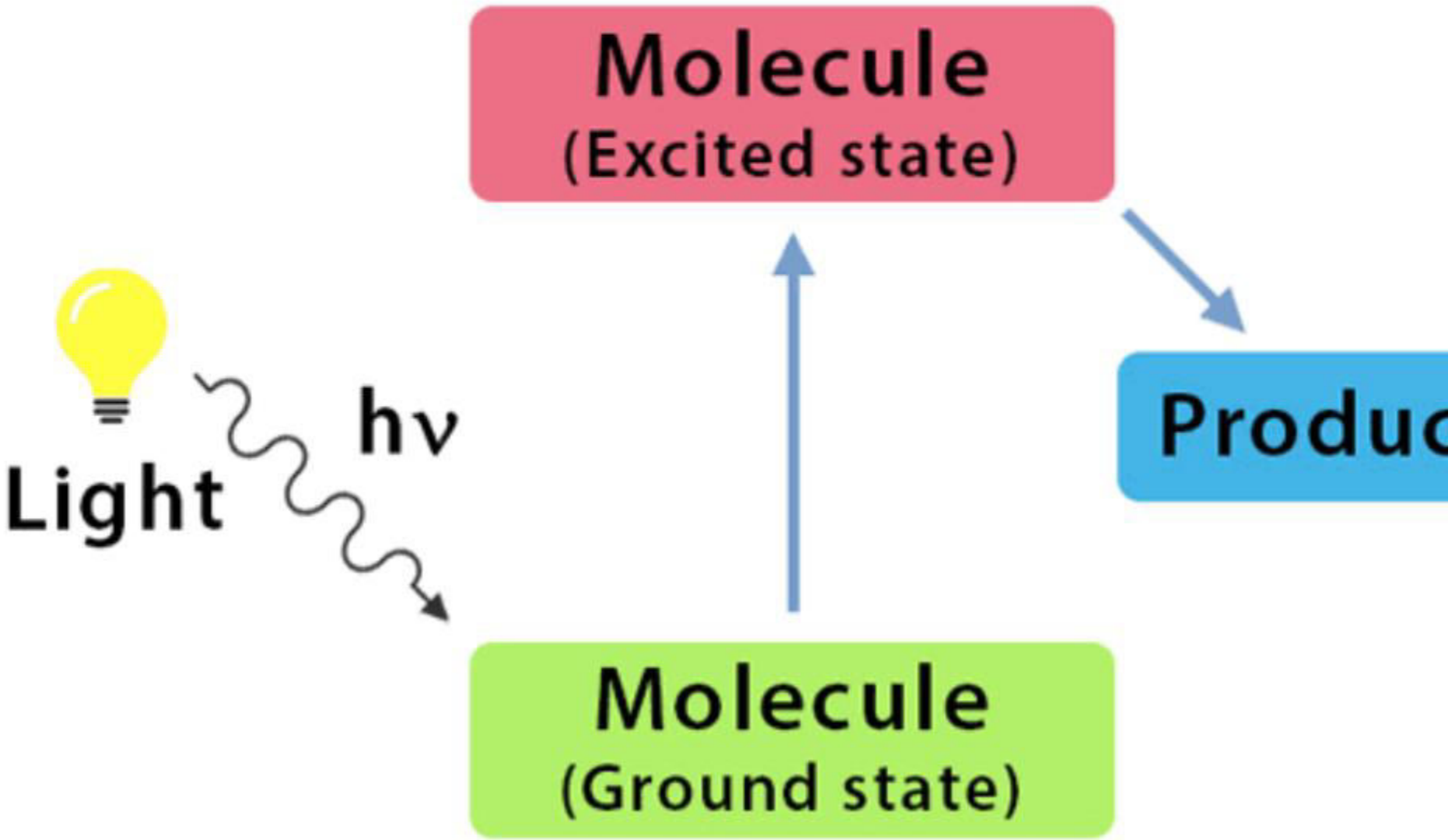
PHOTOCHEMICAL REACTION

- वे अभिक्रियाएँ जो प्रकाश का अवशोषण करने पर ही संपन्न होती है, **प्रकाश-रासायनिक अभिक्रिया (Photochemical Reaction)** कहलाती है।
- प्रकाश-रासायनिक अभिक्रियाएँ **दो** प्रकार की होती है, जो इस प्रकार है- i. प्रकाश संश्लेषण अभिक्रिया ii. तथा प्रकाशअपघटन अभिक्रिया।

Photochemical Reactio



EX. -

$$H_2 + CL_2 \xrightarrow{hv} 2HCL$$

$$Cl_2^* + hv \longrightarrow 2CL^*$$

$$Cl^* + H_2 \longrightarrow HCl + H$$

$$H^* + Cl_2 \longrightarrow HCl + H^*$$

$$Cl^* \longrightarrow \tfrac{1}{2} Cl_2$$

2.2 Derivation of rate constant

According to classical collision theory (hard sphere theory), rate of the reaction as given by equation (1) depends on collision density and exponential factor. Or one can simply say that the rate of a bimolecular gaseous reaction depends on collision frequency and its probability of success.

A + B $\longrightarrow$ products

$$Rate = -\frac{dn_A}{dt} = kn_An_B \qquad ...(5)$$

$$[A] = \frac{n_A}{N_A}, [B] = \frac{n_B}{N_A}, where\ N_A\ is\ the\ Avogadro\ number$$

$$-\frac{dn_A}{dt} = {N_A}^2k[A][B]$$

$$-N_A\frac{d[A]}{dt} = {N_A}^2k[A][B]$$

$$-\frac{d[A]}{dt} = N_Ak[A][B] \qquad ...(6)$$

Substituting the expression of collision density from equation (2) into equation (1) along with n_A and n_B gives the rate as,

$$Rate = {N_A}^2\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2}[A][B]e^{-E_0/RT} \qquad ...(7)$$

$$k = N_A \sigma \left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_0/RT} \qquad \ldots(8)$$

THANK YOU

FOR WATCHING

GOVT. DR. SHYAMA PRASAD MUKHERJEE SCIENCE & COMMERCE COLLEGE

SUBJECT : PHOTOCHEMISTRY

TOPIC
BEER-LAMBERT LAW

DEPARTMENT OF CHEMISTRY

M.Sc. 3rd SEMESTER

Guided By
DR ILA JAIN

Presented By
RIYA JOSHI

LAMBERT'S LAW

- *PIERRE BOUGUER in 1729*
- *JOHAN HEINRICH LAMBERT quoted BOUGER'S discovery in 1760*
- **Equal parts in the same absorbing medium absorb equal fractions of light that enters them**

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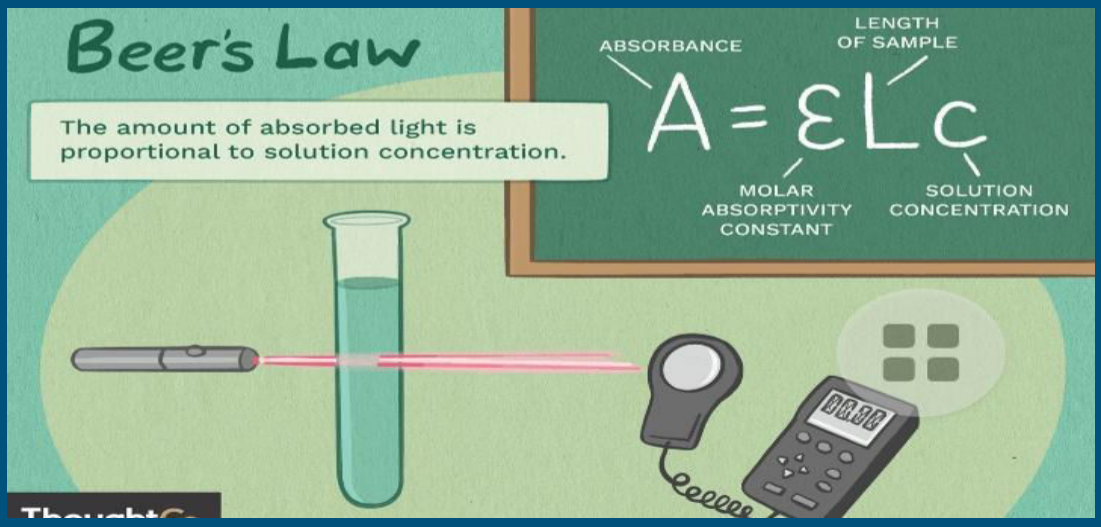


Beer lambert law

- Also known as Beer's law.

- There is a linear relationship between the *concentration* and the *absorbance* of the solution.

