SCH 441E: PHOTOCHEMISTRY

Photochemistry is the study of chemical reactions resulting from the exposure of light radiations. Light supplies the required energy to take place the photochemical reactions. The visible and UV radiations (2000-8000Å wavelength) are mainly used in photochemical reactions.

Thermochemical reactions (dark reactions) are brought about by molecular collisions. These reactions are spontaneous and are accompanied by a decrease in free energy. But certain photochemical reactions are accompanied by an increase in free energy.

All *photochemical reactions* take place in two steps. In the first step, the reacting molecules are activated by absorption of light. In the second step, the activated molecules undergo a photochemical change. For example, in the combination of hydrogen and chlorine, the first step is: $Cl_2 + h\nu \rightarrow 2Cl^{\cdot}$

The activated chlorine atoms ($Cl^{\cdot}$) then undergoes chemical reaction.

It is evident from the above reaction that the second step can occur in absence of light.

Characteristics of photochemical reaction:

1. Photochemical reactions take place by absorption of light.
2. When a light composing number of colours is used, the photochemical reaction may not be initiated by all colours.
3. The free energy change (ΔG) of a photochemical reaction may be either negative or positive.

Differences between photochemical and thermal reactions:

Photochemical reactions	Thermochemical reactions
1. These involve the absorption of light. 2. Take place in presence of light. 3. They are independent of temperature. 4. Rate of reactions is dependent on the intensity of the light absorbed. **5.** The free energy change is negative or positive.	• These involve either absorption or evolution of heat. • Take place in dark or in presence of light. • They are dependent of temperature. • Rate of reactions is not affected by the intensity of light. • The free energy change is always negative.

LAWS OF PHOTOCHEMISTRY:

The First Law of Photochemistry (*Grotthus-Draper Law) - 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.

**The Second Law of Photochemistry (*Stark-Einstein Law of Photochemical Equivalence)- Principle of Quantum Activation:*

It states that in a primary photochemical process (first step) each molecule is activated by the absorption of one quantum of radiation (one photon).

When a molecule absorbs a photon, it is not necessary that only one molecule should react. The absorption of one photon by a molecule is only the first step resulting in the formation of an activated molecule. This further may or may not react or may cause the reaction of many molecules through a chain mechanism.

Reasons for validity of Stark-Einstein Law of Photochemical Equivalence

i. Electronically excited state of a molecule obtained on absorption of a photon has so short a life that absorption of a second photon during its state of excitation may not have a chance.

ii. Compared to the number of available light absorbing molecules in a substance, the number of photons provided by the ordinary intensities of light sources is so low that on this account too absorption of a second photon is not probable.

Other laws

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 .

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

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

Where I = the intensity if incident light of wavelength λ

l = the thickness of the medium

k = the proportionality factor

on integrating equation 1 and putting $I = I0$ when $l = 0$, we get

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

Beer's law:

The intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically.
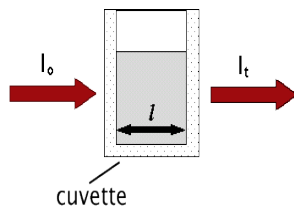
Figure. Schematic representation showing that light of initial intensity, I_o, passing through an absorbing medium in a cuvette with light path, l, will emerge with a final intensity, lt.

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

On combining both laws, we get $\log I_0/I = \varepsilon cl$ ---------- (4)

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

In the above equation;

ε = the molar absorption coefficient

$A = \log I0/I$ is the absorbance (or) optical density (OD)

Example 1

The absorbance of an iron thiocyanate solution containing 0.00500 mg Fe/mL was reported as 0.4900 at 540 nm.

    a.   Calculate the specific absorptivity, including units, of iron thyocyanate on the assumption that a 1.00 cm cuvette was used.

       ε = [A] / [cm X C]

       ε = [0.4900] / [1.00 cm X 0.00500 mg/mL]

        ε = [98.0 cm-1(mg/mL) -1]

    b.   What will be the absorbance if

       (1) the solution is diluted to twice its original volume and

       (2) the solution is placed in a 5.00 cm cuvette?

       (1) $A = \varepsilon lC$

            $A = [98.0 \text{ cm-1(mg/mL) -1}] \times 1.00 \text{ cm} \times [0.00250]$

            $= 0.2450$

       (2) $A = \varepsilon lC$, $A = [98.0 \text{ cm-1(mg/mL) -1}] \times 5.00 \text{ cm} \times [0.00250]$

            $A = 1.225$

    c.   Calculate percentage of light transmitted by the original iron thiocyanate solution.

       $A = -\log[I/I0]$

       $-0.4900 = \log[I/I0]$

       $= 0.3236 = [I/I_0]$

       $[0.3236 \times I0] = I$

       32.36% of the light is transmitted

d. Determine the concentration of iron thiocyanate that will absorb 50% of the entering light.

$50.0\% = 0.500$

$-\log [0.500] = A$

$0.3010 = A = \epsilon lC$

$0.3010 = [98.0 \text{ cm-1(mg/mL) -1}] \times 1.00 \text{ cm} \times [C]$

$C = 0.00307 \text{ mg/mL}$

2. A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution, given that $\varepsilon = 6000 \text{ dm}^3/\text{mol/cm}$.

$\log(I/I_O) = \epsilon lC$

$-\text{Log} (0.4) = 6000 \times 2 \times C$

$0.3979/12000 = C$

Answer: $3.316 \times 10^{-5} \text{mol} / \text{dm3}$

Example

A solution of the red complex formed by Fe^{2+} ion with 1, l0-phenanthroline is taken in a cell of thickness 1.00 *cm*. If **E** for the complex is $1.11 \times 10^3 \text{ m}^2 \text{ mol}^{-1}$ and the absorbance of the solution is 0.391, calculate the concentration of the complex in mol m^{-3} units.

Solution

$A = 0.391; l = 1.00 \text{cm} \times 10^{-2}; \varepsilon = 1.11 \times 10^3 \text{m}^3 \text{mol}^{-1}$

Rearranging the equation,

$$C = \frac{A}{\varepsilon l} = \frac{0.391}{1.11 \times 10^3 \times 1.00 \times 10^{-2}}$$

$= 0.0352 \text{molm}^{-3}$

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.

    iv. if the solution contains impurities or dissociation or association (Deviation may occur).

Quantum Yield (or) Quantum Efficiency (ϕ):

To express the relationship between the number 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,

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

The quantum efficiencies for the formation of a product and for the disappearance of the reactant are defined below:

$$\text{quantum efficiency for the formation of a product } Q_p \;==\; \frac{\text{no of molecules formed per sec}}{\text{no of quanta absorbed per sec}} = \frac{dN_p/dt}{Ia}$$

In this equation, dN_p/dt denotes the rate of formation of the product. The units for dN_P/dt molecules per second. **Ia** refers to the number of photons absorbed per second. Similarly we can define the quantum efficiency for the disappearance of a reactant.

$$\text{quantum efficiency for the disappearance of a reactant } Q_R \;==\; \frac{\text{no of molecules consumed per sec}}{\text{no of quanta absorbed per sec}} = \frac{dN_R/dt}{Ia}$$

Experimentally,

$$\Phi = \frac{\text{rate of chemical reaction}}{\text{quanta absorbed per second}}$$

In certain photochemical reaction,

Number of Einsteins absorbed $= q/(Nhc/\lambda) = q\lambda/Nhc$

$\therefore$ Quantum yield $\phi = n/(q\lambda/Nhc) = nNhc/q\lambda$

In CGS units, $\phi = n/q \times [1.196 \times 10^{16}/\lambda \text{ (in Å)}$

Where;

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),

To calculate the quantum efficiency, use the following steps:

i) **Calculation of Energy Absorbed per Quantum**

Energy Per quantum of radiation absorbed $= h\nu = \boldsymbol{hc/\lambda}$

ii) **Calculation of Ia.**

Usually intensity of light absorbed is given in J s^{-1} units. From this, **Ia** could be calculated using the following equation :

Intensity in terms of number of photons absorbed in 1 second (**Ia**) $= \frac{\text{Intensity in J s}-1\text{units}}{Energy\ per\ quantum}$

iii) **Calculation –dN_R/dt or dN_P/dt**

First we have to obtain the number of moles of reactant consumed or of product formed **in 1second** by dividing the respective amount by the time in second unit.

In order to calculate the rate of formation or rate of disappearance in molecule per second units, we have to use the following equations:

–dN_R/dt = Number of moles of reactant decomposed in 1 second x NA

Also

dN_P/dt = Number of moles of product formed in 1 second x *NA*

iv) **Calculation of Quantum Efficiency**

Quantum efficiency $\Phi = dNp/dt$ */Ia*

Some important relations:

Photons $\equiv$ quanta

One molecule absorbs $\equiv$ one photon

One mole of a substance one mole of quanta (or)

Containing 6.023×10^{23} $\equiv$ 6.023×10^{23} quanta of (Avogadro number)

light (or) one Einstein Molecules absorbs

One Einstein $E = Nh\nu = Nhc/\lambda$ [$\therefore \nu = c/\lambda$]

The energy of photons and Einstein:

The energy of a photon (or quantum) E, is given by the equation $E = h\nu = hc/\lambda$,

where,

$\qquad$ h – Planck's constant (6.625×10^{-34} Js);

$\qquad$ c – velocity of light = 3.0×10^8 ms^{-1};

$\qquad$ λ – wavelength of light.

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

On substituting the values in the above equation it becomes

$\qquad$ E $= (6.023 \times 10^{23}) \times (6.625 \times 10^{-34}) \times (3 \times 10^8)/\lambda$ J mol^{-1}

$\qquad\qquad = 0.1196/\lambda$ J mol^{-1} in SI units

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

$\qquad\qquad \therefore E = (6.023 \times 10^{23}) \times (6.625 \times 10^{-27}) \times (3 \times 10^{10})/\lambda$ erg mol^{-1}

$\qquad\qquad\quad = 1.196 \times 10^{16}/\lambda$ (in Å) erg mol^{-1}

$\qquad$ 1 cal = 4.184×10^7 ergs

$\qquad\qquad \therefore E = 1.196 \times 10^8/4.184 \times 10^7/\lambda$ cal mol^{-1}

$\qquad\qquad\quad = 2.859/\lambda$ cal mol^{-1}

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

$$= 2.859 \times 10^5/\lambda \text{ (in Å) kcal mol}^{-1}$$

Example 1

In photochemical decomposition of acetone using **313** nm light, **7.57** x 10^{-6} mol of carbon monoxide is formed in 20 minutes. If the light absorbed corresponds to 2.41 x J s^{-1}, calculate the quantum efficiency for the formation of carbon monoxide.

Solution

i)   Energy absorbed per quantum = *hc/λ* = *(6.626 x 10^{-34} x 3x10^8)/313 x 10^{-9}*

$$= \textbf{6.35 x } 10^{-19} \text{ joule photon}^{-1}$$

ii) *Ia =* Intensity in joule second^{-1}/6.35 **x** 10^{-19} joule photon^{-1}

= 2.14 **x 10^{-3}** joule second^{-1}/6.35 **x** 10^{-19} joule photon-1

. ,*Ia* = 3.80 *x* 10^{15} photons second^{-1}

iii) Amount of carbon monoxide formed in 1 second =7.57 **x** 10^{-6}mol/20 **x** 60 s

= 6.31 **x 10^{-9}**mol s^{-1}

-dNco/dt = 6.31 **x 10^{-9} x** 6.022 **x** 10^{23} molecule second^{-1}

= 3.80 **x** 10^{15} molecule second^{-1}

jv) Quantum efficiency for the formation of carbon monoxide= dNco/dt */Ia = 1*

Example 2

Hydrogen iodide vapour undergoes photo dissociation to hydrogen and iodine when exposed to a radiation of 2070A wavelength. For every joule of radiation absorbed 4.4x 10^{-4}g of HI is decomposed. What is the quantum efficiency of the reaction?

Solution

V= C/ *λ*

λ = 2070 X 10^{-10}m, c = 3x 10^8m/s

v = 3x 10^8m/s/(2070 x 10^{-10}) = 1.45 x 10^{15}

1 joule of photon energy decomposes 4.4 x 10^{-4}g of HI

1 photon energy = hv= 6.626 x 10^{-34} x 1.45 x 10^{15}

$$= 9.6 \times 10^{-19} \text{ joule}$$

No of photons per joule = 1/(9.6 x 10^{-19}) = 1.04 x 10^{18}

Gram molecular weight of HI = 128

No of molecules = (4.4 x 10^{-4} x 6.023 x 10^{23})/128

$$= 2.07 \times 10^{18}$$

Φ = 2.07 x 10^{18}/1.04 x 10^{18}

= 2 molecules per photon

Example 3.

When a substance *A* was exposed to light, 0.002 mole of it reacted in 20 minutes and 4 seconds. In the same time *A* absorbed 2.0×10^6 photons of light per second. Calculate the quantum yield of the reaction. (Avogadro number *N* = 6.02×10^{23})

SOLUTION

Number of molecules of *A* reacting = $0.002 \times N = 0.002 \times 6.02 \times 10^{23}$

Number of photons absorbed per second = 2.0×10^6

Number of photons absorbed in 20 minutes and 4 seconds = $2.0 \times 10^6 \times 1204$

Quantum yield φ =

No. of molecules reacted

No. of photons absorbed

= $0.002 \times 6.02 \times 10^{23} / (2.0 \times 10^6 \times 1204)$

= $\mathbf{5.00 \times 10^{11}}$

Example 4

In the uranyl oxalate actinometer 5.18×10^{18} molecules were decomposed during the time radiation. 10.58×10^{18} photons of a radiation of 3655A wavelength were absorbed. What is the quantum efficiency of this reaction?

Solution

Quantum efficiency $\Phi = \dfrac{\text{molecules decomposed}}{\text{quanta absorbed}}$

$= \dfrac{5.18 \times 10^{18}}{10.58 \times 10^{18}} = 0.49$ molecule/photon

Example 5

A radiation of 250 nm incident oil HI results in the decomposition 1.85 $\mathbf{x}$ $\mathbf{10^{-2}}$ mol within a particular time interval. Light energy absorbed during this time interval is 4.18 k J. Calculate the quantum efficiency for the decomposition of HI.

1) Energy absorbed per photon $= \dfrac{6.626 \times 10^{-34} \times 3 \times 10^8}{250 \times 10^{-9}}$ joule photon^{-1}

$$= 7.95 \times 10^{-19} \text{ joule photon}^{-1}$$

Assume that the reaction is conducted for t seconds.

