PHOTOCHEMISTRY

Reference: Photochemistry and Pericyclic Reactions

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Photochemistry : It is the study of reactions that are brought about by the action of **visible or ultraviolet light.** e.g. photosynthesis of glucose in the plants by means of sunlight.

$$6\ CO_2 + 6\ H_2O \xrightarrow[\text{chlorophyll}]{\text{sun light}} C_6H_{12}O_6 + 6\ H_20$$

Luminescence

- **Chemical reactions accompanied with light are :**
- By the action of light A → B
- (i) A new molecule is generated by chemical changes (light induced reactions)

  (ii) In some reaction, during chemical reaction light is emitted (chemiluminescence)

Chemiluminescence:

$$P_{4(g)} + O_{2(g)} + H_2O \longrightarrow \longrightarrow \longrightarrow P_4H_{10} + h\nu$$

White phosphorus glows ignites in air to form phosphorus pentoxide.

- Bioluminescence :
- (emission of light by a living organism) - insects

  - fishes

Light : Electromagnetic field vibration spreading in quanta (photons).

Photon: The smallest amount of light carrying energy.

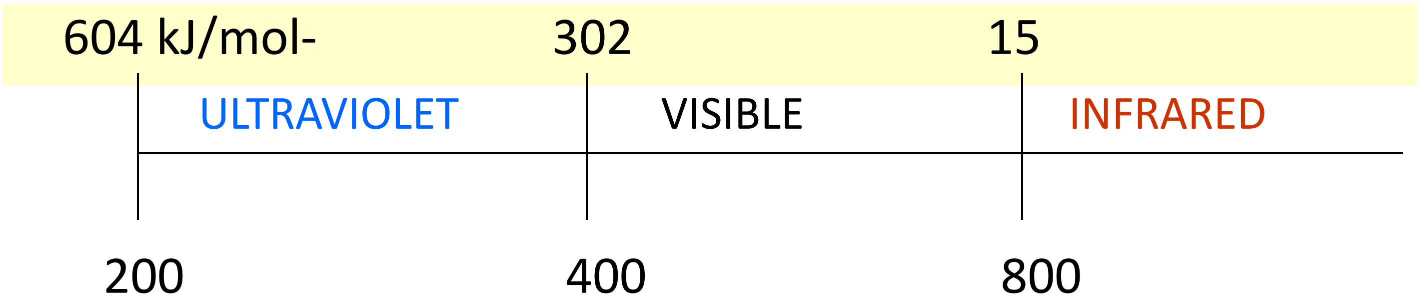
Energy of photons (A. Einstein) $E = h\nu = h\frac{c}{\lambda}$

So one particle of a chemical substance can absorb only one photon from a light beam:

$$\Delta E = h\nu$$

Chemical bond energies: from 100 – 1000 kJ/mol

Light energies:



Laws of Photochemistry

(I) Only light that is absorbed can produce photochemical change (Grotthus, Draper)

(ii) A molecule absorbs a single quantum of light is becoming excited (Stark, Einstein)

Basic Principles of Photochemistry :

Photochemistry is based on following fundamentals.

1. Photochemical Energy.
2. Electronic Excitation.
3. Excited State, Modes of Dissipation of Energy.
4. Energy Transfer.
5. Quantum Efficiency.

1. Photochemical energy:

For any chemical transformation an activation energy, must be supplied to molecules.

Such energy can be provided by different way :

(i) Some molecules undergo **spontaneous transformations**.

(ii) In some cases, energy is supplied by **increasing the temperature** (**thermal condition**) as a result molecules present in the system have same amount of energy throughout the chemical transformation.

(iii) In another method, molecules present in the system involve the **absorption of electromagnetic radiation** in the visible or ultraviolet region (photochemical condition).

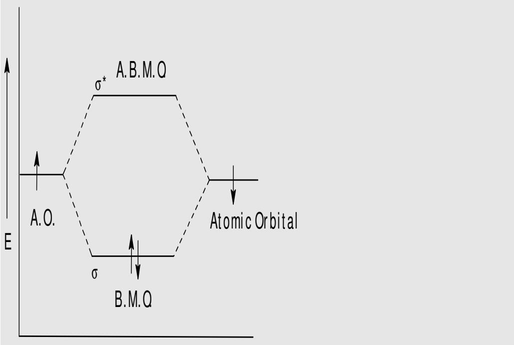
Such absorption of light excites an individual molecule from ground state to an excited electronic state without effecting the surrounding molecules.