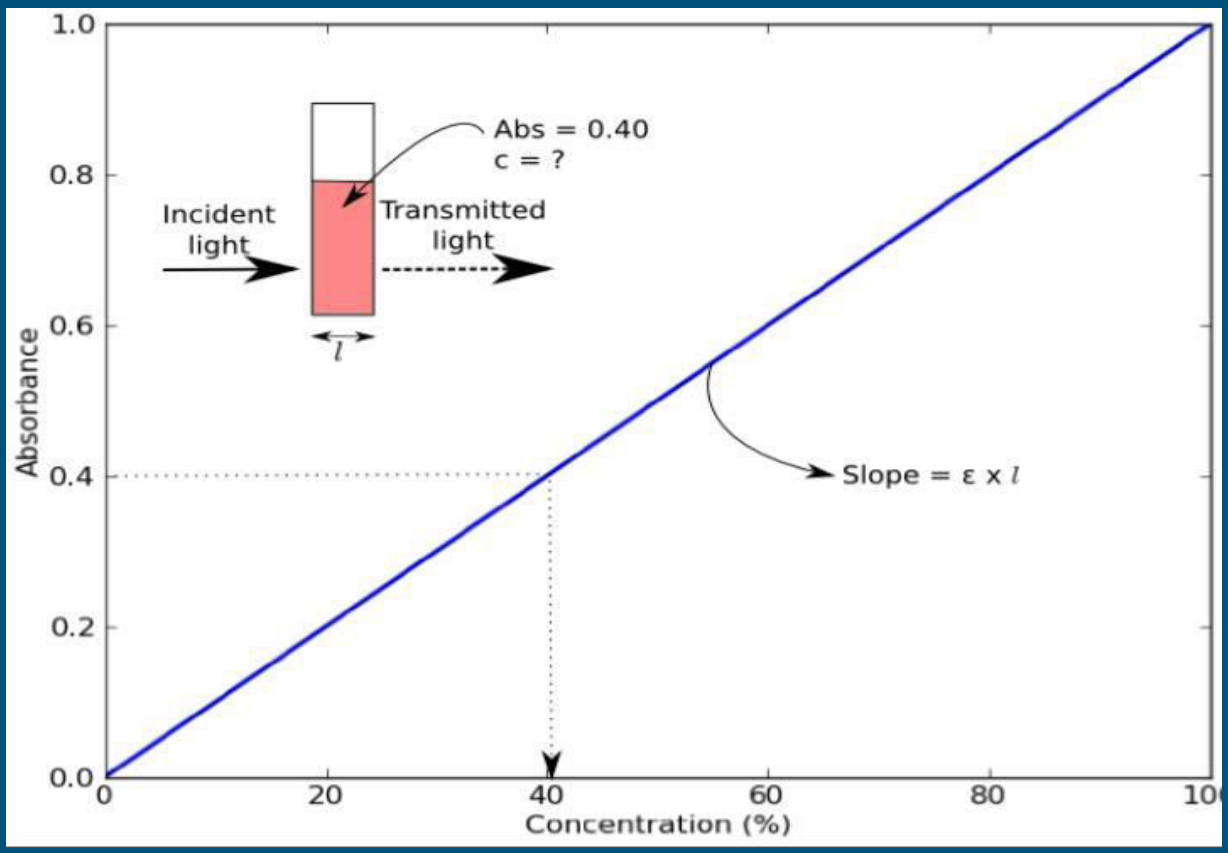
$$A = \varepsilon c l$$

A	Absorbance
ε	Molar absorption coefficient
c	Molar concentration
l	optical path length

GRAPH

- The slope of the graph (absorbance over concentration) equals the molar absorptivity coefficient.

- The linear nature of the curve.



ADVANTAGES OF BEER-LAMBERT LAW

- This law enables the concentration of a solution to be calculated by measuring its absorbance.

- INSTRUMENT : Spectrophotometer is based on the Beer-Lambert law .

Govt. Shyama Prasad Mukherjee Science And Commerce College, Bhopal

Name : Pratyush Mittal

Class : M.Sc. 3 rd Sem

Subject : Photo chemistry

Head of Department
Dr. Sudhanshu dhar dwivedi

Organized by
Ila Jain

Principal
Dr.Saroj Srivastava

Contents:

i. Definition
ii. Jablonski Diagram
iii. Photo Physical Process
iv. Types of Photo Physical Processes
v. Fluorescence
vi. Phosphorescence

Jablonski Diagram define :-

- In molecular spectroscopy, a Jablonski diagram is a diagram that illustrates the electronic states of a molecule and the transitions between them. The states are arranged vertically by energy and grouped horizontally by spin multiplicity

- The diagram is named after the Polish physicist Alexander Jablonski.

Jablonski Diagram

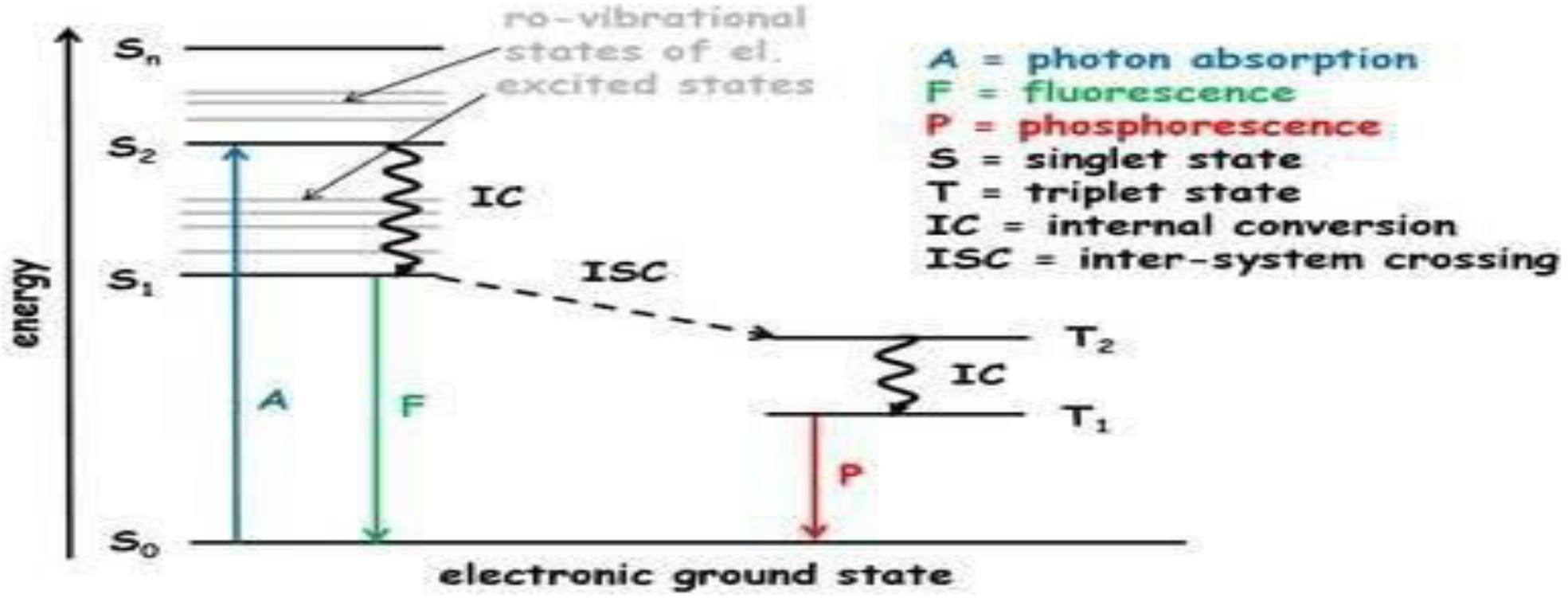


Photo Physical Processes:-

- The photo physical processes are those taking place without chemical change in the system

- Here, absorption (A), fluorescence (F) and internal conversion (IC) occur between singlet states, whereas intersystem crossing (ISC) and phosphorescence (P) involve singlet and triplet states.

Types Of Photo Physical Processes:-

1. Fluorescence
2. Phosphorescence

Fluorescence:-

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation.

a. Its emission ceases as soon as the source of exciting radiation is removed.

b. It can be stimulated in gases, liquids and solids.

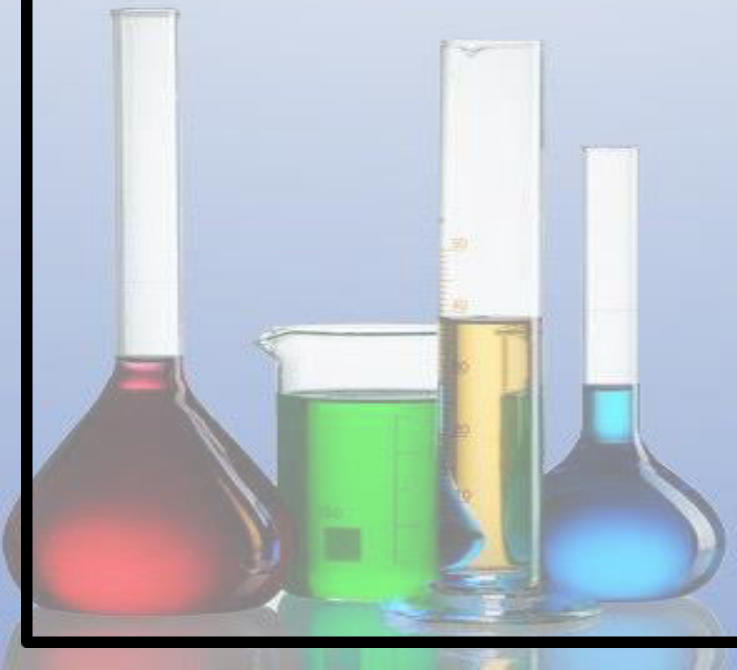
Phosphorescence:-

Phosphorescence is a specific type of photoluminescence related to fluorescence. Unlike fluorescence, a phosphorescent material does not immediately re-emit the radiation it absorbs

(a)If a system absorbs radiant energy and then emits partially or completely after a time lag in the form of radiation.