Hence, $I_a = \dfrac{\text{Intensity in joule second}^{-1}}{7.95 \times 10^{-19} \text{ joule photon}^{-1}}$

$$= \dfrac{4.18 \times 10^3 \text{ joule}/t \text{ second}}{7.95 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= \dfrac{5.26 \times 10^{21}}{t} \text{ photon second}^{-1}$$

Amount of HI decomposed in 1 second $= \dfrac{1.85 \times 10^{-2} \text{ mol}}{t \text{ second}}$

$$\dfrac{-dN_{HI}}{dt} = \dfrac{1.85 \times 10^{-2}}{t} \times 6.022 \times 10^{23} \text{ molecule second}^{-1}$$

$$= \dfrac{1.114 \times 10^{22}}{t} \text{ molecule second}^{-1}$$

Using Eq. 19.3, $\phi_{HI} = \dfrac{-dN_{HI}/dt}{I_a} = \dfrac{1.114 \times 10^{22}/t}{5.26 \times 10^{21}/t}$

$$= 2.12$$

Example 6

If 10% of the energy of a 100w incandescent bulb generates visible light having average wavelength 600 nm, how many quanta of light are emitted in 10 mins? (1W = 1J/s)

(Hint; A tungsten filament bulb is an example of incandescent bulb. Incandescence is light emission due to intense

Energy per quantum $= \dfrac{6.626 \times 10^{-34} \times 3 \times 10^8}{600 \times 10^{-9}}$ joule photon^{-1}

$$= 3.31 \times 10^{-19} \text{ joule photon}^{-1}$$

$\left\{\begin{array}{l}\text{Number of quanta} \\ \text{emitted per second}\end{array}\right\} = \dfrac{\text{Energy emitted per second}}{\text{Energy per photon}}$

$$= \dfrac{10 \text{ joule second}^{-1}}{3.31 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= 3.02 \times 10^{19} \text{ photons second}^{-1}$$

heat

$\left\{\begin{array}{l}\text{Number of quanta emitted} \\ \text{in 10 minutes}\end{array}\right\} = 3.02 \times 10^{19} \times 600 \text{ photons}$

$$= 1.81 \times 10^{22} \text{ photons}$$

Example 7

At 478 nm, hydrogen and chlorine combine to give hydrogen chloride with quantum efficiency of 1·0 x 106. If the absorbed intensity is 2.5 x 10-3 J/s, calculate the amount in moles of hydrogen chloride formed in 10 mins.

$$\text{Energy per quantum} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{478 \times 10^{-9}} \text{ joule photon}^{-1}$$

$$= 4.16 \times 10^{-19} \text{ joule photon}^{-1}$$

$$I_a \left(\begin{array}{l}\text{Number of quanta} \\ \text{per second}\end{array}\right) = \frac{\text{Intensity in joule second}^{-1}}{\text{Energy per photon}}$$

$$= \frac{2.50 \times 10^{-3} \text{ joule second}^{-1}}{4.16 \times 10^{-19} \text{ joule photon}^{-1}}$$

$$= 6.01 \times 10^{15} \text{ photons second}^{-1}$$

$$\phi_{HCl} = \frac{\frac{dN_{HCl}}{dt}}{I_a}; \text{ hence, } \frac{dN_{HCl}}{dt} = \phi_{HCl} \cdot I_a$$

$$i.e., \quad \frac{dN_{HCl}}{dt} = 6.01 \times 10^{15} \times 1.00 \times 10^6 \text{ molecules second}^{-1}$$

$$= 6.01 \times 10^{21} \text{ molecules second}^{-1}$$

$$\left\{\begin{array}{l}\text{Number of molecules of HCl} \\ \text{formed in 10 minutes}\end{array}\right\} = 6.01 \times 10^{12} \times 600 \text{ molecules}$$

$$= 3.61 \times 10^{24} \text{ molecules}$$

$$\left\{\begin{array}{l}\text{Amount of HCl formed} \\ \text{in 10 minutes}\end{array}\right\} = \frac{3.61 \times 10^{24}}{6.022 \times 10^{23}} \text{ mole}$$

$$= 5.99 \text{ mole.}$$

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 fulfill 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.
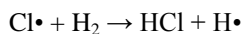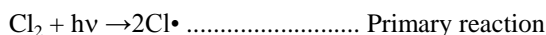
The Quantum Efficiencies of Some Reactions

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:

$HI + h\nu \rightarrow H\bullet + I\bullet$ .... Primary reaction

$H\bullet + HI \rightarrow H2 + I\bullet$

$I\bullet + I\bullet \rightarrow I2$ ....Secondary reaction

Overall reaction : $2HI + h\nu \rightarrow H_2 + I_2$
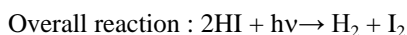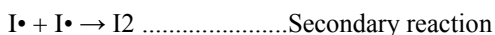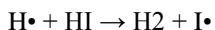
The overall reaction shows that the two HI are decomposed for one photon ($h\nu$). Thus, the quantum yield (ϕ) = 2

2. Formation of HCl: In the primary step, one Cl_2 molecule absorbs a photon and dissociated into two Cl atoms. This is followed by the secondary reaction as shown below:

$Cl_2 + h\nu \rightarrow 2Cl\bullet$ .... Primary reaction

$Cl\bullet + H_2 \rightarrow HCl + H\bullet$

$H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$ .... 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.

$2Cl \rightarrow Cl_2$
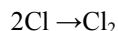
Thus the quantum yield varies from 10^4 to 10^6.

Other photochemical reaction based on quantum yield:

1. The reaction in which the quantum yield is a small integer like 1, 2.

Examples:

    a. Dissociation of HI & HBr;

    b. Combination of $SO_2 + Cl_2$ and

    c. Ozonisation of O_2.

2. The reaction in which the quantum yield is less than 1.

Eaxmples:

    a. Dissociation of NH_3, CH_3COCH_3 & NO_2;

    b. Transformation of maleic acid into fumaric acid.

3. The reaction in which the quantum yield is extremely high.

Examples:

    a. Combination of $CO + Cl_2$;

    b. Combination of $H_2 + Cl_2$.

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 anable them to react.

4. The primary photochemical reaction may be reversed.

5. Recombination of dissociated fragments will give low quantum yield.

Example: Dimerization of anthracene to dianthracene

$$2C_{14}H_{10} + h\nu \rightarrow C_{28}H_{20}$$
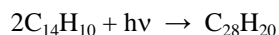
The quantum yield = 2, but actually it is found to be = 0.5 ; the reason is the above reaction is reversible.

$$2C_{14}H_{10} \rightarrow C_{28}H_{20}$$
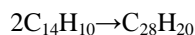
Measurement of Absorbed Intensity:

A photochemical reaction takes place by the absorption of photons of light by the reacting molecules. Therefore, it is essential to determine the intensity of light absorbed by the reacting molecules. An experimental arrangement for the study of rate of a photochemical reaction is shown in figure.
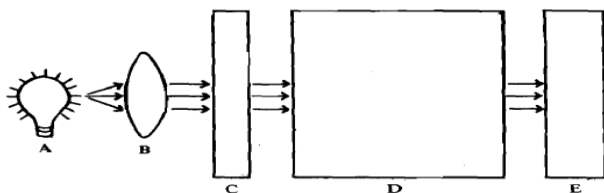
Radiation emitted from a source of light, A (sun light, tungsten filament, mercury vapour lamp) is passed through the lens B, which produces parallel beams. The parallel beams are then passed through a monochromator, C, which yields a beam of the desired wavelength only. This monochromatic light is allowed to enter into the reaction cell, D, immersed in a thermostat, containing the reaction mixture. The part of the light that is not absorbed fall on a detector, E, which measures the intensity of radiation.The most frequently used detector is the chemical actinometer. A chemical actinometer is a device used to measure the amount of radiation absorbed by the system in a photochemical reaction. Using chemical actinometer, the rate of a chemical reaction can be measured easily.Uranyl oxalate actinometer is a commonly used chemical actinometer. It consists of 0.05 M oxalic acid and 0.01 M uranyl sulphate in water. When it is exposed to radiation, oxalic acid undergoes decomposition to give CO_2, CO and H_2O. The residual concentration of oxalic acid can be found out by titrating with standard $KMnO_4$. The amount of oxalic acid consumed is a measure of the intensity of radiation.

Chemical Actinometers

Light intensity could be estimated by a quantitative estimation of a substance formed ox decomposed by light. The photochemical decomposition of $K_3Fe(C_2O_4)_3$ is a widely used chemical method for estimating intensity of light between the wavelength range 250 nm and 577 nm. Light within this wavelength range causes $K_3Fe(C_2O_4)_3$ dissolved in sulphuric acid to react as follows:

$2Fe^{3+} + 2e \rightarrow 2Fe^{2+}$

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e$
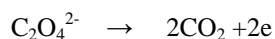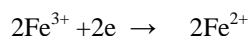
The concentration of Fe^{2+} is estimated colorimetrically through complex formation with 1, 10-phenanthroline. This complex has a deep red colour. The concentration of the complex is equal to the concentration of Fe^{2+} present before complexation. The following example is worked out to illustrate this method.

Example3

In a potassium ferrioxalate actinometer, the quantum efficiency for Fe^{2+} Production, at 480 mn wavelength is 0.95. After irradiating the potassium ferrioxalate solution for 20 minutes, it is completely transferred to a 200 cm^3 volumetric flask, mixed with required quantity of 1,10-phenanthroline for complex formation and made up to mark with a buffer solution. For colorimetric estimation, a sample of this complex is taken in a cell of 1.00 **cm** thickness. The complex has an absorbance value of 0.391 and its **E** is 1.11 **x** 10^3 m^2 mol^{-1}.

Calculate

i) the concentration of the complex,

ii) the number of Fe^{2+} ions formed in the actinometer due to irradiation,

iii) the rate of formation of Fe^{2+} ions (dNp/dt)

iv) **Ia** (number of photons absorbed per second).

Assume that one Fe^{2+} ion forms one complex molecule with 1,10-phenanthroline.

Solution

i) Note that the concentration of the complex is same as that calculated in Example 1

using concentration of complex = 0.0352 mol m^{-3}.

Also, concentration of Fe^{2+} ion = concentration of the complex = 0.0352 mol m^{-3}.

Number of moles of Fe^{2+} ion present in 200 cm^3 of the solution=$[Fe^{2+}]$ x Volume of solution in M^3

= 0.0352 **x** 200 **x** 10^{-6} mol

= 7.04 **x** 10^{-6} mol(because, 200 cm3= 200 **x** 10^{-6} m3)

Hence the number of moles

of Fe^{2+} ion formed in the actinometer = 7.04 **x** 10^{-6} mol

The number of Fe^{2+} ions formed in the actinometer = 7.04 **x** 10^{-6} **x** 6.022 **x** 10^{23} = 4.24 **x** 10^{18} ions

iii) dNp/dt = Number of Fe^{2+} ions formed/time in sec= 4.24 **x** 10^{18}/1200 = 3.53 **x** 10^{15} ions $second^{-1}$

iv) Using quantum efficiency = dNp/dt / **Ia**

Given that quantum efficiency, **p**= 0.95

Hence Ia = dNp/dt x1/0.95

= 3.53 x 10^{15} /0.95photons $second^{-1}$

= 3.72 x 10^{15} photons $second^{-1}$

Calculation of the amount of radiation absorbed:

The empty cell (or) the cell filled with solvent is exposed to radiation and reading is noted = Total incident energy

The cell is filled with the reactants and again the reading is noted = Residual energy

∴ Total energy absorbed by the reacting mixture = Total incident energy – Residual energy transmitted

PHOTOPHYSICAL PROCESS:

Generally atoms or molecules go to excited state by the absorption of suitable radiation. If the absorbed radiation is not used to cause a chemical reaction, it will be re-emitted as light of longer wavelength. This process is called as photophysical process.

The three such photophysical processes which can occur are :

(*a*) Fluorescence (*b*) Phosphorescence (*c*) Chemiluminescence

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, thalium, 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.

i)   **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).

Mechanism of Photophysical Processes (or) Mechanism of Fluorescence and

Phosphorescence (or) Jablonski Diagram

Most molecules possess an even number of electrons and all the electrons are paired in ground state. The spin multiplicity of a state is given by 2S + 1, where S is the total electronic spin.

i) When the spins are paired ($\uparrow\downarrow$), the clockwise orientation of one electron is cancelled by the anticlockwise orientation of other electron. Thus,

$S = s1 + s2 = (\frac{1}{2}) - (\frac{1}{2}) = 0$

$\therefore 2S + 1 = 1$, ie., spin multiplicity is 1. The molecule is in the singlet ground state.

ii) On absorption of a suitable energy, one of the paired electrons goes to a higher energy level. The spin orientation of the two electrons may be either

 a. parallel ($\uparrow\uparrow$), then $S = s1 + s2 = (\frac{1}{2}) + (\frac{1}{2}) = 1$, $\therefore 2S + 1 = 3$, ie., spin multiplicity is 3. The molecule is in the triplet (T) excited state.

 b. or anti-parallel ($\uparrow\downarrow$), then $S = s1 + s2 = (\frac{1}{2}) - (\frac{1}{2}) = 0$, $\therefore 2S + 1 = 1$, ie., spin multiplicity is 1. The molecule is in the singlet (S) excited state.

| Singlet groung state | Singlet excited state s_1 (pair of electrons with opposite spins but each in different orbital | Triplet excited state T_1(pair of electrons with parallel spins in different orbitals |
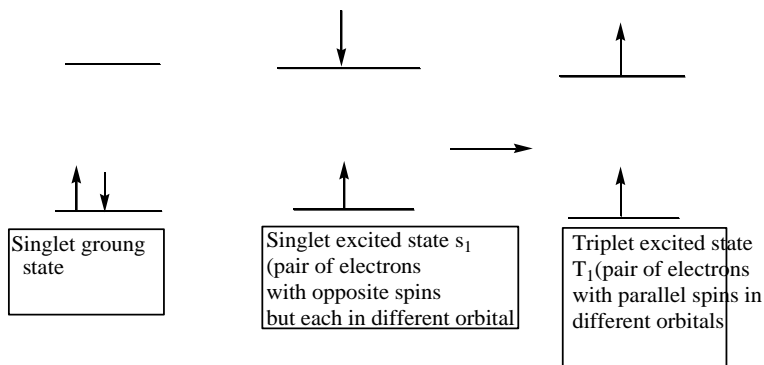
The exicted species can return to the ground state by losing all of its excess energy by any one of the paths shown in jablonski diagram.