- selective excitation
  - chemistry of excited molecules differs from the chemistry of those in the ground state
  - One can change the course of a reaction by activating the reactants by light rather than by heat.

Infrared region is producing Vibrationally or rotationally excited molecules.,

While light in the **visible and ultraviolet region** has sufficient energy to cover the range of chemical bond energies and is able to induce chemical changes by exciting molecules to higher electronic states.

2. Electronic excitation:



Promotion of an electron from the bonding orbital to the corresponding anti-bonding orbital take place .

σ - σ^* ; π - π^* and n- π^*.

3. Excited States, Modes of Dissipation of Energy :

In an organic molecule, even number of electrons are paired in the ground state.

Now when absorption of light of the correct energy occurs, than one of the electron excited from ground state (π) to excited state (π*) by retaining the spin, so the electron spins remain paired in the excited state. This state is called **excited singlet state (S_1).**

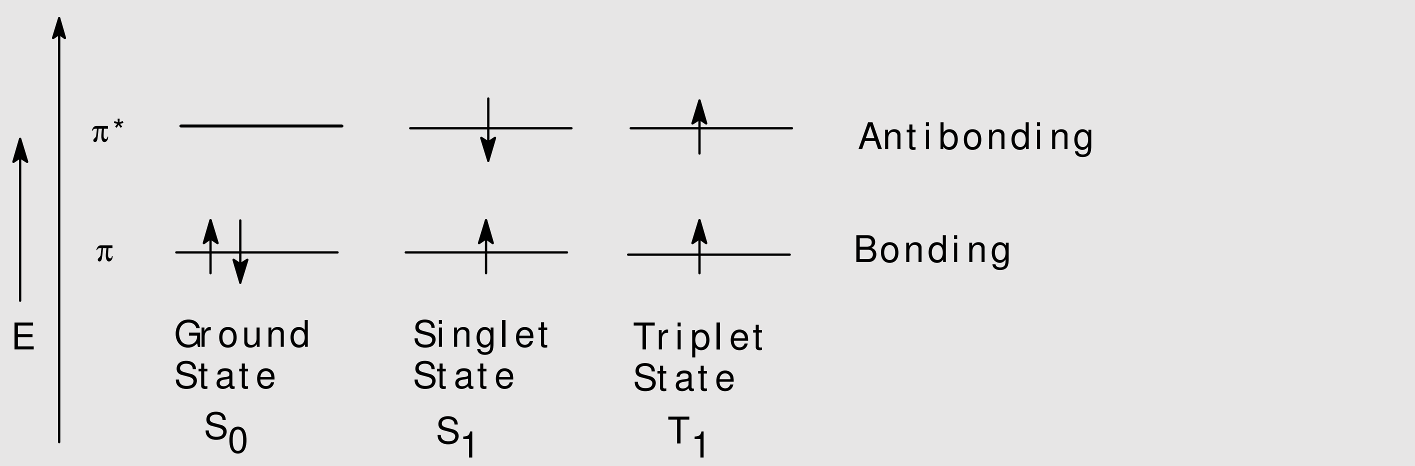
In some cases, spin inversion take places thus giving rise to a new excited state with two unpaired electrons. This state is called an **excited triplet state (T_1).**

4. Energy Transfer and Photosensitization:

It is a one step radiationless transfer of excitation energy from an electronically excited molecule (donor) to the ground state of another molecule (acceptor)." As a result, the donor molecule returns to the ground state and the acceptor molecule gets excited.

For energy transfer the donor molecule should have at least 5 kcal/mole more energy than the acceptor molecule.

A typical mechanism for triplet energy (T_1) transfer is described below :



A **triplet** state is **more stable** than the **singlet** state. Because in triplet state, electrons are unpaired - lesser inter electronic repulsion take place, while in singlet state electrons are paired, -causing inter electronic repulsion and is unstable.

Jablonski Diagram:

(For more detailes refer II sem Material related to Photochemistry)

When a molecule absorbs a photon of energy, electronic transition occurs (S_u or S_2 or S_1).