(b)It continues for some time even after the source of

THANK YOU



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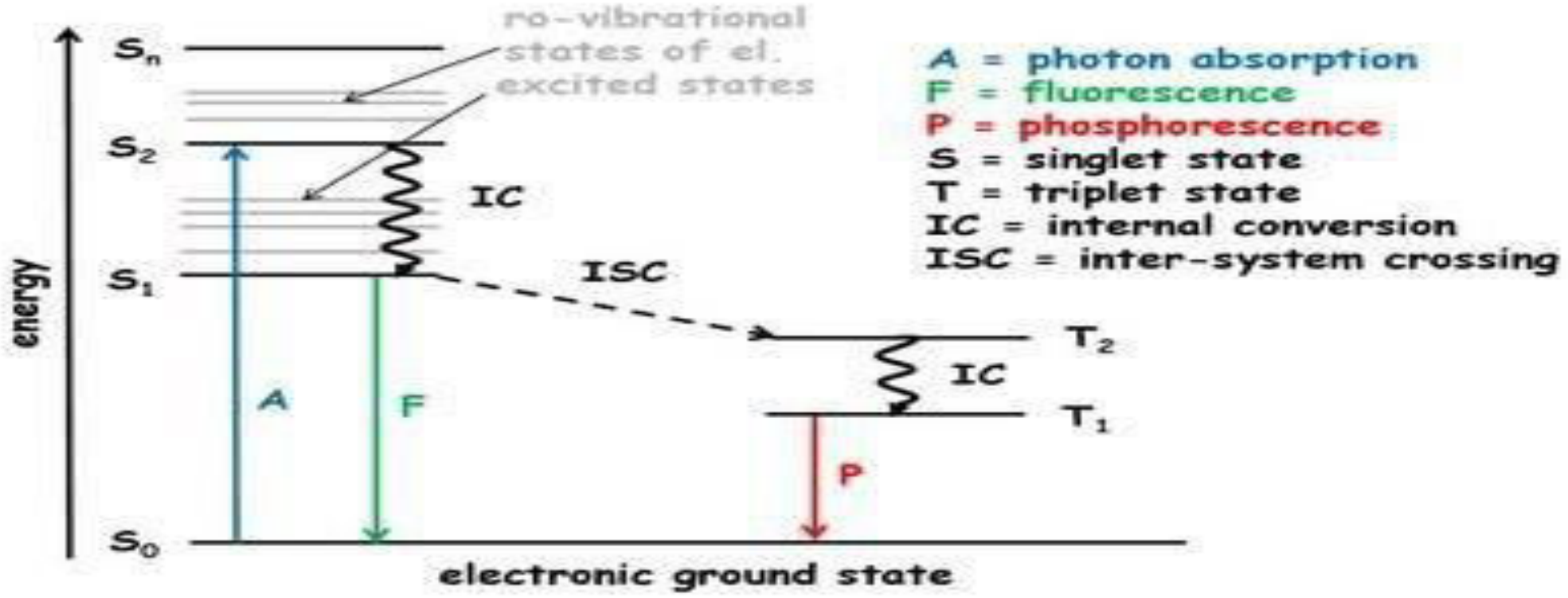

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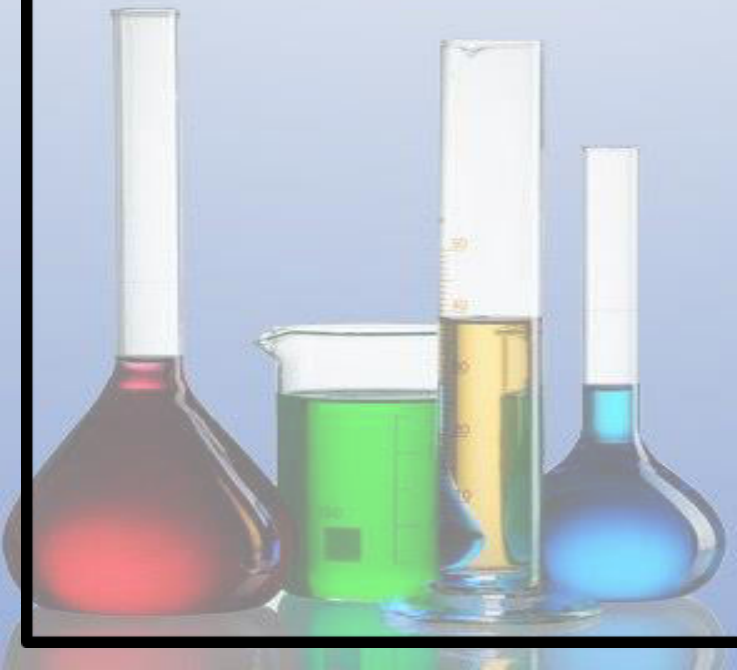

GOVT. DR. SHYAMA PRASAD MUKHERJEE SCIENCE & COMMERCE COLLEGE

SUBJECT : PHOTOCHEMISTRY

TOPIC
BEER-LAMBERT LAW

DEPARTMENT OF CHEMISTRY

M.Sc. 3rd SEMESTER

Guided By
DR ILA JAIN

Presented By
RIYA JOSHI

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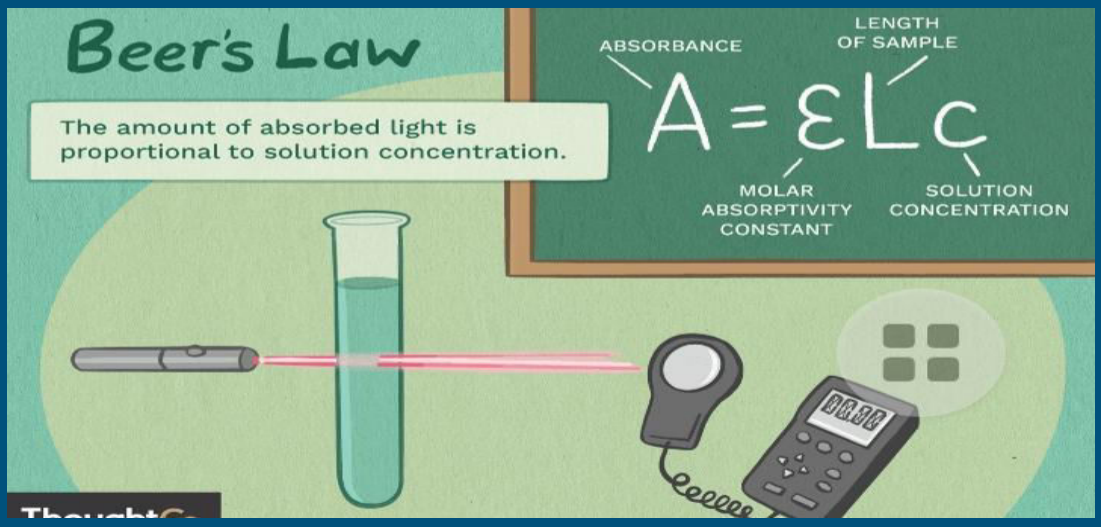

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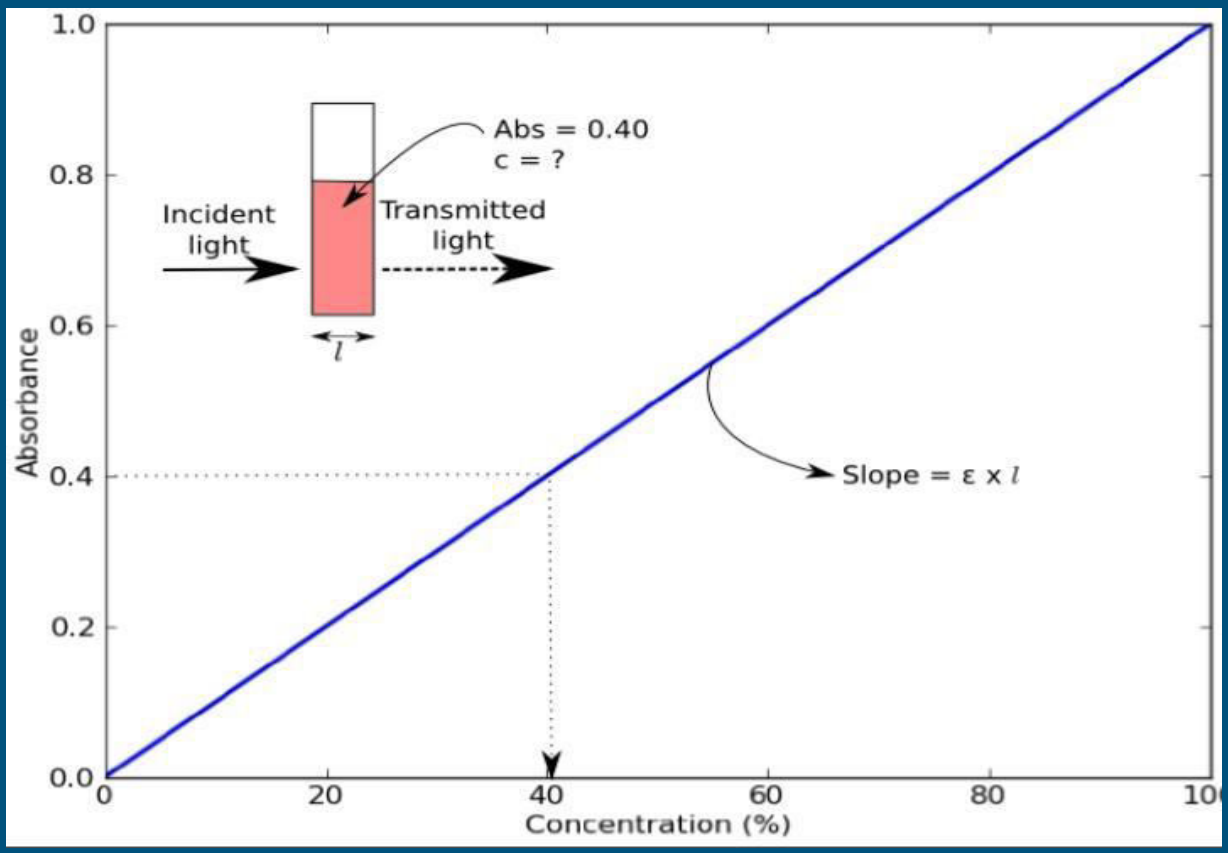

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Name = Arun Kumar Rakse

Class = M.Sc Final Year(chemistry)

Presentation On Photochemistry

Topic= Photo Dissociation And Gas Phase Photolysis

Roll. No= 2100600307

Collage Name = Govt. Dr. SPM Science And Commerce Collage Bhopal(M.P)

PHOTO DISSOCIATION

- **Photo dissociation**, **photolysis**, or **photodecomposition** is a chemical reaction in which a chemical compound is broken down by photons.
- It is defined as the interaction of one or more photons with one target molecule. Photo dissociation is not limited to visible light .
- Any photon with sufficient energy can affect the chemical bonds of a chemical compound.
- Since a photon's energy is inversely proportional to its wavelength, electromagnetic waves with the energy of visible light or higher, such as ultraviolet light, x-rays and gamma rays are usually involved in such reactions.