A Jablonski Diagram

S = singlet state
T = triplet state
ic = internal conversion
isc = intersystem crossing
R = relaxation
F = fluorescence
P = phosphorescence
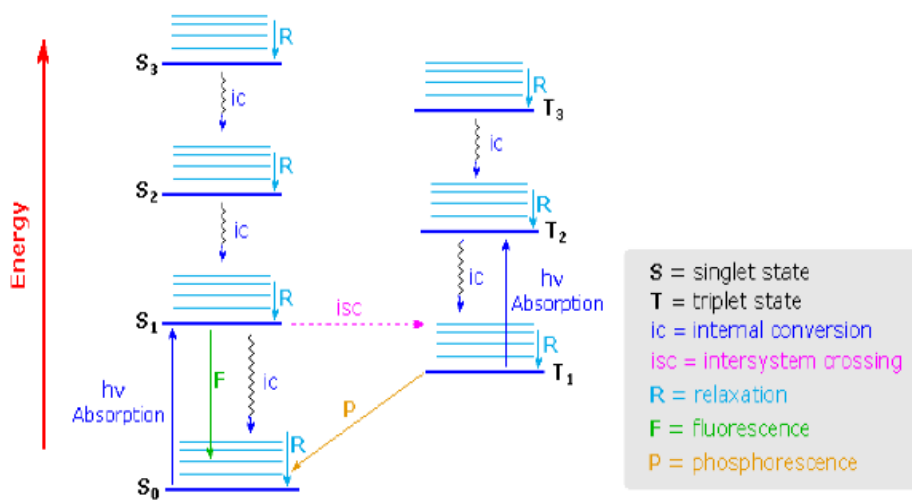
Since the electron can jump from the ground state to any of the higher electronic states depending upon the energy of the photon absorbed we get a series of

 a. singlet excited states ie., S1, S2, S3, etc., (first singlet excited state, second singlet excited state, third singlet excited state, etc.) and

b. triplet excited states ie., T1, T2, T3, etc., (first triplet excited state, second triplet excited state, third triplet excited state, etc.).

Generally singlet excited state has higher energy than the corresponding triplet excited state. Thus, the energy sequence is as follows: ES1> ET1> ES2> ET2> ES3> ET3 and so on.

When a molecule absorbs light radiation, the electron may jump from S0 to S1, S2 (or) S3 singlet excited state depending upon the energy of the light radiation as shown in Jablonski diagram.

For each singlet excited state there is a corresponding triplet excited state, ie.

$$S1 \rightarrow T1; S2 \rightarrow T2; S3 \rightarrow T3, \text{etc.}$$
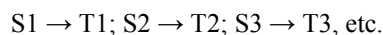
The molecule, whether it is in singlet or triplet excited state, is said to be activated. Thus,

$$A_0 + h\nu \rightarrow A*$$
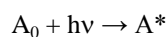
where

A_0 – ground state molecule

A* - excited state molecule.

Types of transitions:

The activated molecules returns to the ground state by emitting its energy through the following general types of transitions.

1. **Non-radiative transitions** do not involve the emission of any radiations, so these are also known as non-radiative or radiationless transitions. Non-radiative transitions involve the following two transitions.

a. *Internal conversion (IC)*: These transitions involve the return of the activated molecule from the higher excited states to the first excited states, ie.

$$S3 \rightarrow S1;$$
$$S2 \rightarrow S1$$

(or)

$$T3 \rightarrow T1;$$
$$T2 \rightarrow T1$$
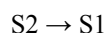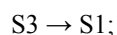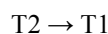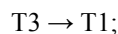
The energy of the activated molecule is given out in the form of heat through molecular collisions. This process is called internal conversion (IC) and occurs in less than about 10-11 second.

b. *Inter system crossing (ISC)*: The molecule may also lose energy by another process called inter system crossing (ISC). These transitions involve the return of the activated molecules from the states of different spins ie. Different multiplicity ie.,

$$S2 \rightarrow T2;$$
$$S1 \rightarrow T1.$$
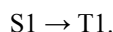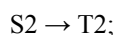
These transitions are forbidden, occurs relatively at slow rates.

2. **Radiative transitions** involve the return of activated molecules from the singlet excited state S1 and triplet state T1 to the ground state S0. These transitions are accompanied by the emission of radiations. Thus, radiative transitions involve the following two radiations.

a. *Fluorescence*: The emission of radiation due to the transition from singlet excited state S1 to ground state S0 is called fluorescence ($S_1 \rightarrow S_0$). This transition is allowed transition and occurs in about 10^{-8} second.

b. *Phosphorescence*: The emission of radiation due to the transition from the triplet excited state T1 to the ground state S0 is called phosphorescence ($T_1 \rightarrow S_0$). This transition is slow and forbidden transition.

3. **Quenching of fluorescence**: The fluorescence may be quenched, when the excited molecule collides with a normal molecule before it fluoresces (the excited molecules are deactivated and the fluorescence stops). During quenching, the energy of the excited molecule gets transferred to the molecule with which it collides. Quenching occurs in two ways;

a. *Internal quenching*: Quenching may also occur, when the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called internal quenching.

b. *External quenching*: Quenching may also occur from the addition of an external substance, which absorbs energy from the excited molecule. This phenomenon is called external quenching.

Summary of Physical processes undergone by excited molecules

$S_o + hv \rightarrow S1$ Excitation .

$S1 \rightarrow S1 + heat$ Vibrational relaxation

$S1 \rightarrow S_o + hv$ Fluorescence

$S1 \rightarrow S_o + heat$ Internal conversion

$S1 \rightarrow T1$ Intersystem crossing

$T1 \quad T1 + heat$ Vibrational relaxation

$T1 \rightarrow S_o + hv$ Phosphorescence

$T1 \rightarrow S_o + heat$ Intersystem crossing

$S1 + S_o \rightarrow S_o + s_1$ Singlet-singlet transfer (photosensitisation)

$T1 + S_o \rightarrow S_o + T_1'$ Triplet-triplet transfer (photosensitisation)
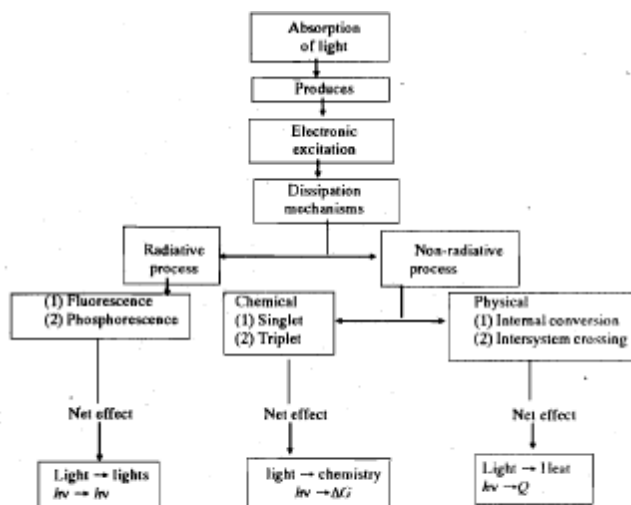
Fig. 13.2 : Important processes involved in a molecular photochemistry

Singlet and triplet excited states often show different reactivity

Singlet	Triplet
• tend to have considerable zwitterionic character • undergo rapid, concerted reactions • stereospecific • must compete with facile photophysical processes • *electrocyclic rearrangements* • *cycloadditions* • *sigmatropic rearrangements*	tend to have biradical character triplet state is longer lived no stereospecificity stepwise reactions *hydrogen abstraction* *additions to unsaturation* *homolytic fragmentation* *radical rearrangements*

Fluorescence lifetime

The fluorescence lifetime is a measure of the time a fluorophore spends in the excited state before returning to the ground state by emitting a photon . The lifetimes of fluorophores can range from picoseconds to hundreds of nanoseconds.

If a population of fluorophores is excited, the lifetime is the time it takes for the number of excited molecules to decay to 1/e or 36.8% of the original population according to:

$$\frac{n^*(t)}{n^*(0)} = e^{-t/\tau}$$
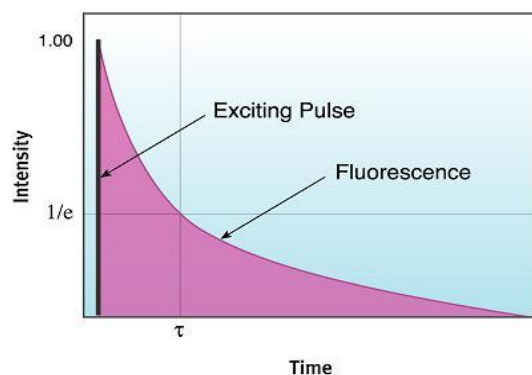
As shown in the intensity decay figure, the fluorescence lifetime, t, is the time at which the intensity has decayed to 1/e of the original value. The decay of the intensity as a function of time is given by:

$$I_t = \alpha\ e^{-t/\tau}$$

Where I_t is the intensity at time t, α is a normalization term (the pre-exponential factor) and τ is the lifetime.

Knowledge of the excited state lifetime of a fluorophore is crucial for quantitative interpretations of numerous fluorescence measurements such as quenching, polarization.

Fluorescence lifetime is an intrinsic property of a fluorophore. FLT does not depend on fluorophore concentration, absorption by the sample, sample thickness, method of measurement, fluorescence intensity, photo-bleaching, and/or excitation intensity. It is affected by external factors, such as temperature, polarity, and the presence of fluorescence quenchers. Fluorescence lifetime is sensitive to internal factors that are dependent on fluorophore structure.[1]

Methods to determine fluorescence lifetime of fluorophores

Fluorescence lifetime can be measured in either the frequency domain or the time domain.

The time domain method

- involves the illumination of a sample (a cuvette, cells, or tissue) with a short pulse of light, followed by measuring the emission intensity against time. The FLT is determined from the slope of the decay curve. Several fluorescence detection methods are available for lifetime measurements, of which, time-correlated single photon counting (TCSPC) enables simple data collection and enhanced quantitative photon counting.

The frequency domain method

-    involves the sinusoidal modulation of the incident light at high frequencies. In this method, the emission occurs at the same frequency as the incident light accompanied with a phase delay and change in the amplitude relative to the excitation light (demodulation).

Advantages of fluorescence lifetime measurement over intensity-based measurement[2]

1. Lifetime measurements do not require wavelength-ratiometric probes to provide quantitative determination of many analytes
2. The lifetime method expands the sensitivity of the analyte concentration range by the use of probes with spectral shifts.
3. Lifetime measurements may be used for analytes for which there are no direct probes. These analytes include glucose, antigens, or any affinity or immunoassays based on fluorescence energy transfer transduction mechanism.

Summary of timelifes

The approximate timelifes for these transitions are given in the following table.

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

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, CaF2, etc.	• Examples: ZnS, sulphides of alkaline earth metals.

CHEMILUMINESCENCE

Chemiluminescence is a process in which visible light is produced by a chemical reaction at a temperature at which a black body will not give out visible radiation. Thus, chemiluminescence is the reverse of a photochemical reaction. As the emission occurs at ordinary temperature, the emitted radiation is also known as "cold light".

In a chemiluminescent reaction, the energy released during the chemical reaction makes the product molecule electronically excited. The excited molecule then emits radiation, as it returns to the ground state. Examples,

   a. The oxidation of ether solution of magnesium p-bromophenyl bromide gives rise to chemiluminescence, the greenish glow that accompanies the exposure of solution to air, being visible in day light.
   b. Glow of phosphorous and its oxide, in which the oxide in its excited electronic state emits light.
   c. When pyragallol is oxidized by H_2O_2, chemiluminescence is produced.
   d. The glow of fire flies/ glow-worms is due to the chemiluminescence of a protein (luciferin) oxidation by oxygen in presence of an enzyme (luciferase).

Mechanism of chemiluminescence can be explained by considering anion-cation reactions.

Example, interaction between the aromatic anions (Ar^-) and cations (Ar^+).

$$Ar^- + Ar^+ \rightarrow {}^1Ar^* + Ar$$

$${}^1Ar^* \rightarrow Ar + h\nu$$
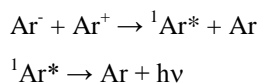
The aromatic anion (Ar^-) contains two paired electrons in the bonding molecular orbital (BMO) and one unpaired electron in the anti bonding molecular orbital (ABMO). The ABMO of the aromatic cation Ar^+ is empty. When the electron is transferred from the ABMO of the anion (Ar^-) to the ABMO of the cation (Ar^+), the singlet excited state ${}^1Ar^*$ is formed. The excited state can be deactivated by the emission of photon $h\nu$.

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*:

Photosensitisation is the process of exciting a molecule by energy transfer from an excited molecule. In this process, a donor molecule (D) absorbs a quantum light and forms an excited molecule (D*). The excited donor molecule then transfers its excitation energy to an acceptor molecule **(A)** in the ground state in order to excite it. This can be explained using the following reaction sequence:

Light absorption rD + hv →   D*

sensitisation   D* + A → A* + D
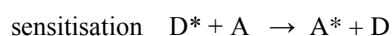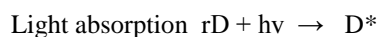
The donor Molecule is called the sensitiser. The excited acceptor molecule A* could take part either in chemical reactions or in physical processes. This process is called photosensitized reaction (or) photosensitization. Examples,

   i.   Atomic photosensitizers : mercury, cadmium, zinc and
   ii.   Molecular photosensitizers: benzophenone, sulphur dioxide.

Requirements of photosensitiser

   i.   It must be excited by the irradiation used.
   ii.   Present in sufficient concentration and absorb more strongly than the other reactants so that it is the major light absorber.
   iii. Energy of triplet state of sensitiser must be greater than that of the reactant.
   iv.   Must be able to transmit energy to reactant.

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.

Mechanism of Photosensitization and Quenching

- can be explained by considering a general donor (D) and acceptor (A) system. In a donor-acceptor system, the donor D (sensitizer) absorbs the incident photon and gets excited from ground state (S0) to singlet state (S1). Then the donor attains the triplet excited state (T1 or ^{3}D). The triplet state of the donor is higher than the triplet state of the acceptor (A). This triplet excited state of the donor collides with the acceptor produces the triplet excited state of the acceptor (^{3}A) and returns to the ground state (S_0). If the triplet excited state of the acceptor (^{3}A) gives the desired products, the mechanism is called photosensitization. If the products are resulted directly from the excited state of the donor (^{3}D), then A is called quencher and the process is called **quenching**.