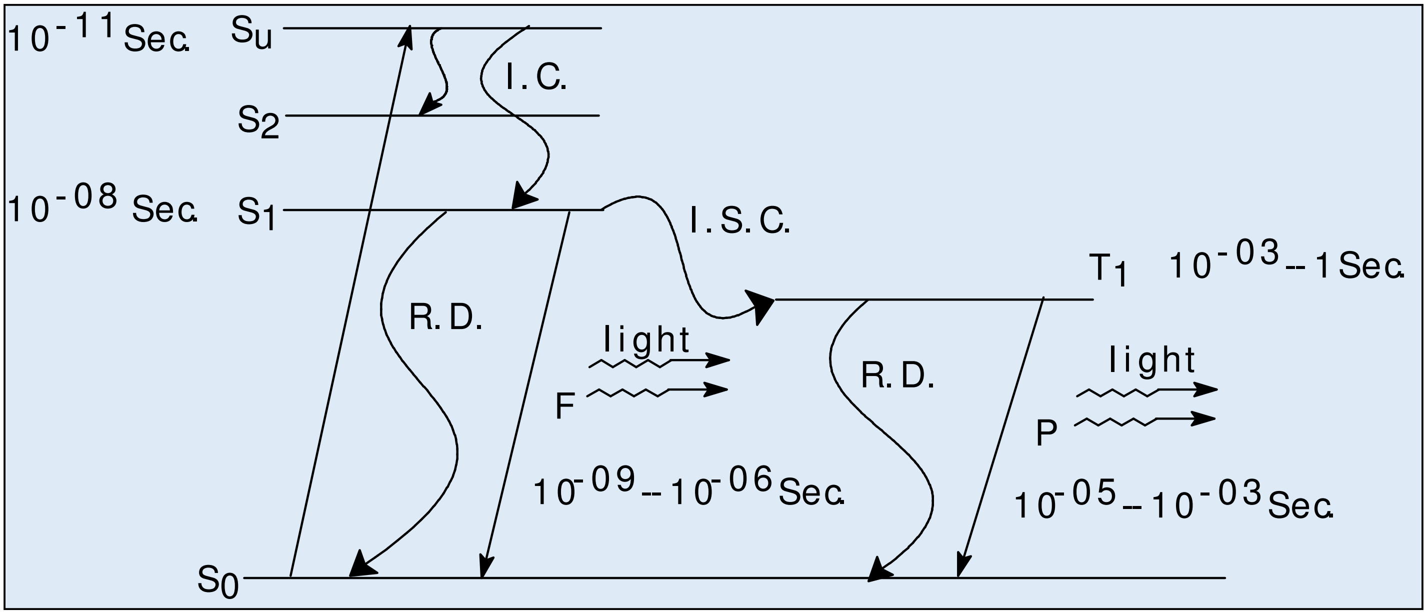
A molecule in S_1 state undergo one of the following four energy degrading (decay) processes to the ground state.

(i) The molecule can undergo chemical reaction or return to the ground state by emission of light by a process called **fluorescence** and generally occurs with in 10^{-9} to 10^{-6} sec.

(ii) It may return to ground state (S_0) by non radiative process in which excess energy of the excited state is shuffled into vibrational modes.

(iii) S_1 may undergo chemical reactions.

(iv) The molecule may undergo spin inversion to the triplet state (spin unpaired) by a process as "**intersystem crossing**", Which is a radiation less process.



ISC = Intersystem crossing. IC = Internal conversion. F = Fluorescence.
P = Phosphorescence. RD = Radiationless decay.