TYPES OF PHOTO DISSOCIATION

- Photolysis in photosynthesis.
- Photo induced proton transfer.
- Photolysis in the atmosphere.
- Astrophysics.
- Atmospheric gamma-ray bursts.
- Multiple photon dissociation.
- Gas phase photolysis

GAS PHASE PHOTOLYSIS

- The gas phase photolysis of $CHFCl_2$

The photolysis of $CHFCl_2$ at 300 K has been investigated at 213.9, 163.3 and 147 nm. Methane, Br_2, HBr and HCl were added as free radical interceptors in order to unravel the primary photodecomposition processes. Analysis of the data shows that at 213.9 and 163.3 nm the photodissociative process occurs with a quantum yield of 0.9 – 1.0, giving stable CHFCl radicals.

At $CHFBr_2$. shorter wavelengths the quantum yield of CHFCl shows a drastic decrease with concurrent appearances of species such as CFCl, CHF and CF. The laboratory experiments indicate that CF is mainly formed via the dissociative process The CF radicals react with CH_3 to yield C_2H_2 ($CF + CH_3 \rightarrow C_2H_2 + HF$) while the CHF species insert readily into HCl to yield CH_2FCl. In the presence of Br_2, CF and CHF undergo reactions which result in the formation of $CFBr_3$ and respectively

GOVT DR. SHAYAM PRASHAD MUKHARJI SCIENCE AND COMMERCE COLLEGE
2021-22

TOPIC : TYPE OF EXCITATION IN PHOTOCHEMISTRY

SUBJECT : PHOTOCHEMISTRY

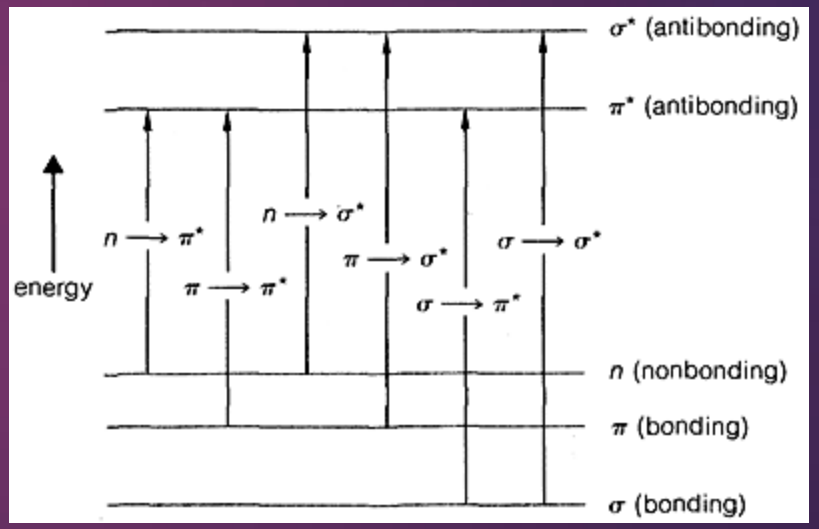
SUBMITTED TO:
DR. ILA JAIN MAM
(PROF. OF PHOTOCHEMISTRY)

SUBMITTED BY:
SHEETAL CHOUKSEY
ROLL NO : 2100600328
(M.SC 3 SEM)

Type of excitations

According to molecular orbital theory, every molecule posses low energy bonding molecular orbitals , non-bonding molecular orbitals and antibonding high energy molecular orbitals . When molecules is excited by absorption of radiation (UV or visible light), its valence electrons are promoted from a bonding orbital to an antibonding molecular orbital. The energy of various molecular orbit is in given order

Only following for transitions of electron from low energy molecular orbit to high energy molecular orbit are allowed.



$\sigma \rightarrow \sigma$ *Transitions

The antibonding molecular orbital associated with the excitation of σ electrons is called σ* [sigma asterisk] and transition of electrons from is termed as $\sigma \rightarrow \sigma$* transition. This transition requires high energy and high energy radiation of vacuum ultraviolet region[> 150 nm] are used for this purpose. Organic compound with all valencies satisfied show this transitions, examples., saturated hydrocarbon-methane, Ethan propane etc.

$n \rightarrow \sigma^*$ Transitions

The transition of electrons from a non bonding orbital to σ^* (antibonding) orbital, is reported in saturated compounds containing one Hetero atom with unshared pair of electrons [Lone pair of electrons] known as non - bonding electrons. For Example , Alcohols, ethers, ketones, aldehydes, saturated halides, amines etc.

This transition requires less energy than $\sigma \rightarrow \sigma^*$ transition and is caused by radiation of wavelength below 200 nm. For example, water absorbed at 167 nm , methyl alcohol at 174 nm and methyl chloride at 169 nm.

$\pi \rightarrow \pi$ * Transitions

The transition from π [bonding orbital] π *[antibonding orbital] occurs on the unsaturated centers of molecules. The organic compounds containing double or triple bonds show this excitation.

This transitions required lesser energy then the previous transition. The absorption of radiation-wavelength is fluctuated and depend on the molecule. For ethylene $\pi \rightarrow \pi$ * transition occurs at 171 nm [700 kJ mol^{-1}] and for butadiene at 214 nm [560 kJmol^{-1}]. This transition occurs at wavelength around 200 nm.

This transition occurs by the promotion of an electron from highest occupied molecular orbital [HOMO] to the lowest unoccupied molecular orbit [LUMO].

n→ π * Transitions

The transition of electron from non-bonding orbital (n) to antibonding(π*) orbital is reported when an electron of unshared electron pair on hetero atom get excited to π* orbital. $n \rightarrow \pi^*$ transitions requires least energy out of all the transitions. Saturated aldehydes[>C=Ö] show both $\pi \rightarrow \pi$ *transitions and n→ π * transitions at 180 and 290 nm respectively.

Deepak kumar

WELCOME

To

प्रकाश वियोजन तथा गैस अवस्था

परिभाषा:- वियोजन अभिक्रिया:- वह अभिक्रिया है जिस मे एक पदार्थ टुटकर दो या दो से अधिक पदार्थ का निर्माण करते है वियोजन अभिक्रिया कहलाता है

उदाहरण :- $Co_2 \xrightarrow{\text{उष्मा}} C + O_2$

$2H_2O \xrightarrow{\text{उष्मा}} 2H_2 + O_2$

प्रकाश वियोजन :- सुर्य के प्रकाश कि उपस्तिथि में होने वाली वियोजन अभिक्रिया प्रकाश वियोजन अभिक्रिया कहलाती है

उदाहरण:- 1. $2AgCl(s) \xrightarrow{\text{सुर्य का प्रकाश}} 2Ag(s) + Cl_2(g)$

2. $2AgBr(s) \xrightarrow{\text{सुर्य का प्रकाश}} 2Ag(s) + Br_2(g)$

या AgBr के प्रकाश वियोजन अभिक्रिया Use black and white photography में किया जाता है,

उष्मीय वियोजन:- वह वियोजन अभिक्रिया जिसमें उष्मा कि उपस्तिथि में वियोजन होता है उष्मीय वियोजन अभिक्रिया कहलाता कहलाती है

- उदाहरण :- $CaCO_3(s) \xrightarrow{\text{उष्मा}} CaO(s) + CO_2(g)$

वैधुत वियोजन:- वह वियोजन जिसमें वैधुत धारा के प्रवाहित होने के कारण होने वाला वियोजन वैधुत वियोजन अभिक्रिया कहलाती है

उदाहरण:- $2H_2O(l) \xrightarrow{\text{वैधुत धारा}} 2H_2(s) + O_2$

गैस अवस्था :-

गैस पदार्थ की तीन अवस्थाओं में से एक अवस्था का नाम है । गैस अवस्था में पदार्थ का न तो निश्चित आकार होता है न नियत आयतन। ये जिस बर्तन में रखे जाते हैं उसी का आकार और पूरा आयतन ग्रहण कर लेते हैं।

बर्फ से पानी बनना

• जब ठोस अवस्था को उष्मा देने पर वह द्रव अवस्था में परिवर्तन हो जाती है तथा द्रव अवस्था गैस अवस्था में परिवर्तन होती है