The sequence of photosensitization and quenching may be represented as follows:

$$D + hv \rightarrow {}^1D$$
$$1D \rightarrow {}^3D$$
$${}^3D + A \rightarrow D + {}^3A$$

$^3A \rightarrow$ Products (photosensitization)

$^3D \rightarrow$ Products (quenching)
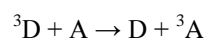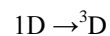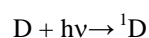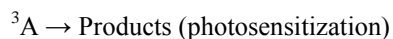
It is necessary that the energy of the triplet excited state of the donor (sensitizer) must be higher than the triplet excited state of the acceptor (reactant). Thus the energy available is enough to excite the reactant molecule to its excited state. The dotted line indicates the transfer of energy from the sensitizer to reactant.

Examples for photosensitized reactions are;

      a.   ***Dissociation of hydrogen molecule***: (discussed)

      b.   ***Photosynthesis in plants***

PHOTOCHEMICAL REACTIONS

Types of photochemical reactions:

a) Photosynthesis: when a larger molecule is formed from simple ones

b) Photodissociation when a larger molecule is decomposed to simple ones

c) Photosensitized reactions: when an excited molecule supplies activation energy for the reactants

Photochemical reactions processes:

The overall photochemical reaction consists of;

ii)   *Primary reaction.* In the primary reaction, the quantum of light is absorbed by a molecule 'A' resulting in the formation of an excited molecule 'A*'

$$A + h\nu \rightarrow A^*$$
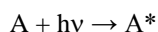
Primary effects of absorption of radiations by molecules are;

- *Excitation of molecules*; includes electronic, vibrational and rotational excitations of molecules.
- *Isomeric change to new molecules*; a direct photochemical effect.
- *Dissociation of molecules to atomic or multi atomic units*- direct photochemical effect.
- *Ionization of molecules through ejection of an electron (photoionization)*.

iii)   *Secondary reaction*. In the secondary reaction, the excited molecules react further to give the product of higher quantum yield. $A^* \rightarrow B$

If dissociation or ionization of light absorbing molecules does not occur by direct absorption of a radiation, energies of excited molecules can give rise to the following **secondary effects**;

- Photosensitization of reactions
- Delayed photochemical changes
- Rise in temperature of the system
- Fluorescence of the substance
- Phosphorescence of the substance

   1.   Photochemical combination of H_2 and Cl_2

The equation for the reaction;

$H_2 + Cl_2 \rightarrow$ 2HCl
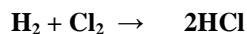
The quantum efficiency for the photochemical combination of hydrogen and chlorine is very high.

When exposed to light of wavelength 478 nm, the primary process in the photochemical reaction is the decomposition of chlorine,

$Cl_2 + \boldsymbol{hv} \rightarrow 2\ Cl\bullet$
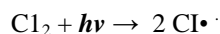
This is followed by the following secondary processes:

$Cl\bullet + H_2 \rightarrow HCl + H\bullet$

$H\bullet + Cl_2 \rightarrow HCl + Cl.\bullet$
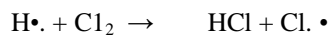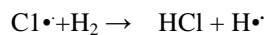
The reaction between Cl_2 and H_2 is exothermic and much fast. This results in the **propagation of chain reaction** with high quantum efficiency. The **chain-terminating** step is the recombination of chlorine atoms on the walls of the vessel to form chlorine molecule.

$Cl\bullet. + Cl\bullet \rightarrow Cl_2$
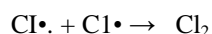
2. Photochemical combination of H_2 and Br_2

In this case too, the primary process is the dissociation of Br2 molecules by absorbing of light.

$Br_2 + hv \rightarrow 2Br\bullet$

Secondary steps;

$Br\bullet + H_2 \rightarrow HBr + H\bullet$ (endothermic and slow)

$Br\bullet + Br\bullet \rightarrow Br_2$

Other chain reactions

$H\bullet + Br_2 \rightarrow HBr + Br\bullet$

$H\bullet + HBr \rightarrow H_2 + Br\bullet$
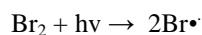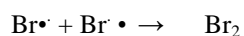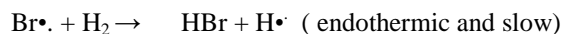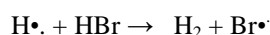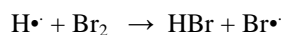
3. Photo decomposition of HI

$2HI \rightarrow H_2 + I_2$
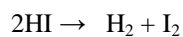
It takes place in the radiation of wave length between 2070 Å - 2820 Å. The quantum yield of the reaction is found to be closer to 2.0.

Primary process

$HI + hv \rightarrow H\bullet + I\bullet$.

Secondary process

$H\bullet + HI \rightarrow H_2 + I\bullet$.

$I\bullet + I\bullet \rightarrow I_2$
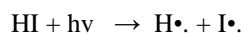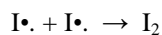
The quantum efficiency of photodecomposition of HI is 2. The number of molecules of absorbing substance, which undergo chemical transformation, directly and through secondary reactions per quantum of radiation absorbed has been called *quantum efficiency* of a photo chemical reaction.

4. Photolysis of ammonia

The Overall reaction is represented by the equation

$2NH_3 \rightarrow N_2 + 3H_2$
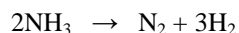
The reaction has the quantum yield less than 1

Initiation step;

$NH_3 + hv \rightarrow \bullet NH_2 + H\bullet$

Secondary steps;

$\bullet NH_2 + \bullet NH_2 \rightarrow N_2 + 2H_2$

$\bullet NH_2 + \bullet NH_2 \rightarrow N_2H_4$

$\bullet NH_2 + H\bullet \rightarrow NH_3$

$N_2H_4 + H\bullet \rightarrow \bullet NH_2 + NH_3$

$H\bullet + H\bullet \rightarrow H_2$
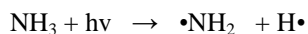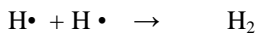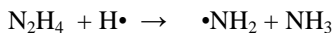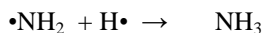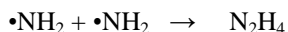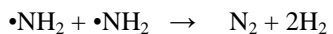
Above combination of steps explains the reduced quantum efficiency and its observed dependence on pressure of ammonia

5. Photo formation of ozone

Equation of reaction

$3O_2 \rightarrow 2O_3$
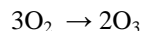
Oxygen absorbs strongly radiations in the range 2600A to 1800A which occurs in upper parts of atmosphere.

Primary step;

$O_2 + hv \rightarrow 2O\bullet$
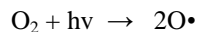
Dark or thermal reaction

$2O\bullet + 2O_2 \rightarrow 2O_3$
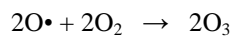
However in these regions, oxygen also exists as atoms and ozone molecules can react with oxygen atoms forming oxygen molecules and ozone molecules can also be photochemically converted to oxygen.

$O_3 + hv \rightarrow O_2 + O\bullet$
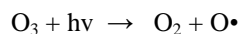
6. Photo excitation reactions

i. Photo decomposition of NOCl

The change occurs over a wide range of 3650A to 6400A with a quantum of efficiency of 2.

Mechanism;

$NOCl + hv \rightarrow NOCl^*$

$NOCl^* + NOCl \rightarrow 2NO + Cl_2$
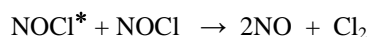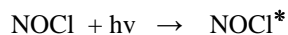
$NOCl^*$ - excited molecule

ii. 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.

$$Hg + hV \rightarrow Hg^*$$
$$Hr^* + H2 \rightarrow H2^* + Hg$$
$$H2^* \rightarrow 2H$$
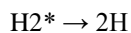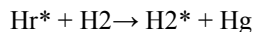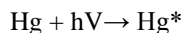
2. *Photosynthesis in plants*: During photosynthesis of carbohydrates in plants from CO_2 and H_2O, chlorophyll of plants acts as a photosensitizer. The energy of the light absorbed by the chlorophyll (due to the presence of conjugation in chlorophyll) is transformed to CO_2 and H_2O molecules, which then react to form glucose.

In the presence of light and chlorophyll ΔGo becomes negative; thereby the reaction proceeds and produces glucose. But in the absence of chlorophyll, the ΔGo for this reaction is +2875 kJ. Since ΔGo is positive, the above reaction is not possible.

$$6CO_2 + 6H_2O \xrightarrow{\text{hv, chlorophyll}} \underset{\text{carbohydrate}}{C_6H_{12}O_6 + 6O_2}$$
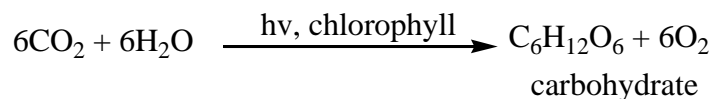
QUIZ

Look at the reaction sequence for the photolysis of acetaldehyde:

$$CH_3CHO + hv \rightarrow CH_3 + CHO \quad \begin{matrix}\text{Rate of}\\\text{photolysis}\end{matrix} = I_a \qquad \text{...(1)}$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO \qquad \text{...(2)}$$

$$CH_3CO \xrightarrow{k_3} CH_3 + CO \qquad \text{...(3)}$$

$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6 \qquad \text{...(4)}$$
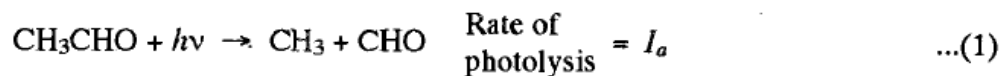
I_a is the absorbed light intensity and it represents the rate of photochemical excitation (as per Eq. (1)).

Using the above mechanism, derive expressions for the following:

i) $\dfrac{d\,[\,CH_3CO\,]}{dt}$ —   ii) $\dfrac{d\,[\,CH_3\,]}{dt}$

(Hints: CH_3CO and CH_3 are active species. CH_3CO is formed as per Eq. (2) and consumed as per Eq. (3). CH_3 is formed as per Eqs. (1) artd (3), and used up as per Eqs. (2) and (4). The answers for (i) and (ii) are to be arrived at using Eqs. 19.21 and 19.22 as models. Note that as per Eq. (4), two CH_3 radicals are consumed for every molecule of ethane formed).

iii)   Derive the combined expression for $\dfrac{d\,[\,CH_3CO\,]}{dt} + \dfrac{d\,[\,CH_3\,]}{dt}$

(Hint: Add up the expressions you have got as answers for (i) and (ii)).

iv)   Find the relationship between $[\,CH_3\,]$ and I_a.

(Hint: Rearrange the answer for (iii)).

v)   State the relationship between $\dfrac{d\,[\,CO\,]}{dt}$ and $[\,CH_3CO\,]$.

(Hint: Use Eq. (3)).

vi)   Find the relationship between the rate of formation of CO and the absorbed light intensity.

(Hints: First combine answers for (v) and (i). Then use the answer for (iv)).

i) $\dfrac{d\,[\,CH_3CO\,]}{dt} = 0 = k_2\,[\,CH_3\,]\,[\,CH_3CHO\,] - k_3\,[\,CH_3CO\,]$

ii) $\dfrac{d\,[\,CH_3\,]}{dt} = 0 = I_a - k_2\,[\,CH_3\,]\,[\,CH_3CHO\,] + k_3\,[\,CH_3CO\,] - 2k_4\,[\,CH_3\,]^2$

iii) $\dfrac{d\,[\,CH_3CO\,]}{dt} + \dfrac{d\,[\,CH_3\,]}{dt} = 0 = I_a - 2k_4\,[\,CH_3\,]^2$

iv) $[\,CH_3\,] = \left(\dfrac{I_a}{2k_4}\right)^{\!1/2}$

v) $\dfrac{d\,[\,CO\,]}{dt} = k_3\,[\,CH_3CO\,]$

vi) $\dfrac{d\,[\,CO\,]}{dt} = k_2\,[\,CH_3\,]\,[\,CH_3CHO\,]$

$= k_2 \left(\dfrac{I_a}{2k_4}\right)^{\!1/2} [\,CH_3CHO\,]$

ATMOSPHERIC CHEMISTRY AND PHOTOCHEMICAL REACTIONS

Atmospheric chemistry refers to chemical processes that occur in the atmosphere. Atmospheric chemistry occurs in the gas phase where molecules are relatively far apart. A second major aspect of atmospheric chemistry is the occurrence of **photochemical reactions**.

- Initiated when a photon of ultraviolet radiation is absorbed by a molecule
- The energy of a photon, E, is given by $E = h\nu$ where h is Planck's constant and ν is the frequency of the radiation.
- Electromagnetic radiation of a sufficiently short wavelength can cause chemical bonds to break in molecules
- This can lead to the formation of reactive species that can participate in reaction sequences called **chain reactions**.

Photochemical and Chain Reactions

Atmospheric oxygen and nitrogen

N_2 and O_2 are by far the most abundant gases in the atmosphere.

Crucial importance of the stratospheric layer of ozone, O_3

Oxygen reacts with atmospheric chemical species.

- Through action of intermediate species, particularly **hydroxyl radical**, HO•
- SO_2 is converted to H_2SO_4
- CO is converted to CO_2

Atmospheric oxygen comes from photosynthesis

$$CO_2 + H_2O + h\nu \rightarrow \{CH_2O\} + O_2$$
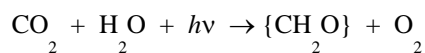
where $\{CH_2O\}$ is a generic formula representing biomass

Nitrogen in the atmosphere

Atmospheric N_2 is very unreactive

Most important reaction of N-containing species in the atmosphere

$$NO_2 + h\nu \rightarrow NO + O$$
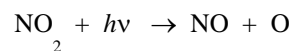
Reactive O atom initiates many tropospheric photochemical reactions

Nitrogen Oxides in the Atmosphere

Nitrous oxide (N_2O), colorless, odorless, nitric oxide (NO), and pungent-smelling, red-brown nitrogen dioxide (NO_2) occur in the atmosphere.

Nitrous oxide generated by bacteria

In the stratosphere: $N_2O + h\nu \rightarrow N_2 + O$
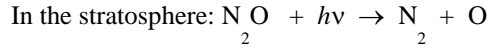
Both NO and NO_2, collectively designated as NO_x, are produced from natural sources, such as lightning and biological processes, and from pollutant sources.

Pollutant concentrations can become too high locally and regionally.

In the internal combustion engine,

$N_2 + O_2 \rightarrow 2NO$
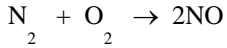
Combustion of fuels that contain organically bound nitrogen also produces NO.

Atmospheric chemical reactions convert some of the NO emitted to NO_2.