Fluorescence : Emission of a photon from a singlet excited state to a singlet ground state, or between any two energy levels with the same spin, is called fluorescence. Fluorescence, decays rapidly after the excitation source is removed. Lifetime of the electron is only 10^{-5} to 10^{-8} s

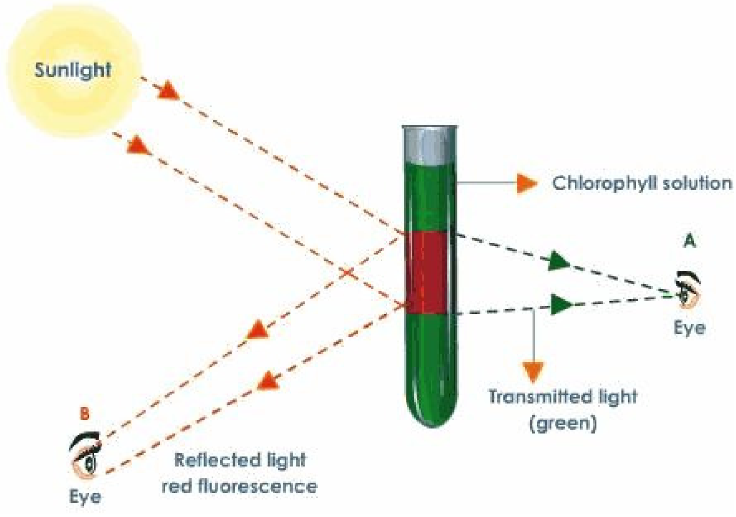
Phosphorescence : Emission between a triplet excited state and a singlet ground state is called phosphorescence. phosphorescence may continue for some time after removing the excitation source. Lifetime for phosphorescence ranges from 10^{-4} to 10^{4} s.

FLUORESENCE:

Certain molecules (or atoms) when exposed to light radiation of short wavelength, emits light of longer wavelength.

EXPLANATION: When a molecule absorb high energy radiation, it is excited to higher energy states. Then it emits excess energy through several transitions to the ground state. Thus the excited molecule emits light of longer frequency. The colour of fluorescence depends on the wavelength of light emitted.

Ex: A solution of chlorophyll in ether shows blood red fluorescence.



PHOSPHORESCENCE

When a substance absorbs radiation of high frequency and emits light even after the incident radiation is cut off, the process is called phosphorescence.

Phosphorescence is chiefly caused by ultraviolet and visible light. It is generally shown by solids.

Ex: Phosphorescent powder under visible light, UV and total darkness.

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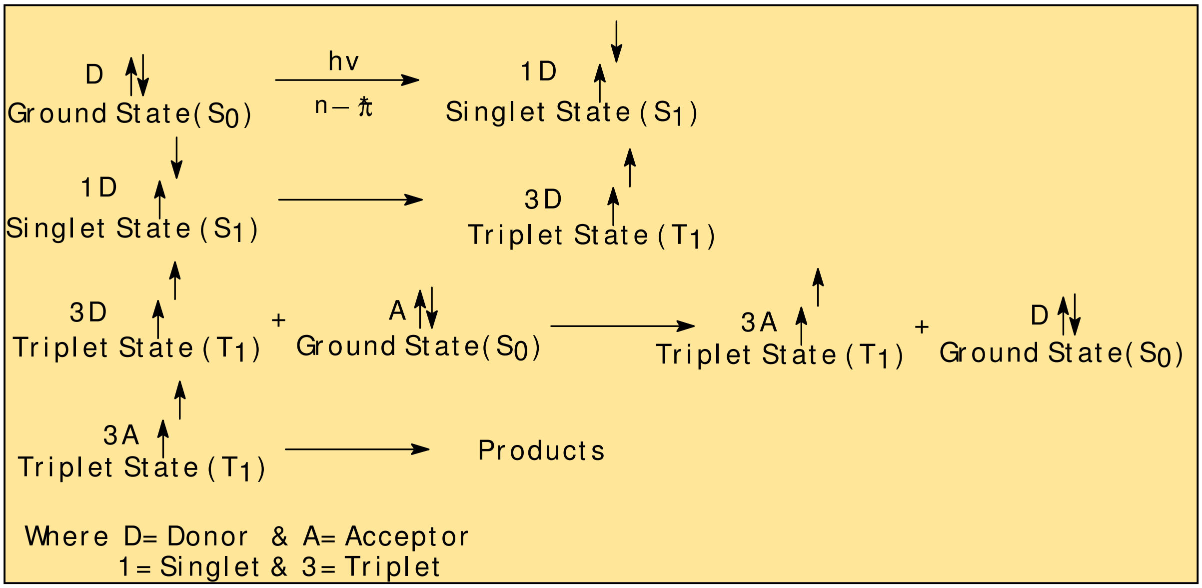
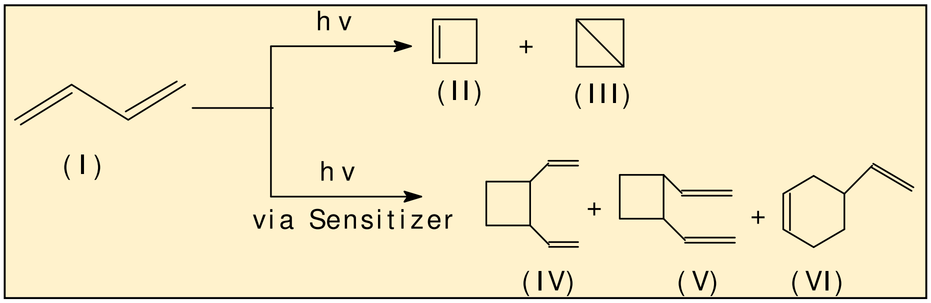