GOVT.DR.SHYAMA PRASAD MUKHERJEE SCIENCE AND COMMERCE COLLEGE BHOPAL

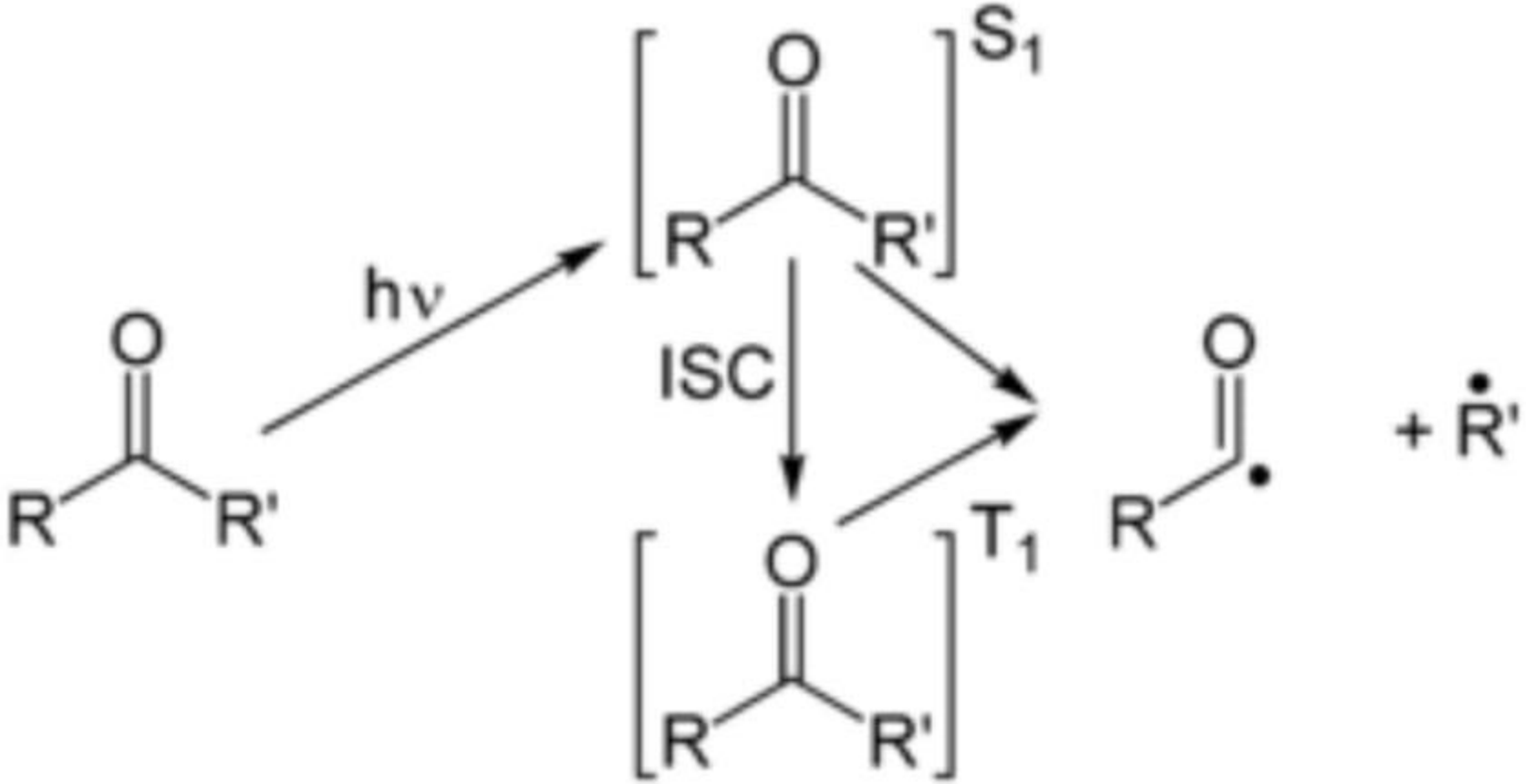
- *SUBJECT – PHOTOCHEMISTRY* *TOPIC :NORRISH TYPE 1*

  MSC 3RD SEMESTER

  Presented –**SANJAY GOUR**

A Norrish reaction in organic chemistry is a photochemical reaction taking place with ketones and aldehydes. Such reactions are subdivided into Norrish type I reactions and Norrish type II reactions.[1] The reaction is named after Ronald George Wreyford Norrish. While of limited synthetic utility these reactions are important in the photo-oxidation of polymers such as polyolefins,[2] certain polycarbonates and polyketones.

The Norrish type I reaction is the photochemical cleavage or homolysis of aldehydes and ketones into two free radical intermediates (α-scission). The carbonyl group accepts a photon and is excited to a photochemical singlet state. Through intersystem crossing the triplet state can be obtained. On cleavage of the α-carbon bond from either state, two radical fragments are obtained.[3] The size and nature of these fragments depends upon the stability of the generated radicals; for instance, the cleavage of 2-butanone largely yields ethyl radicals in favor of less stable methyl radicals.[4]

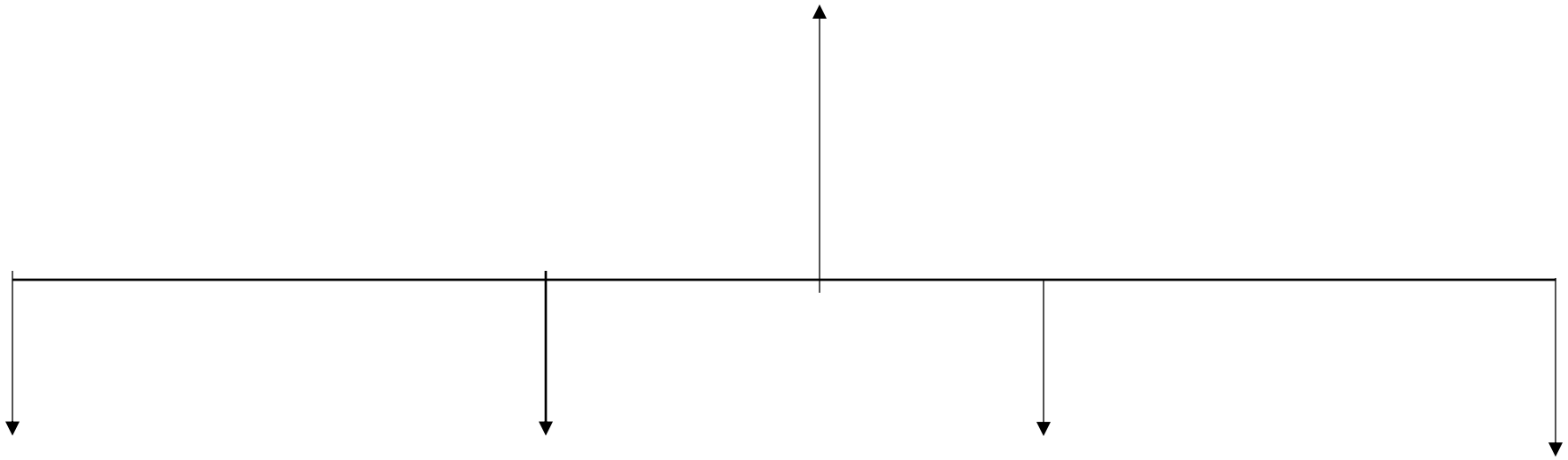

O
R
R'
hν
O
R
R'
S1
ISC
O
R
R'
T1
O
R
+ R'

Several secondary reaction modes are open to these fragments depending on the exact molecular structure.The fragments can simply recombine to the original carbonyl compound, with racemisation at the α-carbon.The acyl radical can lose a molecule of carbon monoxide, forming a new carbon radical at the other α-carbon, followed by formation of a new carbon–carbon bond between the radicals.[3] The ultimate effect is simple extraction of the carbonyl unit from the carbon chain. The rate and yield of this product depends upon the bond-dissociation energy of the ketone's α substituents. Typically the more α substituted a ketone is, the more likely the reaction will yield products in this way.[5]

The abstraction of an α-proton from the carbonyl fragment may form a ketene and an alkane.The abstraction of a β-proton from the alkyl fragment may form an aldehyde and an alkene.

THANK YOU

TYPES OF EXCITATION IN PHOTOCHEMICAL REACTION



$(\sigma \rightarrow \sigma^*)$ $(n \rightarrow \sigma^*)$ $(\pi \rightarrow \pi^*)$ $(n \rightarrow \pi^*)$

Different types of electronic excitation-

- 1. **Sigma to Sigma Star Transaction** **($\sigma \rightarrow \sigma^*$)**

  A transition of an electron from bonding sigma orbital to higher energy antibonding sigma orbital is designated sigma to sigma star transition in Ultraviolet visible spectroscopy. In **alkanes,** there are only sigma bond are avilable. Therefore, alkanes are showing this type of transition. In general, sigma bonds are very strong. Therefore, high energy is requaired for showing this type of transition. In general, sigma bonds are very strong. Therefore, high energy is requaired for sigma to sigma star transition.

- 2. **n to sigma star transition** $(n \rightarrow \sigma^*)$

  n to sigma star transition involves saturated compouds with one hetero atoms like **oxygen, nitrogen, fluorine, chlorine,** etc. normally, saturated halides, alchohols, ethers, aldehydes, ketones, and amines participate in this type of transition. These transation require comparatively less energy than the sigma -sigma transition. In saturated alkyl halides, the energy reaquired for n to sigma star transition decrease with the increase in the size of the halogen atom or decrease in electronegativity of the atom. Due to greater electronegativity of chlorine than iodinen, the n electron on the chlorine atom is comparatively difficult to excite. The n electrons on the iodine atom are loosely bound.

- 3. **pi to pi star transition** $(\pi \rightarrow \pi^*)$

  pi to pi star transition in uv vis spectroscopy is available in compound with unsaturated centers like unsaturated hydrocarbons and corbonyl compounds. It requires lesser energy than n to sigma star transition. In simple alkenes several transitions are available but n to pi star transition required the lowest energy.

- 4. **n to pi star transition** $(n \rightarrow \pi^*)$

  in n to pi star transition an electron in unshared pair on hetero atom is excited to pi antibonding orbital. It involves the least amount of energy than all types of transition in ultraviolet visible

spectroscopy. Therefore, the n to pi transition gives the absorption with a longer wavelength. In saturated ketones, n to pi star transition around 280 nm are the lowest energy transition. n to pi star forbidden by symmetry consideration. Thus the intensity of the band due to this transition is low, although the wavelength is long.