NO_2 in the Atmosphere

Electromagnetic radiation below 398 nm causes

$NO_2 + h\nu \rightarrow NO + O$
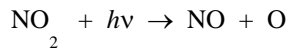
- Produces highly reactive O atoms
- O atoms can participate in a series of chain reactions through which NO is converted back to NO_2, which can undergo photodissociation again to start the whole cycle over. NO_2 more toxic than NO
- Exposure to 100-500 ppm of NO_2 causes a lung condition called *bronchiolitis fibrosa obliterans*
- Exposed plants may suffer decreased photosynthesis, leaf spotting, and breakdown of plant tissue. Reducing release of NO from combustion sources
- Limiting excess air so that there is not enough excess oxygen to produce NO
- Exhaust catalytic converters reduce NO_x emissions from automobile exhausts.

Formation and removal of NO_3 from atmosphere

NO_3 is formed by the reaction of ozone and nitrogen dioxide, but is present in significant concentrations only during the night, since it is quickly photolyzed by sunlight yielding either NO_2 or NO.

$NO_2 + O_3 \rightarrow NO_3 + O_2$
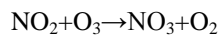
During the day time, NO_3 is destroyed primarily by rapid photolysis, having a lifetime of only 5 s for overhead sun and clear sky conditions

$NO_3 + h\nu \rightarrow NO + O_2$

$NO_3 + h\nu \rightarrow NO_2 + O(^3P)$
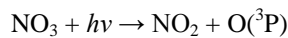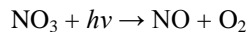
Formation and depletion of ozone layer

Stratospheric Ozone and Atomic Oxygen Production, Cycling, and Loss

$O_2 + \text{hard UV} \rightarrow O + O$ Production

$2(O + O_2 + N_2 \rightarrow O_3 + N_2)$

Cycling

$O_3 + UV \rightarrow O_2 + O$
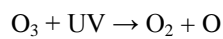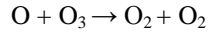
$O + O_3 \rightarrow O_2 + O_2$ Loss

Net: UV $\rightarrow$ higher T

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$
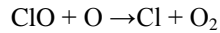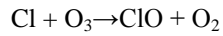
The Stratospheric Chlorine Catalytic Cycles That Destroy Ozone

Generation of OH in the atmosphere

OH is formed in the atmosphere when ultraviolet light (UV) from the sun strikes ozone in the presence of water vapour (H_2O). The initial reaction involves the photolysis of O_3 by solar radiation.
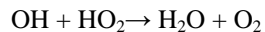
O_3 + UV light --> O_2 + O
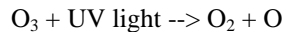
Then the oxygen atom (O) reacts with water vapour to produce two OH radicals.

O + H_2O --> 2 OH
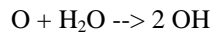
The key production reactions for OH in the stratosphere and mesosphere are

$H_2O + O(1D) \rightarrow 2OH$

$H_2O + h\nu \rightarrow OH + H$
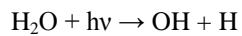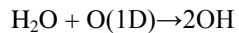
While the loss is determined mainly through

$OH + HO_2 \rightarrow H_2O + O_2$

Chlorofluorocarbons, or CFC's.

CFC's are chlorine and fluorine containing hydrocarbons that were used as refrigerants, electronic cleaners, etc. A common CFC is Freon 12, CF_2Cl_2 (dichlorodifluoromethane). In the atmosphere CF2Cl2undergoes the following reaction;

$CCl_2F_2 + h\nu \rightarrow \bullet CCl_2F_2 + Cl\bullet$ (Stratosphere)

Species with unpaired electrons such as Cl• are very reactive and are called **free radicals**.

Reaction of Cl• with stratospheric ozone and the O atoms required for ozone formation

$\qquad Cl\bullet + O_3 \rightarrow O_2 + ClO\bullet$

$\qquad ClO\bullet + O \rightarrow O_2 + Cl\bullet$

Net reaction: $\qquad O_3 + O \rightarrow O_2 + O_2$
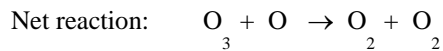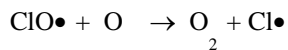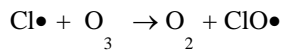
One Cl atom can bring about the destruction of as many as 10,000 ozone molecules!

Photochemical Smog

Smog is a mixture of smoke and fog. It forms when photons of sunlight hit molecules of different kinds of pollutants in the atmosphere. The photons make chemical reactions happen. The pollution molecules turn into other kinds of nasty chemicals. That mixture of bad chemicals is called photochemical smog.

The chemicals in photochemical smog include nitrogen oxides, Volatile Organic Compounds (VOCs), ozone, and PAN (peroxyacytyl nitrate).

- Nitrogen oxides mostly come from the engines of cars and trucks.

- VOCs are given off by paint, gasoline, and pesticides.
- Ozone is a form of oxygen that is harmful.
- PAN is a type of pollution that is made by chemical reactions between other kinds of pollution.

Smog smells bad and makes it hard for people to breath. It can also damage materials. Smog is a very harmful kind of air pollution.

Formation of Photochemical Smog

Photochemical smog is formed due to photochemical oxidation of hydrocarbons and nitrogen oxides.

Photochemical smog reactions

Step 1: From car engines, nitrogen is burned or oxidized

$$N_2 + O_2 \rightarrow 2NO \ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Step 2: In this reaction, Nitric Oxide (NO) emitted from various combustion processes combines with oxygen in the atmosphere to form nitrogen dioxide (NO_2), which has a characteristic brown color that should be familiar to anyone who has lived in a smoggy region.

$$2NO + O_2 \rightarrow 2NO_2 \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

Step 3: u.v. rays of sunlight strike the NO_2, it breaks off a single oxygen radical (O) that triggers many subsequent reactions of photochemical smog.

$$\textbf{NO}_2 + u.v. \dashrightarrow \textbf{O} + NO$$
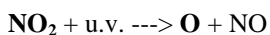
Step 4: In this second reaction, the single oxygen radical helps form ozone (O_3). A variety of molecules can act as catalysts for this reaction.

$$\textbf{O} + O_2 \dashrightarrow \textbf{O}_3$$
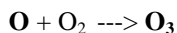
Step 5: scavenging reaction: It happens normally in the evening. Because it converts ozone to O_2, the net result is a drop in the ozone concentration in the evenings.

$$\textbf{O}_3 + NO \dashrightarrow \textbf{O}_2 + NO_2$$
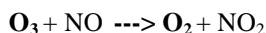
Step 6: When hydrocarbons (represented as RC) combined with the oxygen free radical, it forms RCO, which represents a variety of aldehydes and ketones. Some of these constiutents can combine with oxygen to form peroxide readicals (RCO_3)**.**

$$\textbf{RC} + O \dashrightarrow \textbf{RCO} + O_2 \dashrightarrow \textbf{RCO}_3$$

Step 7: $\textbf{O}_2 + RCO_3 \dashrightarrow \textbf{O}_3 + RCO_2$

This reaction it enhances the formation of ozone.

Step 8: $\textbf{NO} + RCO_3 \dashrightarrow \textbf{NO}_2 + RCO_2$

The peroxide radicals enhance the formation of nitrogen dioxide, which will go on to form more ozone.

If nitric oxide is also present in the air, reaction takes place as follows –

$NO + O_2 \rightarrow NO_2 + O_2$
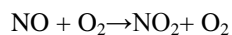
If ozone is present in excess, then

$2 NO_2 + O3 \rightarrow N_2O_5 + O_2$
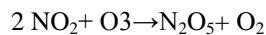
If water vapour is present, then $N_2O_5 + H_2O \rightarrow 2 HNO_3$

Thus nitric acid may be formed.

Summary of photochemical smog formation in urban airsheds

1) Nitrogen oxide (**NO**) generates oxygen atoms (via **NO$_2$** photolysis)

2) Oxygen atoms form hydroxyl radicals, **OH** (via **O$_3$** photolysis)

3) Hydrocarbons generate hydrocarbon radicals (**Ṙ**) (via H-abstraction by **OH**)

4) Hydrocarbon radicals form hydrocarbon peroxyl radicals (**RȮ$_2$**)

5) Hydrocarbon peroxy radicals form aldehydes (via **RȮ** radicals)

6) Aldehydes form aldehyde peroxides, **RC(O)Ȯ$_2$** (via H-abstraction by **OH** and addition of **O$_2$**)

7) Aldehyde peroxides (+ **NO$_2$**) form peroxyacylnitrates (PAN)

8) Aldehydes form aerosols

Effect of photochemical smog

The effects of photochemical smog on human beings, plants and materials have been studied where it usually occurs. Additional information has also been obtained by stimulating photochemical smog in environmental chambers. Following are the important effects of photochemical smog –

i.   Eye irritation: Probably, the compounds responsible for eye irritation are formaldehyde, acrolein, PAN and peroxy benzoyl nitrate.

ii.   *Vegetation damage*: The effects observed are silvering and bronzing of underside of leaves followed by collapse of cells, and necrosis. Growth retardation has also been reported. The three principal phytoxicants are ozone, nitrogen dioxide and PAN. This has resulted in economic loss.

iii. Visibility reduction: This is perhaps the most commonly observed effect of photochemical smog. The aerosol particles causing the photochemical smog contain compounds of carbon, oxygen, hydrogen, nitrogen, sulphur, and halides.

iv.   Cracking of rubber: This is primarily due to the ozone constituents of photochemical smog. An important economic effect of smog is deterioration of the side walls of automobile tyres. To overcome this problem, an antiozonant is being used.

v.   Fading of dyes:This is another important economic effect of photochemical smog.

Organic Photochemistry

Types of Excitation

When an electron is excited, it usually goes into the **lowest available vacant orbital**.

For typical organic molecules, there are 4 possible type of electron excitation:

1) σ → σ*
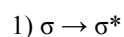
Common for alkanes or things that do not have lone pairs or π bonds.

2) n → σ*
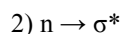
Common for amines, alcohols, ethers or things that have lone pairs but not π bonds.

3) π → π*
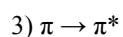
Common for alkenes, aldehydes, carboxylic acids, esters, or things that have π bonds.

4) $n \rightarrow \pi$ *

Common for aldehydes, ketones, esters, things that have lone pairs and π bonds.

Almost all organic photochemistry is $\pi \rightarrow \pi$* or $n \rightarrow \pi$ *

Most common examples are Alkenes undergoing $\pi \rightarrow \pi$*, and carbonyl compounds undergoing $\pi \rightarrow \pi$* or $n \rightarrow \pi$ *

Organic photochemical reactions

There are 3 common types of **photochemical** reaction:

1) α Cleavage (Norrish type I reaction)

2) Hydrogen Abstraction (by Norrish type II cleavage)

3) Cyclo addition (Paterno Buchi reaction)

Other reactions

- reduction

- cis-trans isomerisation

Norrish reaction

The Norrish reaction in organic chemistry describes the photochemical reactions taking place with ketones and aldehydes. This type of reaction is subdivided in Norrish type I reactions and Norrish type II reactions. The reaction is named after Ronald George Wreyford Norrish.

Type I (α Cleavage)

The Norrish type I reaction is the photochemical cleavage or homolysis of aldehydes and ketones into two free radical intermediates. The carbonyl group accepts a photon and is excited to a photochemical singlet state. Through intersystem crossing the triplet state can be obtained.

Carbonyl compounds when irradiated can undergo cleavage of the Carbonyl C - α bond.
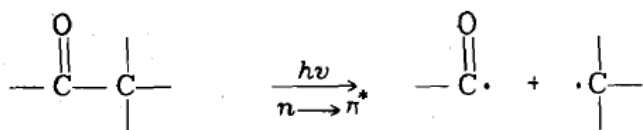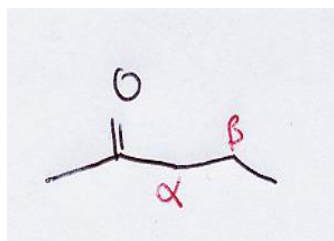
The size and nature of these fragments depends upon the stability of the generated radicals; for instance, the cleavage of 2-butanone largely yields ethyl radicals in favor of less stable methyl radicals.
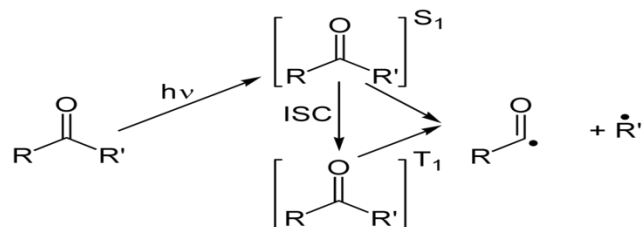
Several secondary reaction modes are open to these fragments depending on the exact molecular structure.

- 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. 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.
- 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.
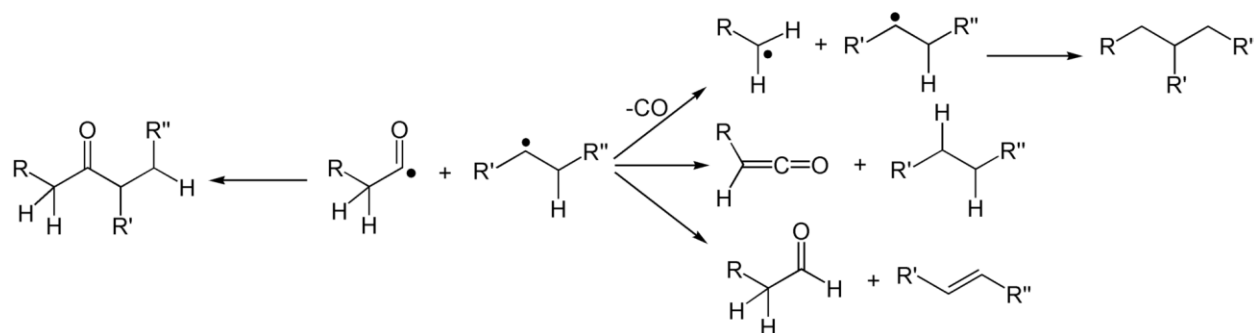
The synthetic utility of this reaction type is limited, for instance it often is a side reaction in the Paternò–Büchi reaction. One organic synthesis based on this reaction is that of bicyclohexylidene.

More examples

Photolysis of Propanone (Acetone)

The term photolysis is used when light absorption of molecules leads to cleavage of bonds. Absorption of light by propanone results in the formation of an excited state which has sufficient energy to undergo cleavage of α- C-C bond (the weakest bond in molecule). The nature of products is dependent on temperature and physical state.