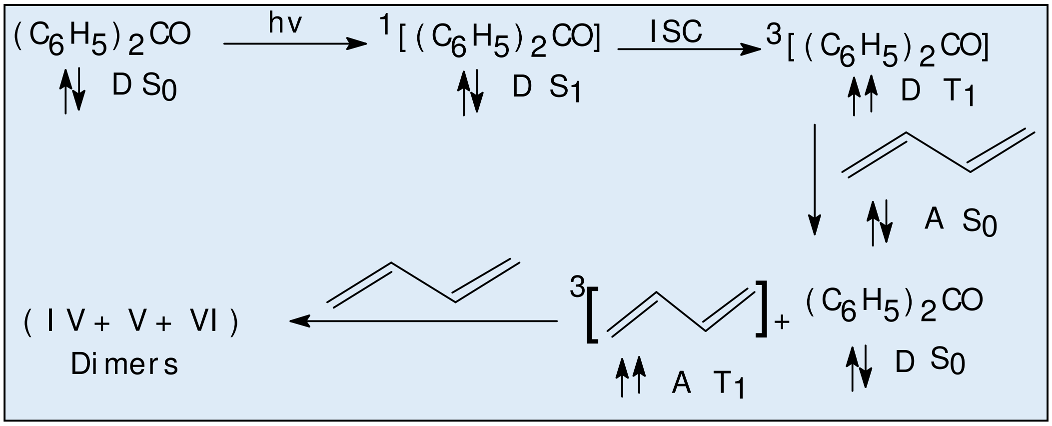
Energy transfer between butadiene as an acceptor and benzophenone as donor.

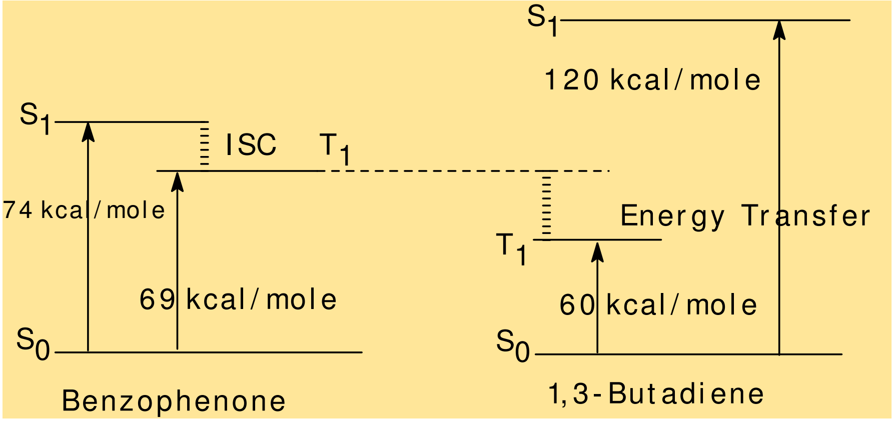
Butadiene (I) **(acceptor)** upon direct irradiation leads to produce product (II) and (III) via ring closure



When butadiene is mixed with benzophenone **(donor)** and is irradiated at 366 nm, than butadiene undergoes photochemical change to yield dimmers (IV) (V) and (VI).