GOVT. DR. SHYAMA PRASAD MUKHERJEE SCIENCE AND COMMERCE COLLEGE BHOPAL

SUBJECT - PHOTOCHEMISTRY

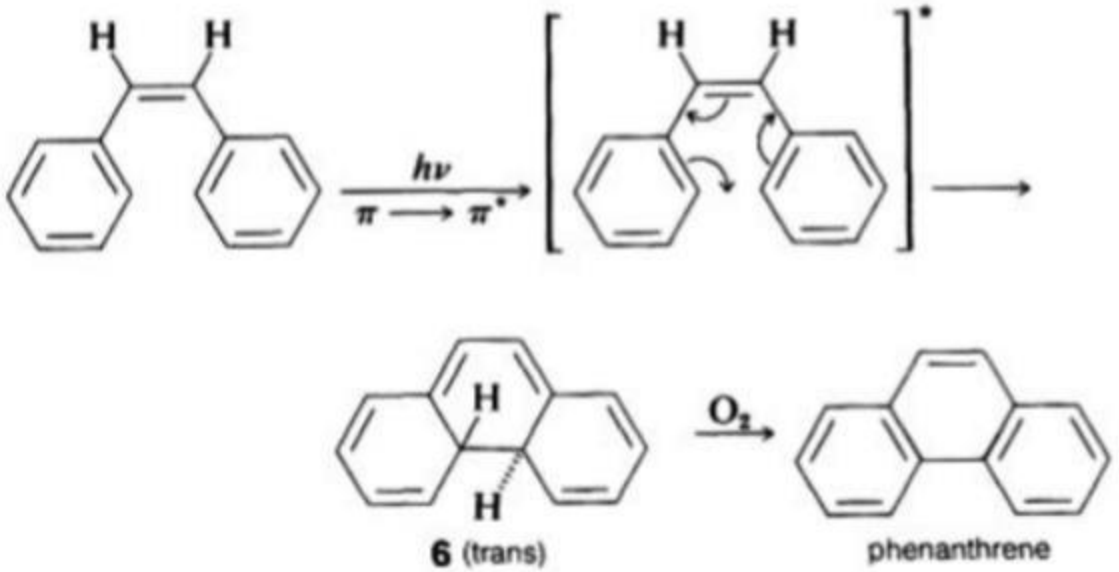
1. ***TOPIC – PHOTOCHEMICAL CYCLIZATION OF ALKENE***

2. ***CLASS – MSC 3RD SEMESTER***

PRESENTED BY – ABHISHEK SINGH RAJPOOT

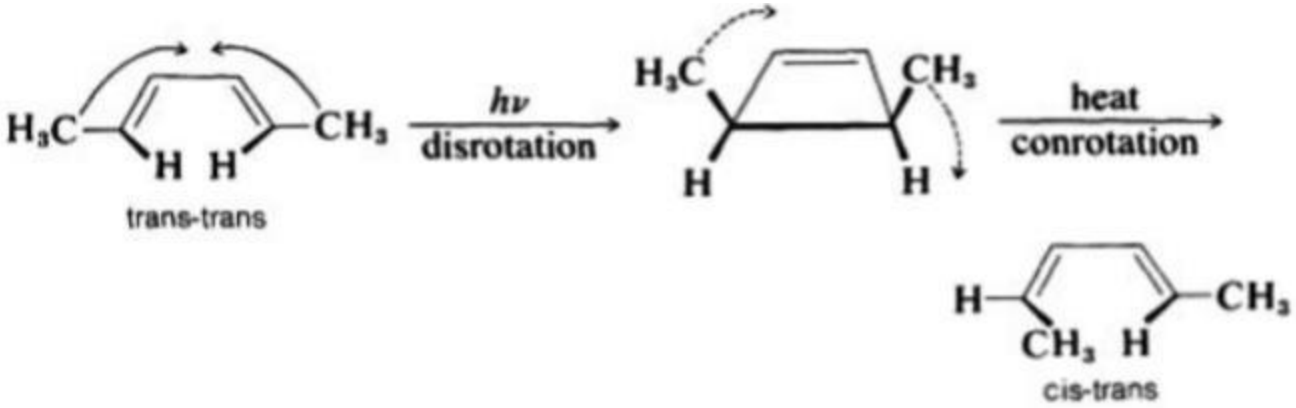
Photochemical Cyclization reaction of alkene

One may well ask why the isomerization of alkenes discussed in the preceding section requires a sensitizer. Why cannot the same result be achieved by direct irradiation? One reason is that a singlet excited state (5_1) produced by direct irradiation of an alkene or arene crosses over to the triplet state (7) inefficiently compared to a excitation of ketones). Also, the S, state leads to other reactions beside isomerization which, in the case of 1.2-diphenyl ethene and other conjugated hydrocarbons, produce cyclic products. For example, cir-1.2-diphenylethene irradiated in the presence of oxygen gives phenanthrene by the sequence of Equation 28-8. The primary photoreaction is cyclization to a dihydrophenanthrene intermediate, & which, in the presence of oxygen, is converted to phenanthrene:



(28-8)

- The cyclization step of Equation 28-8 is a photochemical counterpart of the electrocyclic reactions discussed in Section 21-10D. Many similar photochemical reactions of conjugated dienes and trienes are known, and they are of great interest because, like their thermal relatives, they often are stereo specific but tend to exhibit stereochemistry opposite so what is observed for formally similar thermal reactions. For example.


H3C
CH3
H H
trans-trans
hν
disrotation
H3C
CH3
H
H
heat
conrotation
H
CH3
CH3 H
cis-trans

- These reactions are 4n-electron concerted processes controlled by the symmetry of the reacting orbitals. The thermal reaction is most favorable with a Mobius transition state (achieved by conrotation), whereas the photochemical reaction is most favorable with a Hückel transition state.

PRESENTED BY LALIT DEVANGAN

DR. SHYAMA PRASAD MUHARJEE
SCIENCE AND COMMERCE COLLEGE
BHOPAL

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.

$$\Phi = \frac{\text{number of molecules undergoing the process}}{\text{number of quanta absorbed}}$$

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

- In some reaction deactivation of activated molecule take place in primary process before transfer to product.
- The product of primary process may react back to form reactants.

Eg. Decomposition of HI and HBr,
Polymerization of anthracene.

Reasons for high Quantum yield:Φ>1

- The product of primary process may co
with 2nd molecule & transfer energy. 2nd to
and so on. Thus chain reaction starts and
of reacting molecule will be high.
- Due formation of intermediate product w
act as a catalyst.
- Exothermic reaction may activate m
molecules.

Eg. Reaction between Hydrogen and Halogen

Reasons for unite Quantum yield:

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

Factors affecting quantum yield:-

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

THANK YOU

FOR WATCHING

Govt. Shyama Prasad Mukherjee Science And Commerce College, Bhopal

Name – Shivdayal Shukla

Class – M.Sc. 3rd sem

Subject - Photochemistry

Head of Department
Dr. Sudhanshu Dhar Dwivedi

Organized by
Dr. Ila Jain

Principal
Dr. Saroj Srivastava

Contents:

i. Define Quantum Yield

ii. Quantum yield determination

1. Determination of quanta absorbed (E)
2. Determination of total number of molecules changed Reacted(M)

- **It is define as -**
- The efficiency of photochemical reaction is often expressed in term of quantum yield or quantum efficiency. Which is denoted by Φ.

- When a molecule dissociates after absorbing a light quantum, quantum yield is the no. Of destroyed molecule divided by no of photons.

- The quantum yield (Φ) is a measure of the efficiency of photon emission as defined by the ratio of the number of photons emitted to the number of photons

$$\Phi = \frac{\text{No Of molecule reacting in give Time (Decomposed molecules)}}{\text{No of quantum radiation absorbed in same time}}$$

- Quantum yield in product formation-

$$\Phi = \frac{\text{No of Molecules formed}}{\text{No of photons absorbed}}$$

Experiment to determination of quantum yield It consists of two parts:-

1. Determination of quanta absorbed (E)

2. Determination of total number of molecules changed Reacted (M) .

1. Determination of number of quanta absorbed or light absorbed (E) :-

1. Source of light : Hg- vapour lamp, sodium lamp
2. Monochromator
3. Detector
   - i). Photoelectric cell (photon counter)
   - ii). Radio micrometer
   - iii). Thermopile
   - iv). Chemical actinometer

2. Determination of total number of molecules changed (Reacted) (M):-

Reaction cell – glass / quartz (UV-Visible Light)

- Using chemical Kinetics
- For gaseous reaction – change in pressure
- For Liquid reaction Change in optical rotation, electrical conductivity, absorption

Thank you

DR. SHYAMA PRASHAD MUKHARJEE SCIENCE & COMMERCE COLLEGE KOLAR BHOPAL

PRESENTED TO: DR. ILA JAIN

PRESENTED BY: ANURADHA SHARMA
MSC 3RD SEM

TOPIC: EQUATION DERIVATION OF RATE CONSTANT PHOTOCHEMICAL REACTION

SCHEME1

$S \longrightarrow S^*$ $= W(CONSTANT)$

(1) $S^* \xrightarrow{K_R} P$ $=K_R[S^*]$

(2) $S^* \xrightarrow{K_{ISK}} T^*$ $=K_{ISK}[S^*]$

(3) $S \xrightarrow{KIC} S^*$ $=K_{IC}[S^*]$

(4) $S^* \xrightarrow{KF} S+HV'$ $=K_F[S^*]$

The rate of product formation is

$d[p]/dt=k_r[s^*]$

Where

K_f =rate constant of spontaneous emission

K_{ic} =rate constant of internal conversion

K_{isc} =rate constant of inter system crossing

$$d[s^*]/dt=W-(K_f + K_{isc} + K_{ic} +K_r)[s^*]$$

Apply steady state approximation

$$0= W-(K_f + K_{isc} + K_{ic} +K_r)[s^*]$$

$$d[p]/dt=K_r.W/ \ K_f+ K_{isc} + K_{ic} +K_r$$

K_r is the rate constant of chemical reaction

The steady state approximation is applicable under condition of time dependent excitation if a very short laser phase is used to produce the excited species the light absorption rate W can be neglected and equation

$$D[S^*]/DT=W-(K_F + K_{ISC} + K_{ic} + K_R)[S^*]$$

$$[S^*]= [S^*]_0 \, E^{-(KF + KISC + Kic + KR)}$$

$$=[S^*]^{E-T/(TAU)}{}_0$$

Where (tau)0 is the life time of singlet excited state

$$(TAU)0= (K_F + K_{ISC} + K_{ic} + K_R)^{-1}$$

THANKS

Presentation Work

M.sc. III sem
Physical chemistry
Photochemistry
Quantam yield

Submitted To :
Dr.ila jain ma'am
(Chemistry Department)