At high temperature;

- carbon monoxide and ethane are formed.

The reaction path is shown as :

$$CH_3COCH_3 \xrightarrow[(i)]{h\nu} [CH_3COCH_3]^* \xrightarrow{(ii)} \dot{C}H_3 + CH_3\dot{C}=O$$

$$CH_3\dot{C}=O \longrightarrow \dot{C}H_3 + CO$$

$$2\dot{C}H_3 \longrightarrow C_2H_6$$
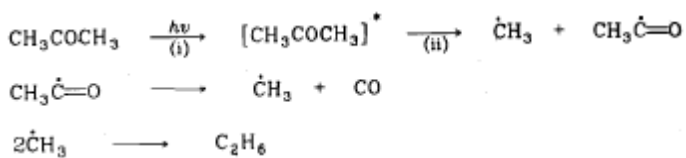
At room temperature;

Photolysis of propanone gives **2,3-** butanedione (biacetyl), ethanol (acetaldehyde), methane and 2,5 hexanedione.
The reaction path is shown as:

$$CH_3COCH_3 \xrightarrow{h\nu} [CH_3COCH_3]^* \longrightarrow CH_3\dot{C}=O + \dot{C}H_3$$

$$2CH_3\dot{C}=O \longrightarrow \underset{\substack{\text{2,3-butanedione}\\\text{(biacetyl)}}}{CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_3}$$

$$CH_3\dot{C}=O + CH_3COCH_3 \longrightarrow \underset{\text{ethanal}}{CH_3\overset{H}{\underset{|}{C}}=O} + \dot{C}H_2COCH_3$$

$$\dot{C}H_3 + CH_3COCH_3 \longrightarrow \underset{\text{methane}}{CH_4} + \dot{C}H_2COCH_3$$

$$2\dot{C}H_2COCH_3 \longrightarrow \underset{\text{2,5 -hexanedione}}{CH_3COCH_2CH_2COCH_3}$$
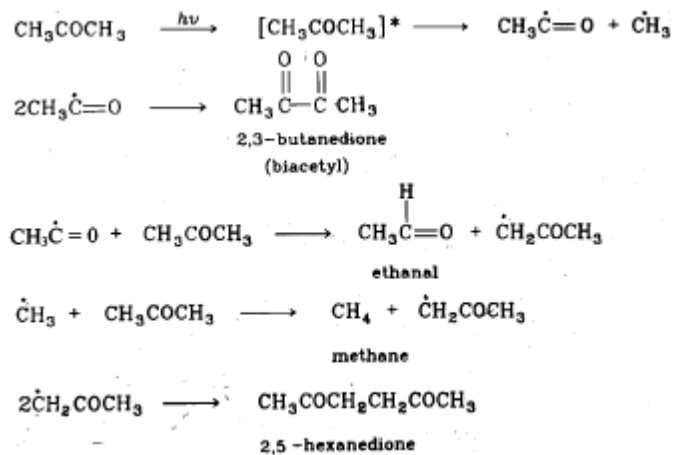
Physical state

a) **In gas phase;**
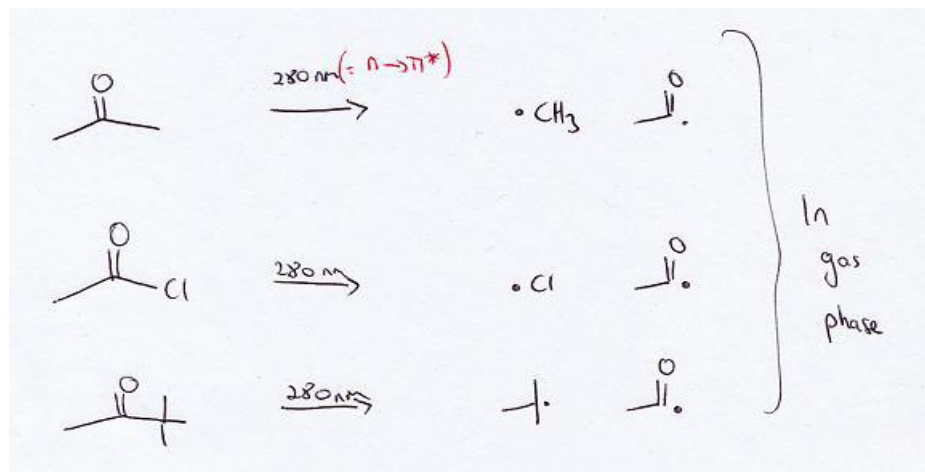
In the gas phase the radicals are generated and detected (longer lifetime) but undergo further reactions to give other **products**.

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α - cleavage

- CO
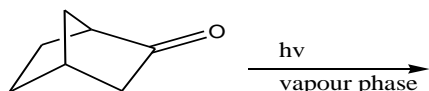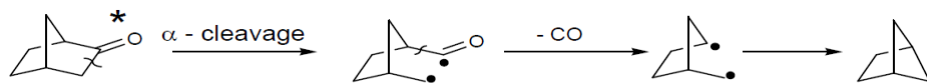
b) In solution phase

In solution the radicals undergo further reactions to give **products.**
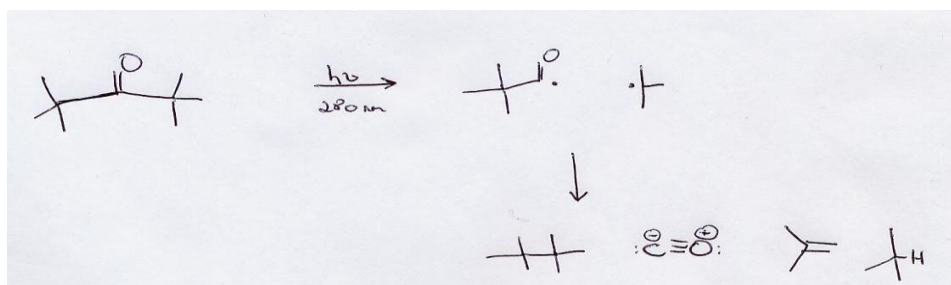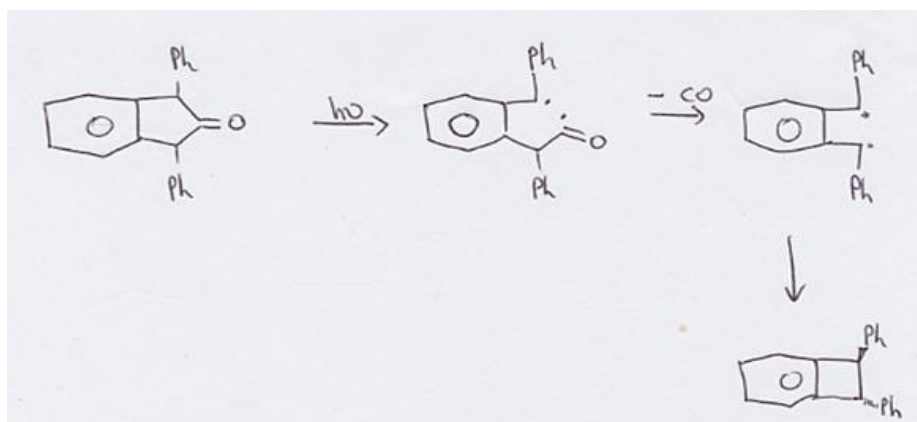
Example

Reaction Mechanism,

- the **cleavage** is a two-step process.

The radicals can undergo further reactions to give **products**.

Example 2

then

and

Disproportionation

Dimerization

Example 3

hν
EtOH

and
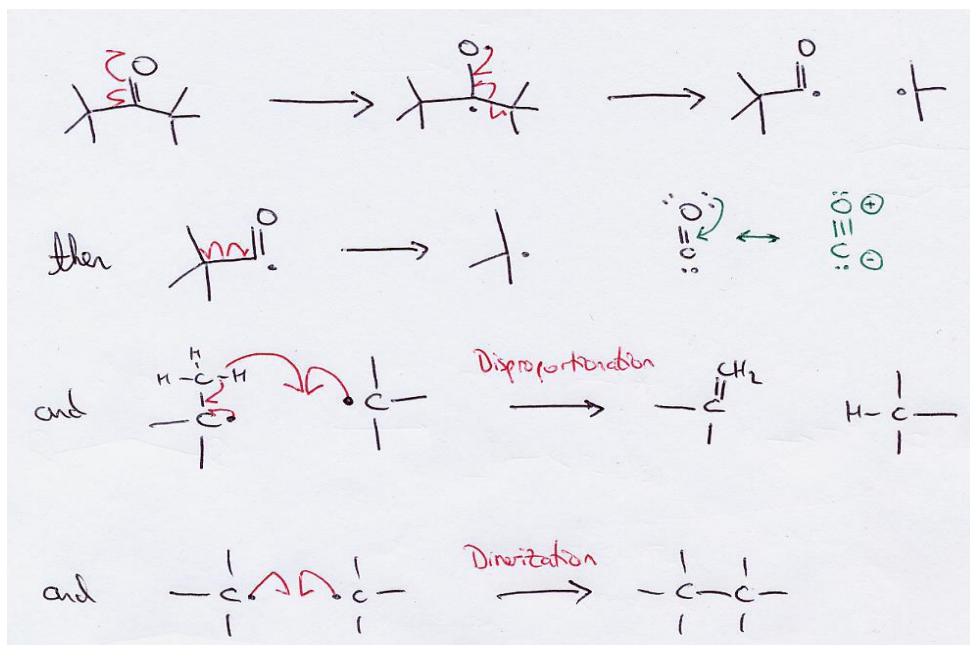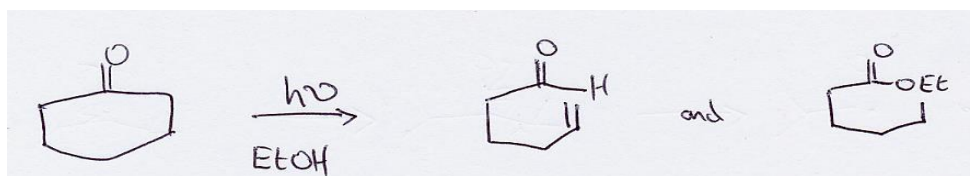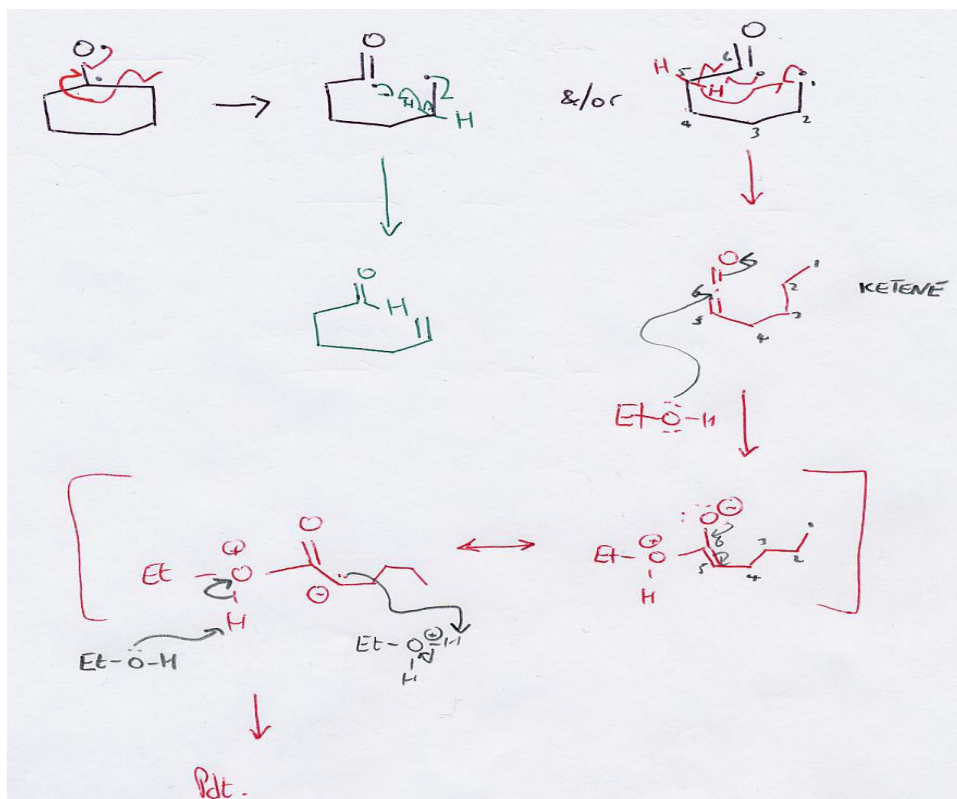
Mechanism

SAQ 4

Give the mechanistic paths in the following reactions.

a) [cyclobutanone structure] $\xrightarrow{h\nu}$ $CH_2{=}C{=}O$ + $CH_2{=}CH_2$

b) $C_6H_5CCH_2CH_2CH_3$ (with C=O) $\longrightarrow$ C_6H_5 [ring structure with OH] + $C_6H_5CC_6H_5$ (with C=O) + $CH_2{=}CH_2$

diphenylmethanone
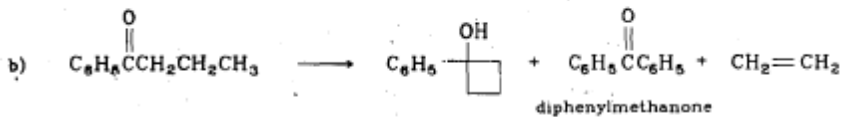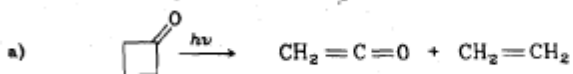
Type II (Hydrogen Abstraction)

A Norrish type II reaction is the photochemical intramolecular abstraction of a γ-hydrogen (a hydrogen atom three carbon positions removed from the carbonyl group) by the excited carbonyl compound to produce a 1,4-biradical as a primary photoproduct. Norrish first reported the reaction in 1937.