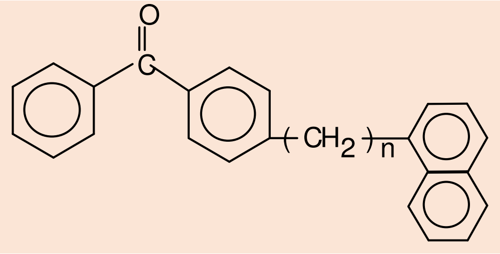
In this process light is absorbed by benzophenone **(donor)** but the reaction is taking place with butadiene **(acceptor)** . Here benzophenone **(donor)** is functioning as a photosensitizer, while **butadiene** is good **acceptor** as it has 9 kcal/mole less triplet energy than benzophenone.





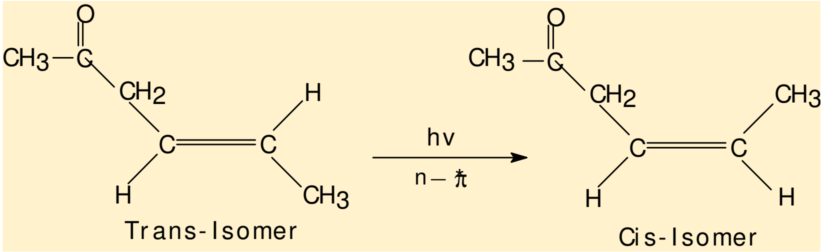
Benzophenone (69 Kcal/mole) **(donor)** triplet energy transfer to 1,3 - Butadiene (60 Kcal/mole) **(acceptor)** (Intermolecular energy transfer).

Intramolecular energy transfer in benzophenone (donor) and naphthalene.



Irradiation of these compounds with light of about 366 nm wavelength absorb by benzophenone showed that there is an efficient transfer of triplet excitation from the benzophenone moiety to the naphthalene moiety.

Energy transfer in Cis – Trans Isomers of 4-hexen-2-one.



Cis - trans isomerization of 4-hexen-2-one shows intramolecular energy transfer when light is absorbed by the carbonyl group.

During this photoreaction energy transfer from the carbonyl group to the carbon-carbon double bond takes place.

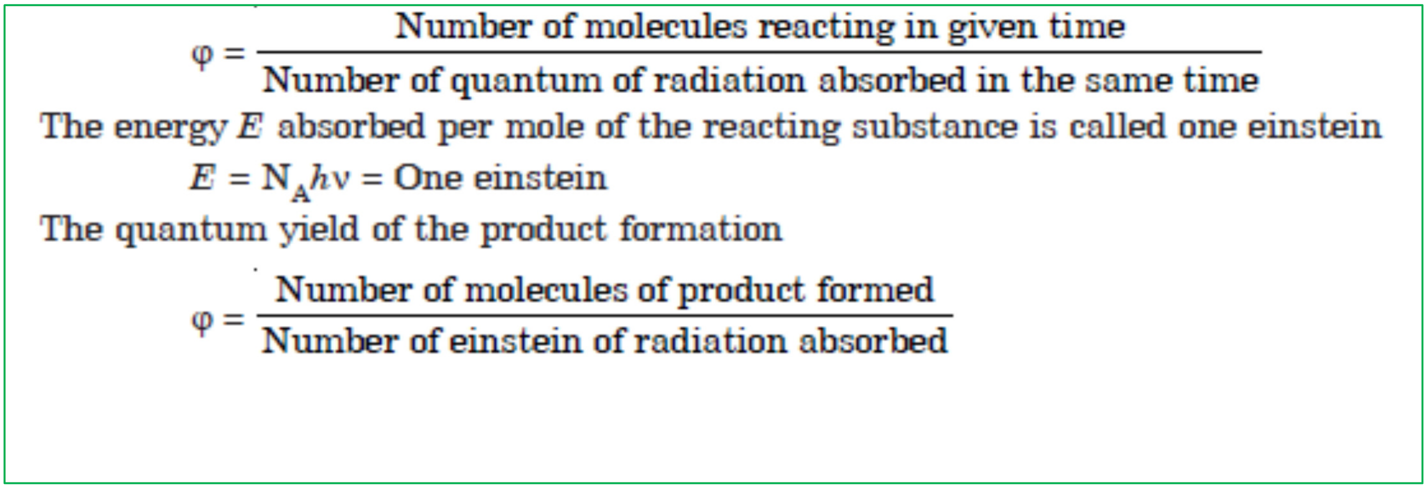
5. Quantum Efficiency.