Submitted by :
Shailesh Narware

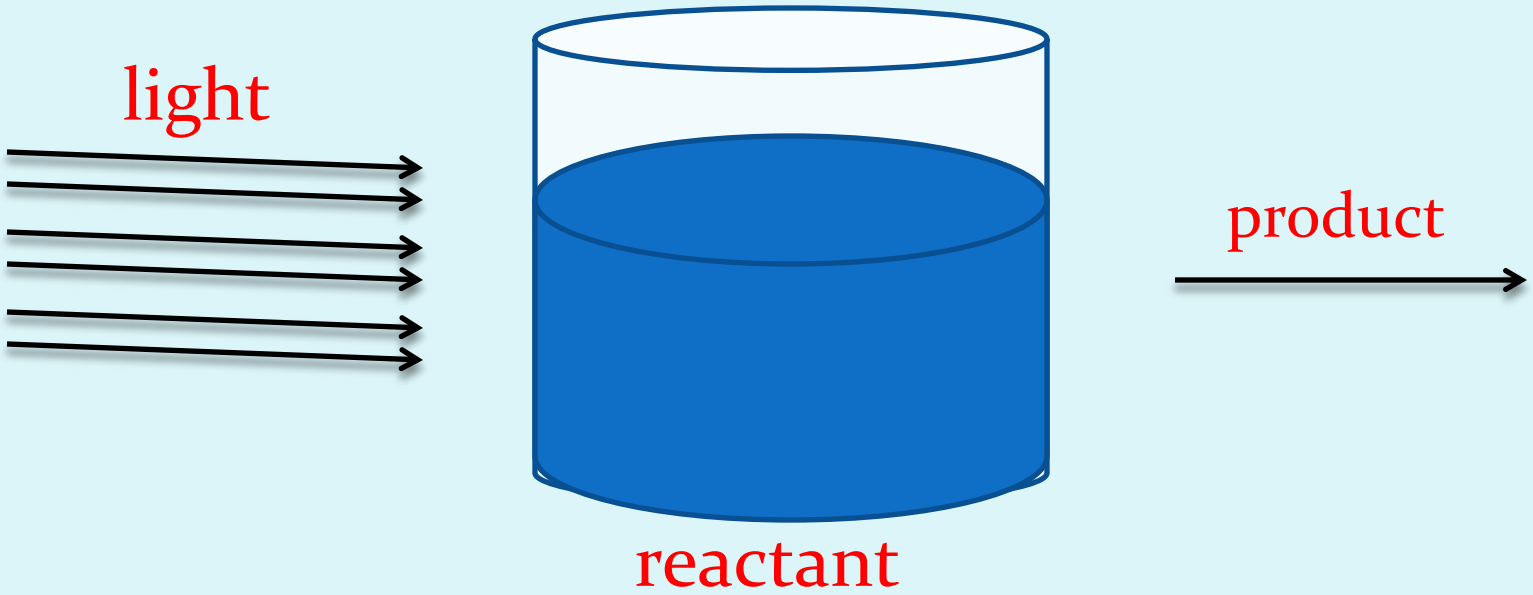
Quantum Efficiency Definition

"**प्रकाश के प्रति** क्वाण्टम **से** अभिकारक के **molecules** की कितनी संख्या **reaction** कर उत्पाद **(product)**बनती है उसे क्वाण्टम दक्षता कहते ϕ ***है।***

यदि ϕ का **value 1** आता है अथात एक क्वाण्टम अवशोषण से केवल **1 molecule** ही **react** करता है तो **reaction** आइंस्टीन के नियम का पालन करता है |

$$\text{Quantum Yield } \phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}}$$

$$\phi = \frac{\text{किसी निश्चित समय में अपघटित होने वाले अभिकारक अणुओं की संख्या}}{\text{उसी समय में अवशोषित Dok.Ve की संख्या}}$$



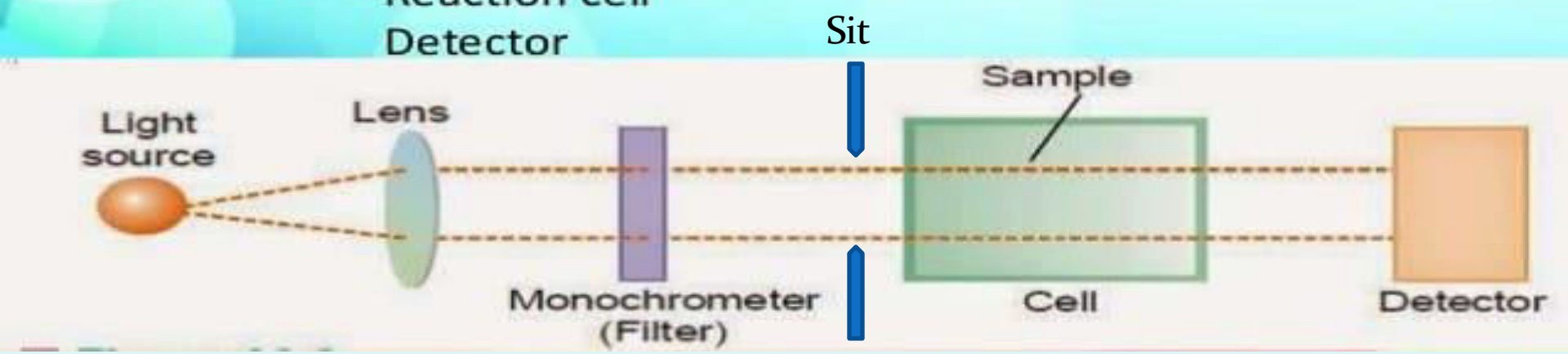
Experimental Determination of Quantum Yield

1. Determination of number of moles reacted.

2. Determination of number of Einstein's absorbed.

3.

Source of light
Monochromator
Reaction cell
Detector



i)Light Source :-

इस उपकरण में Right Source के लिये (uv radiation) mercury lamp का use किया जाता है या इसके जगह sunlight का भी use कर सकते हैं।

ii)Slit, lens : -

इन radiation को slit में से होकर फिर lens में से गुजारा जाता है।

iii) Monochromatar :-

अब इन Radiations को filters में से प्रवाहित कर monochromatic Right की Radiation प्राप्त की जाती है, ये filter Colousfull glass के बने होते है, जब light इनमें से होकर गुजरती है तब ये उन radiation को आगे जाने से रोके देते है जो एक वर्ण नहीं होती है इस प्रकार एक वर्णी प्रकाश ही अंदर जा पता है |

iv)Reaction cell:-

Reaction cell, glass का बना होताहै, Reaction cell में Reaction मिश्रण होता है जिसका प्रकाश रासायनिक अध्ययन करना होता है. जब ये radiation इस cell से होकर गुजरती है, then light detector पर पड़ती हैं।

v) Detector: -

Detector के द्वारा transmitted light की तीव्रता ज्ञात की जा सकती है, detector द्वारा प्रकाश की तीव्रता का मापन दो बार करते हैं, पहली बार जब सेल खाली रहता है या उसमें शुद्ध विलायक (water)भरा रहता है, तथा दूसरी बार जब से कोई मिश्रण (reactent) भरा होता है, प्रकाश की तीव्रता मापने के लिये Photo cell का प्रयोग करते है

Thank you

Govt Dr Shyama Prasad Mukharjee Science and Commerce College Bhopal

Presentation Work

M.Sc. Chemistry (Semester-3)

Submitted To :Dr.ila jain ma'am
(Chemistry Department)

Submitted by ; Shailesh pandey

Lambert-Beer's law (अवशोषण नियम)

The law was first developed by Pierre Bouguer before 1729. It was later attributed to Johann Heinrich Lambert who cited Bouguer's findings. The law included path length as a variable that affected absorbance. Later, Beer extended in 1852 the law to include the concentration of solutions, thus giving the law its name Beer-Lambert Law.

इस नियम को पहली बार 1729 से पहले **Pierre Bouguer** द्वारा विकसित किया गया था। बाद में इसका श्रेय **Johann Heinrich Lambert** को दिया गया जिन्होंने बौगुएर के निष्कर्षों काs प्रमाणस्वरूप उल्लेखित किया। नियम में पथ की लंबाई एक चर के रूप में शामिल थी जो अवशोषण को प्रभावित करती थी। बाद में, **Beer** ने 1852 में समाधान की एकाग्रता को शामिल करने के लिए कानून का विस्तार किया, इस प्रकार नियम को बीयर-लैम्बर्ट नियम का नाम दिया।

Definition & Equation

यदि किसी एकवर्णी प्रकाश को किसी अवशोषक पदार्थ के विलयन में से गुजारा जाये तो इस अवशोषक विलयन में विकिरणों की तीव्रता में हुई कमी आपतित विकिरणों की तीव्रता के साथ साथ विलयन की सांद्रता के समानुपाती होता है।

$-dI/dx \propto I.C$ (यहाँ ऋणात्मक चिन्ह विकिरणों में कमी को दर्शाता है।)

$dI/I = -k'Cdx$ (I = आपतित विकिरणों की तीव्रता में हुई कमी)

यहाँ k' समानुपाती स्थिरांक है जिसे मोलर अवशोषण गुणांक कहते है इसका मान अवशोषक पदार्थ की प्रकृति पर निर्भर करता है।

c = सान्द्रता

लैम्बर्ट का नियम क्या है?