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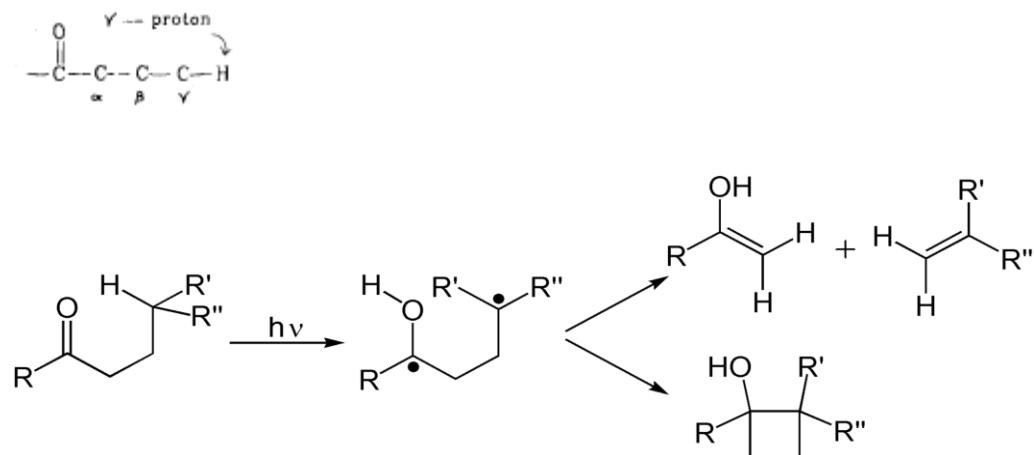
Secondary reactions that occur are fragmentation to form an enol and an alkene, or intramolecular recombination of the two radicals to a substituted cyclobutane (the **Norrish–Yang reaction**)

Example

a) Photolysis of 2-Hexanone

Photolysis of 2-hexanone gives propene and propanone as shown below:
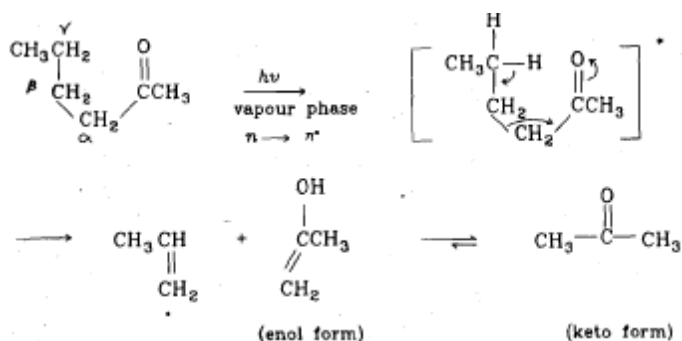
The hydrogen attached to γ-carbon atom (which gets transferred later), oxygen and four carbon atoms **constitute** a six-membered transition state. Such a transition state is considered much favourable for bond making and breaking to occur. Elimination of CO (Norrish type 1 process) could also take place but to a lesser extend. Propanone, the product of photo cleavage of 2-hexanone can undergo **Norrish type 1 reaction**. Thus photolysis of 2-hexanone gives complex mixture of products consisting of propene, propanone, ethane and CO.

b) Photolysis of 2-pentanone
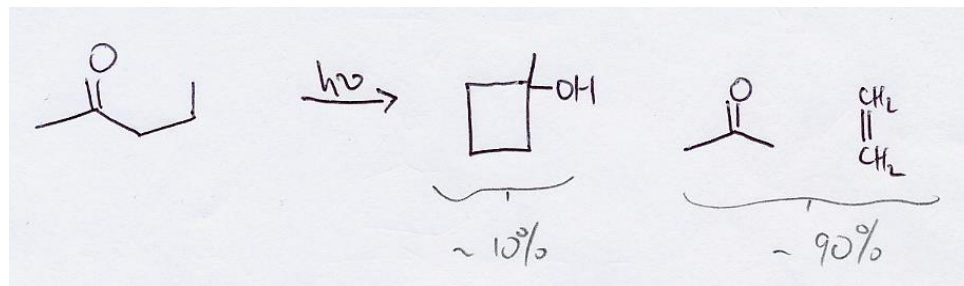
Mechanism

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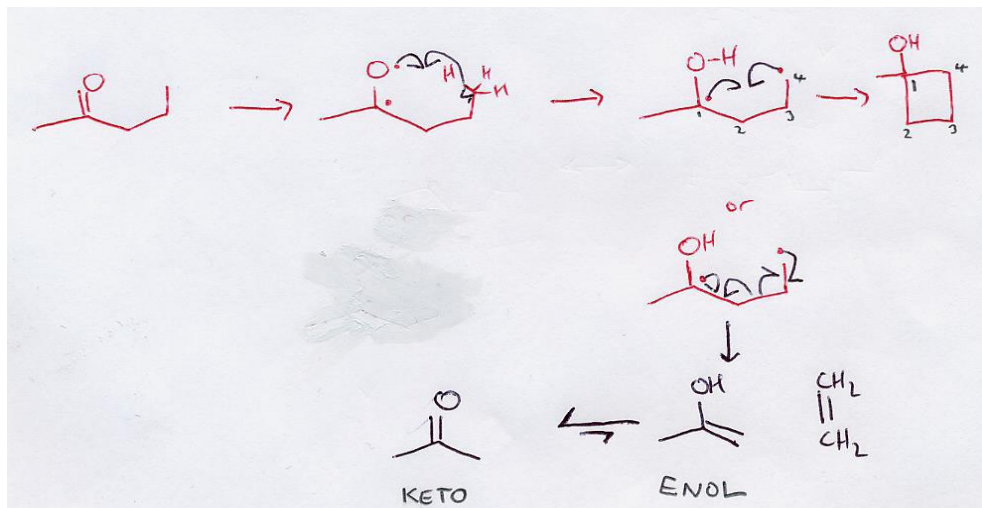
3) Cycloaddition

The allowed concerted thermal (4+2) cycloaddition (Diels Alder), and the thermally forbidden concerted (2+2) cycloaddition, and *the photochemically allowed (2+2) cycloaddition*. Carbonyls will undergo cycloadditions with alkenes under photochemical excitation (of the carbonyl).

---

a) Paternò–Büchi reaction

The **Paternò–Büchi reaction**, named after Emanuele Paternò and George Büchi who established its basic utility and form, is a photochemical reaction that forms four-membered oxetane rings from a carbonyl and an alkene.
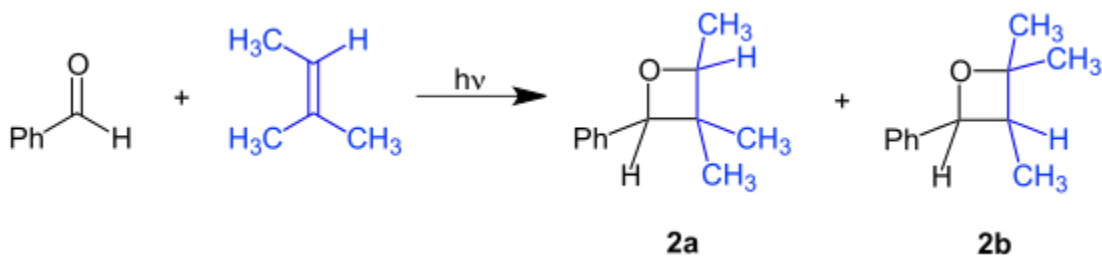
The photochemical [2+2] cyclo addition of a carbonyl with an olefin to give an oxetane.

Mechanism of the Paterno-Buechi Reaction
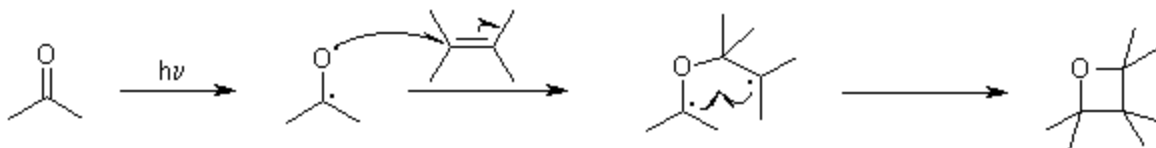
Heterocycles are formed when one of the multiple bonds includes a heteroatom,

Example
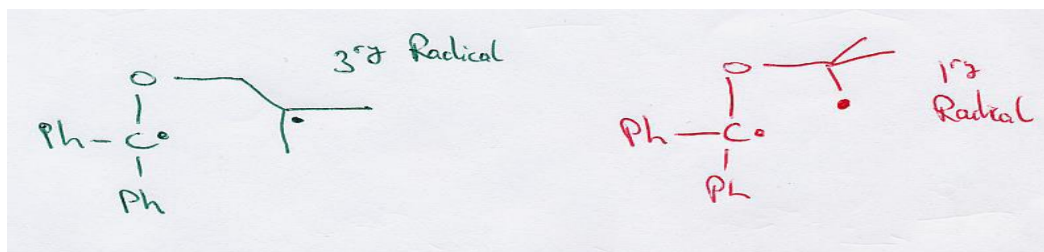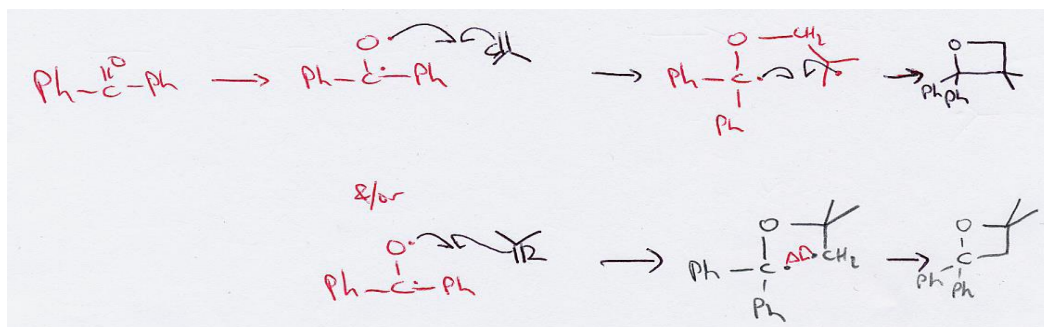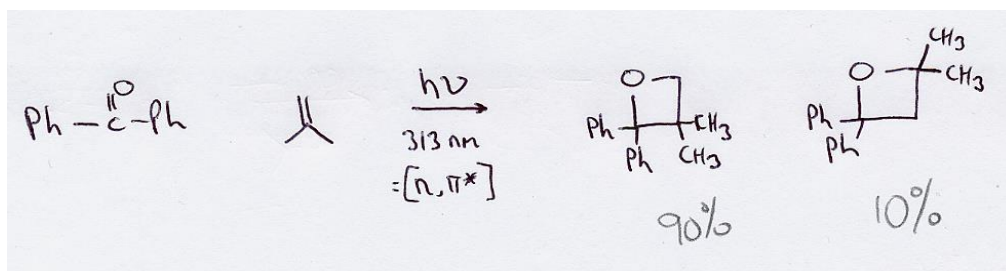
**An intramolecular cyclo addition**

Example:
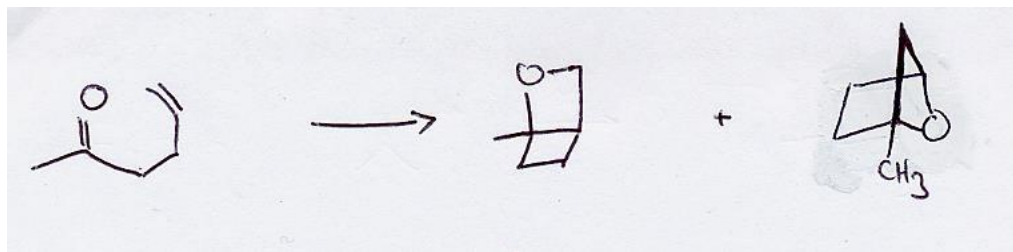
Mechanim
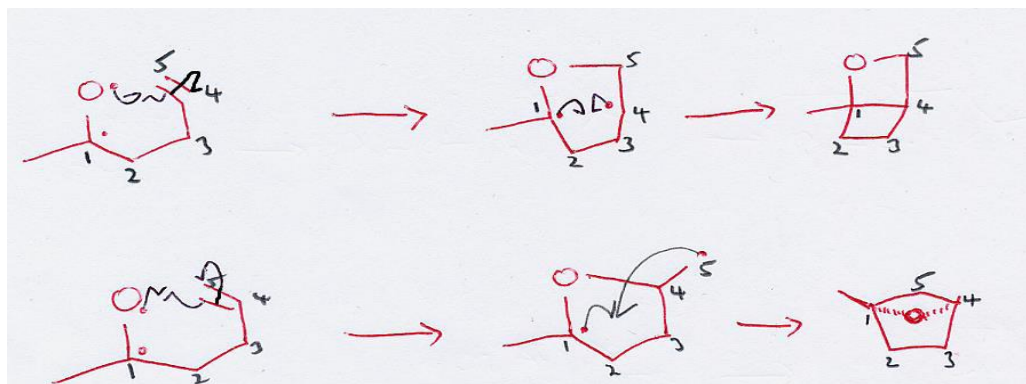
Cyclo addition in alkenes

Photochemical cyclo addition of olefines to give four-membered rings is a synthetically useful process. One familiar example is the dimerisation of cyclo pentenone on irradiation with light in dichloromethane solution to give a mixture of "head to head" and "head to **tail**" dimers. These dimers may be formed via an **excimer** (excited dimer) derived from the **(n-d)** cyclo pentenone and a molecule of ground state cyclo pentene.
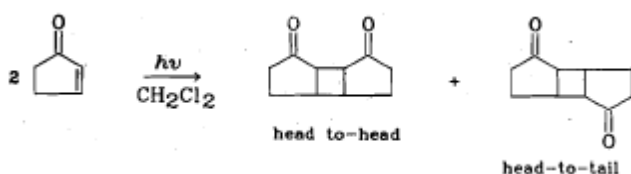
The photo cycloaddition could also proceed in an intramolecular fashion. For example,

1.3 − cycloctadiene   ·   bicyclo[4.2.0] oct−7 ene

norbornadiene $\xrightarrow{h\upsilon}$ quadricyclene
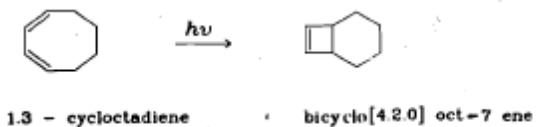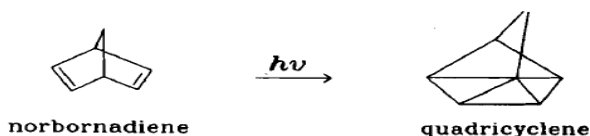
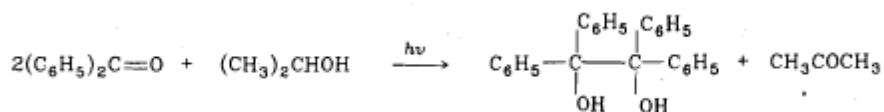## Photo isomerisation of Cis- and Trans-l,2-diphenylethene (Stilbene)

Geometrical isomerisation is a typical photoreaction of many olefinic compounds. The photochemical cis-trans isomerisation of 1, 2-diphenylethenes (stilbenes) has been studied in great detail. Irradiation of a solution of trans- 1, 2-diphenylethene in hexane with UV light results in the formation of the cis-isomer. After sometime the cis-trans ratio becomes constant and does not change as the irradiation is continued. This condition is called a Photo stationary state (the rates of formation and disappearance of each of the transient molecular entities formed are equal) and is also reached on irradiation of the cis-isomer. It has been observed that the equilibrium favours the formation of the cis-isomer.

trans −1,2− diphenylethene
λ_{max} (ε) = 295mm (16300)

cis − 1,2 − diphenylethene
276mm (2280)
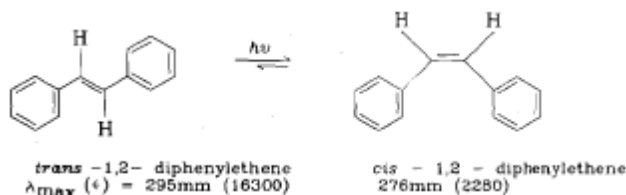
The trans isomer is more stable as cis-1, 2 –diphenyl ethene is distorted from planarity due to the non-bonded interaction between the ortho hydrogens in the benzene rings. Thermal equilibrium would favour the conversion of cis-1, 2- diphenyl ethene to its trans- isomer.