It is the number of moles of a reactant disappearing, or the number of moles of a product produced, per einstein of monochromatic light absorbed

ϕ = NUMBER OF MOLECULES UNDERGOING THE REACTION **/**

NUMBER OF PHOTONES ABSORBED BY THE PHOTOREACTIVE SUBSTANCE

QUANTUM YIELD OR QUANTUM EFFICIENCY



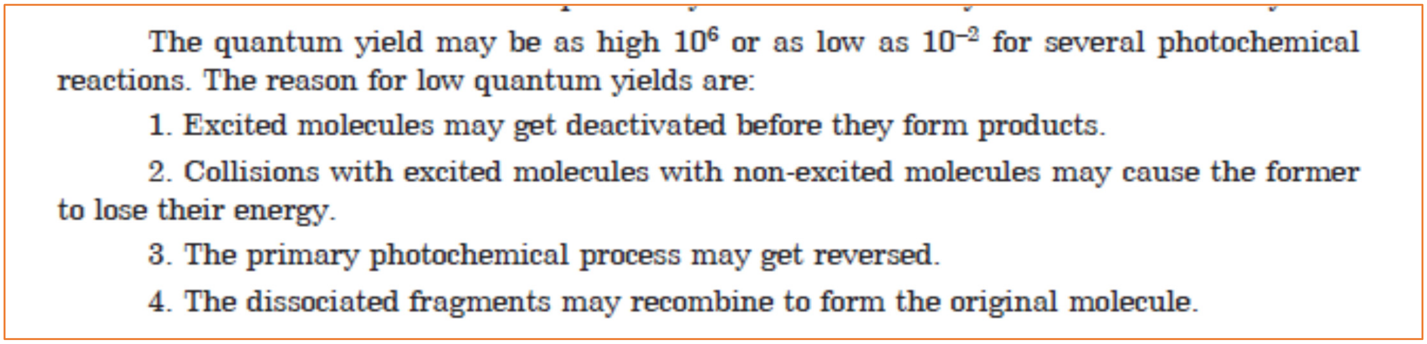
$$\varphi = \frac{\text{Number of molecules reacting in given time}}{\text{Number of quantum of radiation absorbed in the same time}}$$

The energy E absorbed per mole of the reacting substance is called one einstein

$$E = N_A h\nu = \text{One einstein}$$

The quantum yield of the product formation

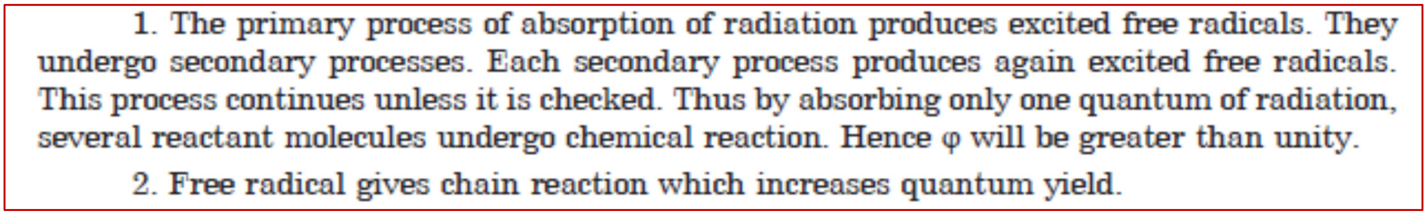
$$\varphi = \frac{\text{Number of molecules of product formed}}{\text{Number of einstein of radiation absorbed}}$$