जब किसी समांगी अवशोषक माध्यम से एकवर्णी प्रकाश को गुजारा जाता है तो अवशोषक माध्यम की मोटाई के साथ विकिरणों की तीव्रता में हुई कमी आपतित विकिरणों की तीव्रता के समानुपाती होती है।

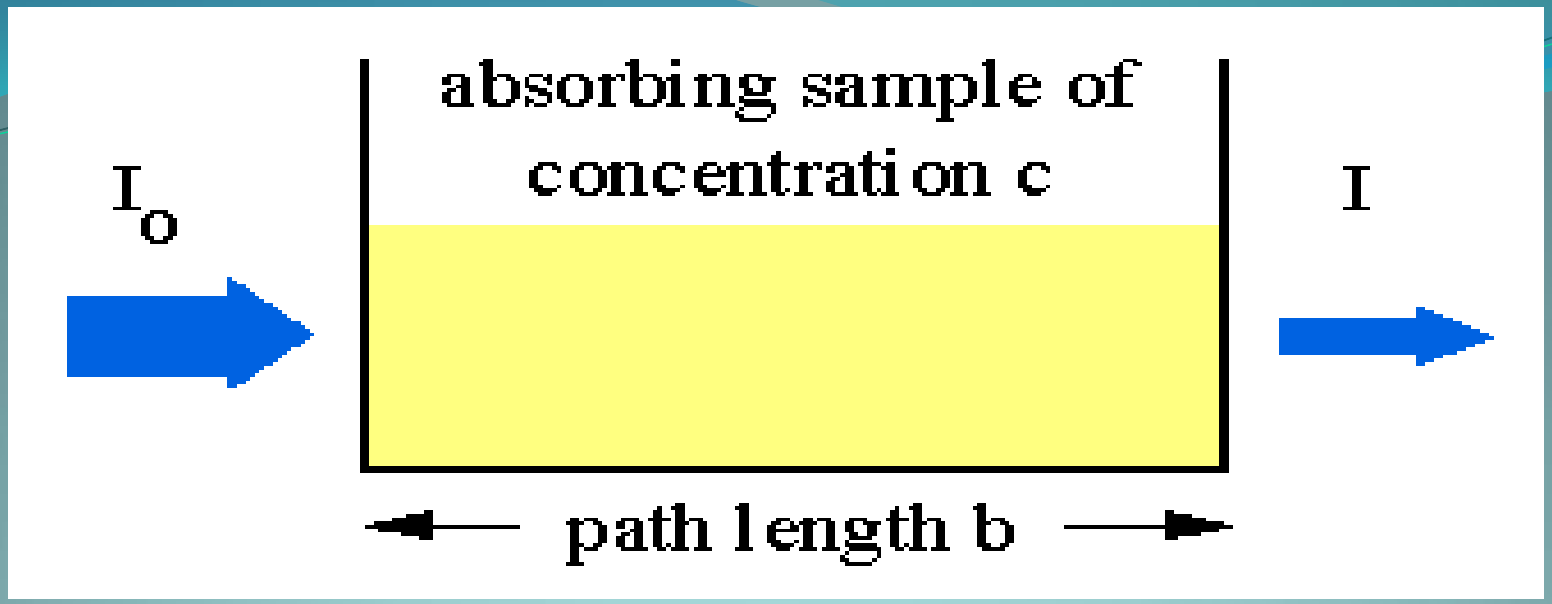
$-dI/dx \propto I$ (यहाँ ऋणात्मक चिन्ह विकिरणों में कमी को दर्शाता है)

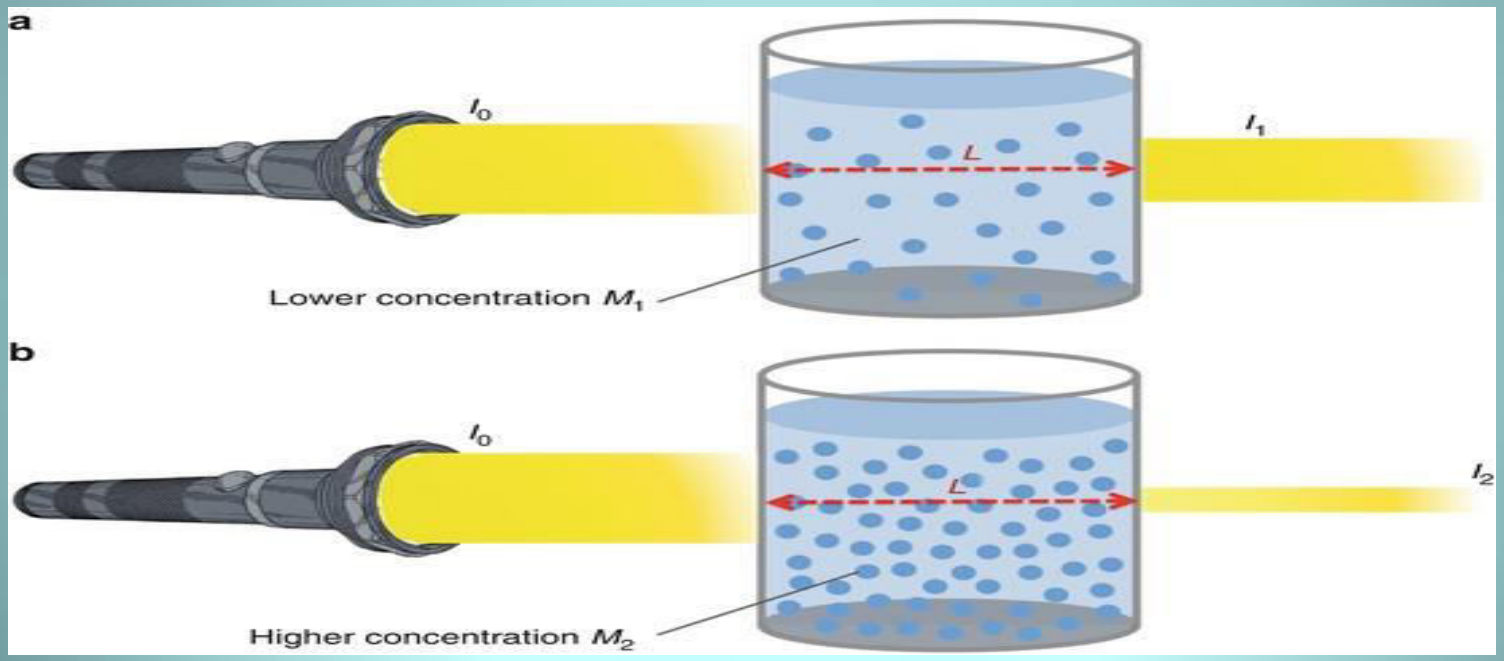
$dI/dx = -kI$ (यहाँ I = आपतित विकिरणों की तीव्रता में हुई कमी)

$dI/I = -kdx$ (K = अवशोषण स्थिरांक जिसका मान अवशोषक पदार्थ की प्रकृति पर निर्भर करता है।

बीयर का नियम क्या है?

जब किसी एकवर्णी प्रकाश की किरण को समांगी अवशोषक माध्यम में से गुजरा जाता है तो अवशोषक माध्यम की मोटाई के साथ विकिरण की तीव्रता में कमी की दर आपतित विकिरण की तीव्रता तथा विलियन की सांद्रता के समानुपाती होती है


absorbing sample of
concentration c
I_0
I
path length b


a
I_0
L
I_1
Lower concentration M_1
b
I_0
L
I_2
Higher concentration M_2

Derivation of Law

मान लें कि प्रकाश की एक किरण समांगी अवशोषक माध्यम में प्रवेश करती है। z को बीम की दिशा के समानांतर अक्ष के रूप में परिभाषित करें। समांगी अवशोषक माध्यम को पतली स्लाइस में विभाजित करें, प्रकाश की किरण के लंबवत, मोटाई dz के साथ पर्याप्त रूप से छोटा है कि एक टुकड़ा में एक कण एक ही टुकड़े में दूसरे कण को अस्पष्ट नहीं कर सकता है जब z दिशा के साथ देखा जाता है।

एक स्लाइस से निकलने वाले प्रकाश का उज्ज्वल प्रवाह $d\Phi e(z) = -\mu(z)\Phi e(z)\, dz$ द्वारा प्रवेश किए गए प्रकाश की तुलना में कम हो जाता है, जहां μ (Napierian) क्षीणन गुणांक है, जो निम्नलिखित प्रथम-क्रम रैखिक ओडीई उत्पन्न करता है:

Limitations of the Beer-Lambert law

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

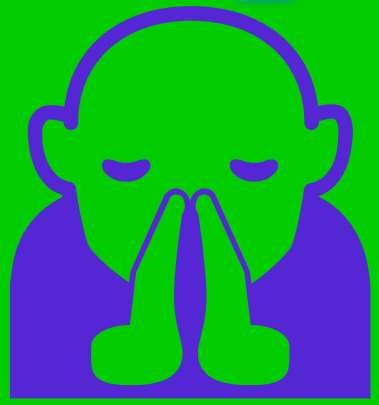
•deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity .

•scattering of light due to particulates in the sample .

• fluoresecence or phosphorescence of the sample .

• changes in refractive index at high analyte concentration.

•shifts in chemical equilibria as a function of concentration .

1. आपतित प्रकाश 1 वर्णी होना चाहिए अर्थात आपतित विकिरणों की तरंग दैर्ध्य एक समान होनी चाहिए।
2. प्रयुक्त विलयन अत्यधिक तनु होना चाहिए।
3. प्रयोग के दौरान ताप स्थिर रहना चाहिए।
4. विलेय पदार्थ का विलयन में स्कंदन नहीं होना चाहिए। वरना प्रकाश का प्रकीर्णन हो जायेगा।
5. विलेय पदार्थ का विलयन में आयनन अथवा जल अपघटन नहीं होना चाहिए।

Thank you