## Photoreductive Dimerisation of Diphenylmethanone (Benzophenone)

This reaction also occurs when a solution of diphenylmethanone in an alcoholic solvent (preferably 2-propanol) is exposed to sunlight. It is known as the photo reductive dimerization.

$$2(C_6H_5)_2C{=}O \ + \ (CH_3)_2CHOH \ \xrightarrow{h\upsilon} \ C_6H_5{-}\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{C}}{-}\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{C}}{-}C_6H_5 \ + \ CH_3COCH_3$$

# APPLICATIONS OF PHOTOCHEMICAL REACTIONS

Photosynthesis

Photosynthesis is a complex process in which carbon dioxide is reduced to give simple sugars and sugar derivatives. This is catalysed by the green pigment chlorophyll and various enzymes. Many other cellular constituents are also involved. Sunlight is absorbed and acts as the source of energy :

$$nCO_2 \ + \ nH_2O \ \xrightarrow[chlorophyll]{h\upsilon} \ (CH_2O)_n \ + \ O_2$$
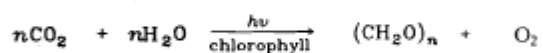
Absorption of sunlight is usually shown to proceed in two stages in which activation of chlorophyll by sunlight appears to provide the energy needed. In the first step, water is oxidized to oxygen and NADP+ (nicotinamide adenine dinucleotide phosphate) is reduced to NADPH :

$$NADP^+ + H_2O \xrightarrow[chlorophyll]{h\upsilon} NADPH + 1/2O_2 + H^+$$

In the second step, ADP (adenosine diphosphate) is converted to ATP (adenosine triphosphate) in the photosynthetic phosphorylation :

$$ADP + H_3PO_4 \xrightarrow[chlorophyll]{h\upsilon} ATP + H_2O$$
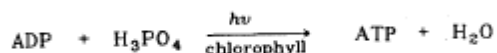
It is believed that NADPH and ATP store in them the light energy and provide **it** to convert carbon dioxide to sugars.

Formation of vitamin D2.

Irradiation of the steroid ergosterol with light leads to cis-trachysterol (pre vitamin D2) by a ring opening process.

ergosterol   *cis*-trachysterol   vitamin D₂
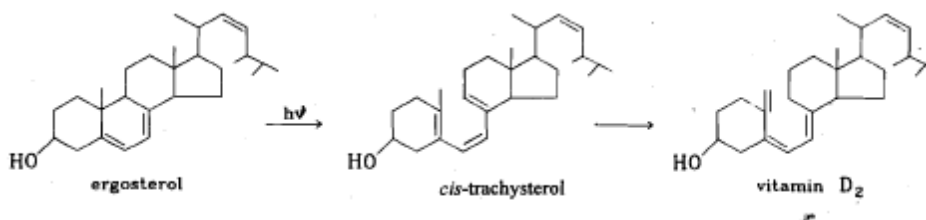
3. *Cis-Trans Isomerization* in the chemistry of vision

e.g., all-*trans* retinal can be converted to 11-*cis* retinal.

The photochemical cis-trans isomerisation **occurs** in the chemistry of vision. Cis-retinal combines with opsin (a protein) in the dark to give rhodopsin (a light sensitive compound).This compound is present in rods of the retina in the eye. It absorbs light at 500 nm and breaks down to opsin and trans-retinal. Tbe isomerisation of cis-to trans-retinal is accompanied by configurational change which excites the nerve cell. The trans-isomer is converted to cis-retinal by an enzyme and the cycle is repeated.

ALL-TRANS RETINAL

II-CIS RETINAL
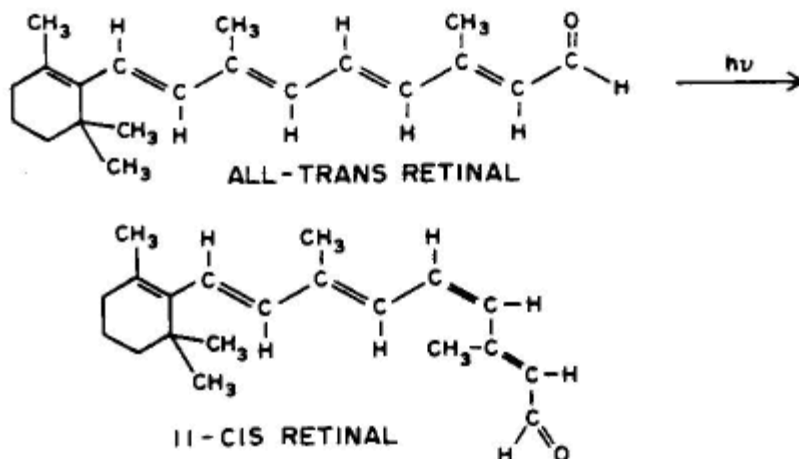
4. The destructive effects of uv radiation

This is due to changes in the DNA of cells by photochemical

a) Linear addition to an unsaturated molecule,

e.g., the pyrimidine base, thymne, in DNA can combine with the amino acid residue, cysteine, in proteins. This is a model for the photochemical crosslinking of DNA and proteins by UV radiation.

THYMINE   CYSTEINE

5-S-CYSTEINYL-6-HYDROTHYMINE
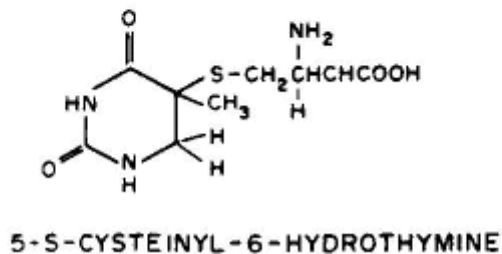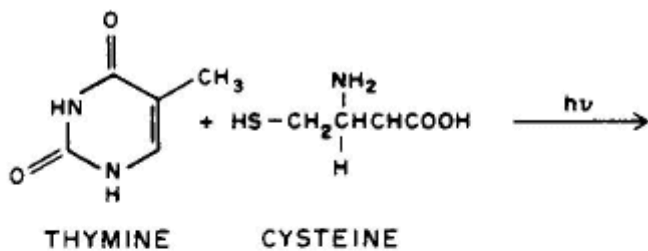
b. *Cycloaddition of unsaturated molecules,*

e.g., two thymines can react to form a ring product, the thymine dimer, an important class of products formed in DNA by UV radiation

THYMINE   THYMINE DIMER
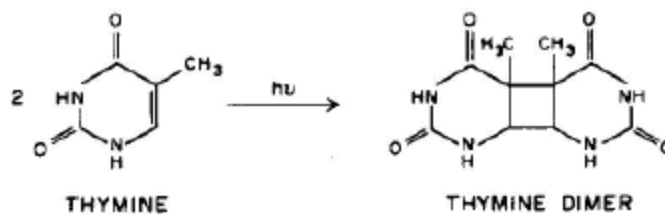
5. Conservation of solar energy by Photocyclisation reaction.

Example

Photoconversion of norbornadiene to quadricyclene.


norbornadiene   quadricyclene
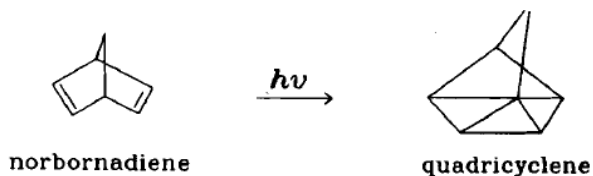
Different norbornadiene derivatives and analogues have been tried to achieve the storage of solar energy. In general, a molecule **A** absorbs sunlight and through its electronically excited state is converted to another molecule B. The ground state energy of B is greater than of **A.** The difference of energy *(H)* is stored in B. This is released when B is converted to **A** via a transition state T
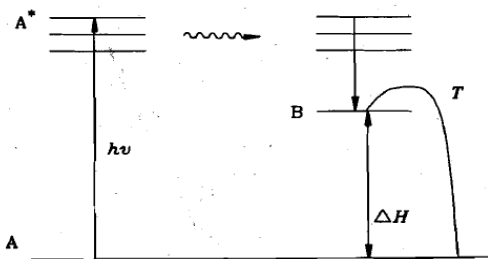

6. *Photorearrangement*, e.g., 7-dehydrocholesterol can be converted to vitamin D_3.

Vitamin- **D3** is formed **from** 7-dehydro cholesterol. Milk and other food are irradiated with light to increase the vitamin D content.
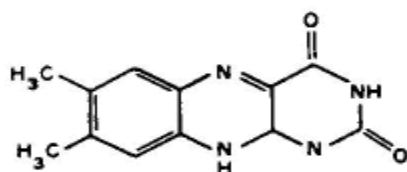
7-DEHYDROCHOLESTEROL

VITAMIN D₃
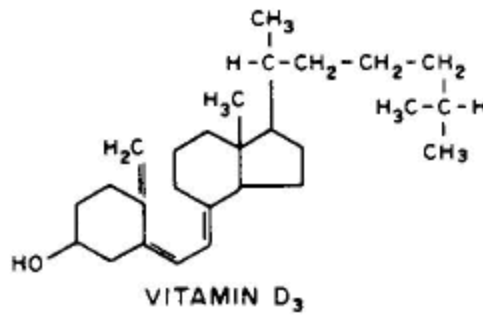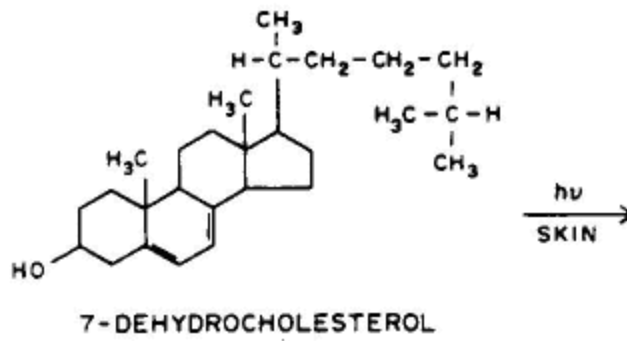
7. *Photohydration*, e.g., uracil can add a molecule of water to it 5-6 double bond when UV irradiated.

URACIL   6-HYDROXY-5-HYDROURACIL
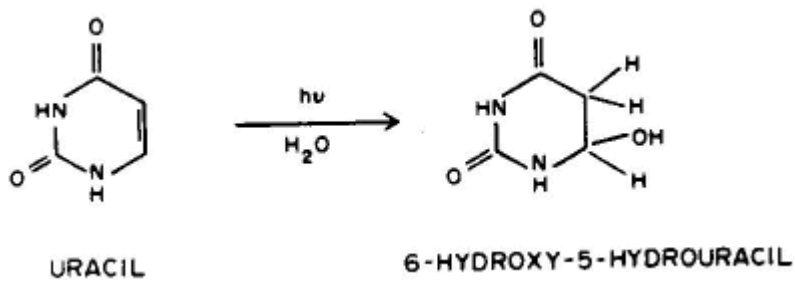
8. *Photofragmentation*, e.g., the side chain of riboflavin can split off to form lumiflavin.

47
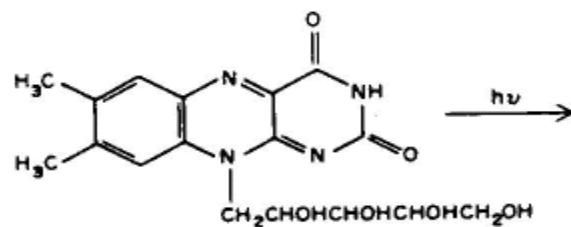
RIBOFLAVIN

LUMIFLAVIN

$$+ \; CH_3\overset{O}{\overset{||}{C}}CHOHCHOHCH_2OH$$

9. *Photooxidation*, e.g., the ring structure of cholesterol can add a peroxy group.
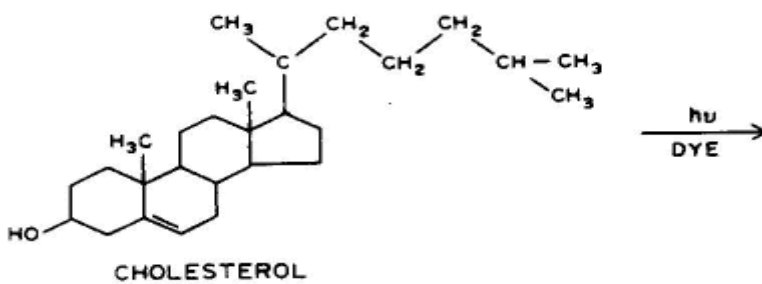
CHOLESTEROL
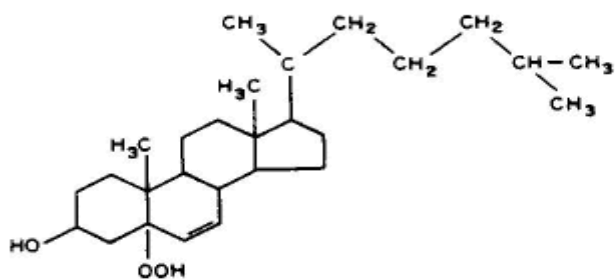
3β-HYDROXY-5α-HYDROPEROXY-Δ^6-CHOLESTENE