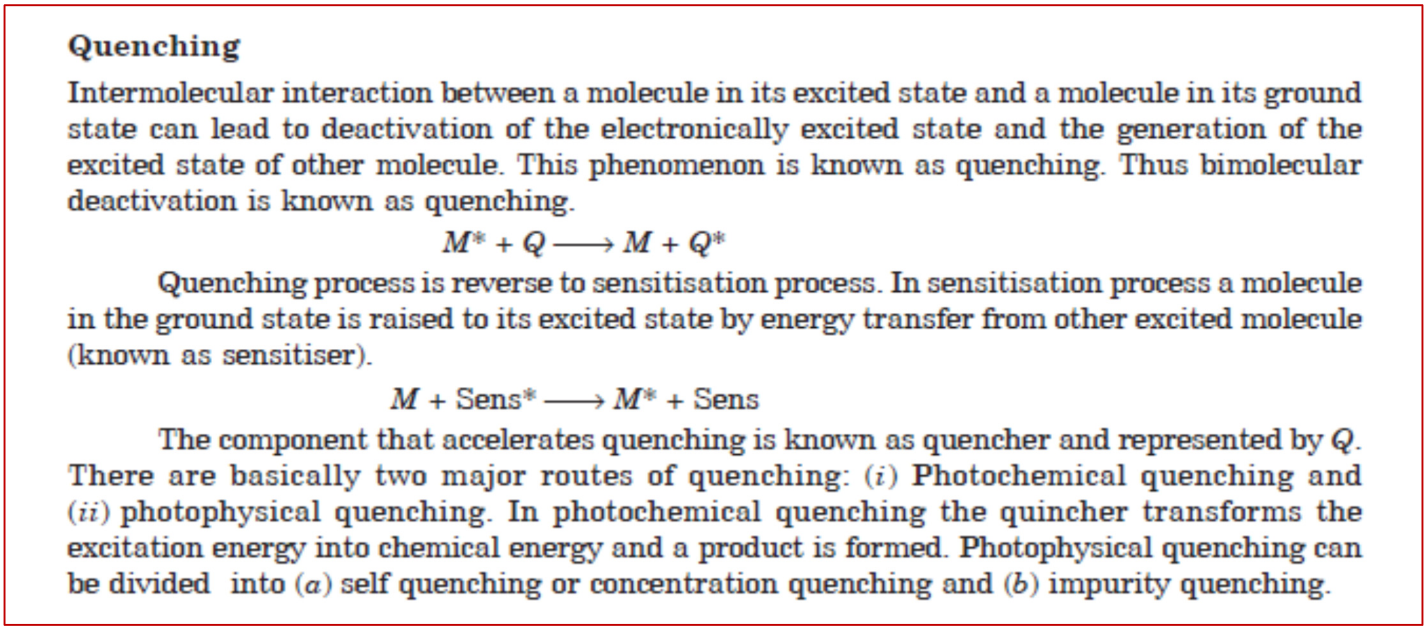
The quantum yield may be as high 10^6 or as low as 10^{-2} for several photochemical reactions. The reason for low quantum yields are:

1. Excited molecules may get deactivated before they form products.
2. Collisions with excited molecules with non-excited molecules may cause the former to lose their energy.
3. The primary photochemical process may get reversed.
4. The dissociated fragments may recombine to form the original molecule.

The Reasons for High Quantum Yield



1. The primary process of absorption of radiation produces excited free radicals. They undergo secondary processes. Each secondary process produces again excited free radicals. This process continues unless it is checked. Thus by absorbing only one quantum of radiation, several reactant molecules undergo chemical reaction. Hence φ will be greater than unity.
2. Free radical gives chain reaction which increases quantum yield.



Quenching

Intermolecular interaction between a molecule in its excited state and a molecule in its ground state can lead to deactivation of the electronically excited state and the generation of the excited state of other molecule. This phenomenon is known as quenching. Thus bimolecular deactivation is known as quenching.

$$M^* + Q \longrightarrow M + Q^*$$

Quenching process is reverse to sensitisation process. In sensitisation process a molecule in the ground state is raised to its excited state by energy transfer from other excited molecule (known as sensitiser).

$$M + \text{Sens}^* \longrightarrow M^* + \text{Sens}$$

The component that accelerates quenching is known as quencher and represented by Q. There are basically two major routes of quenching: (*i*) Photochemical quenching and (*ii*) photophysical quenching. In photochemical quenching the quincher transforms the excitation energy into chemical energy and a product is formed. Photophysical quenching can be divided into (*a*) self quenching or concentration quenching and (*b*) impurity quenching.
