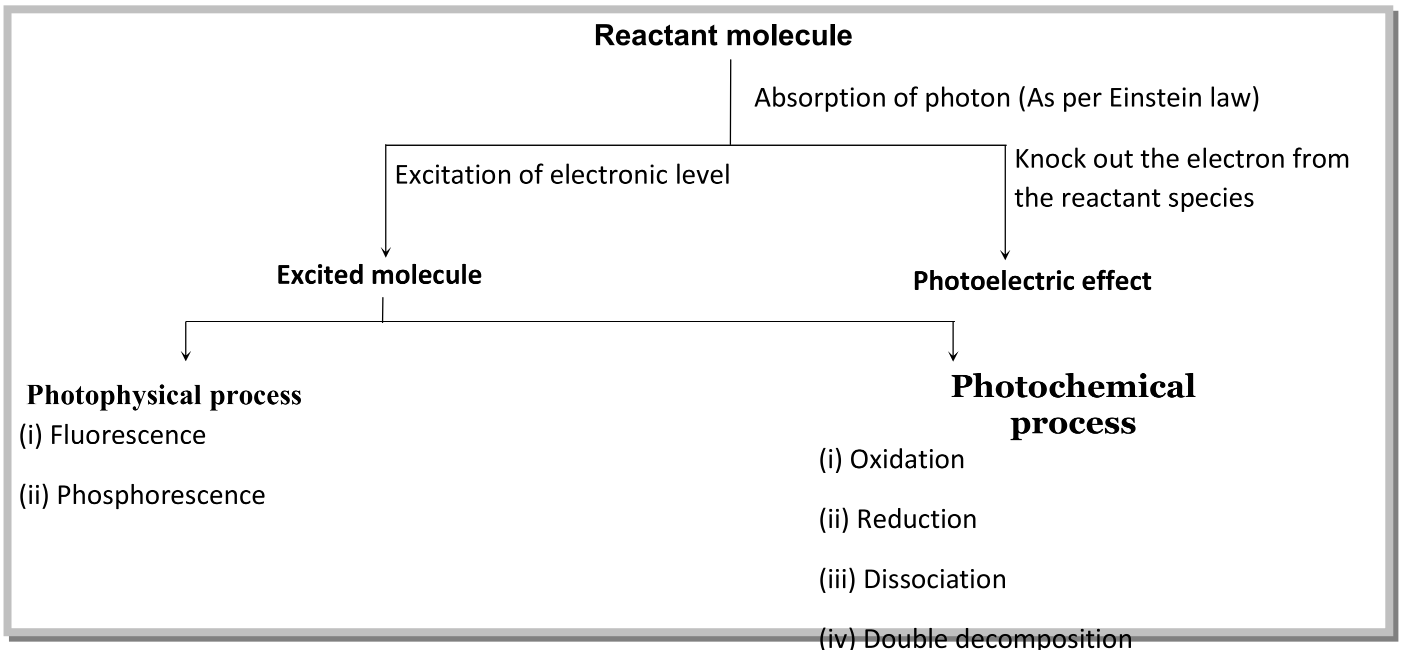
Photochemical reactions:

Absorption of radiant energy by reactant molecules brings in photo physical as well as photochemical changes. According to ***Einstein's law*** of photochemical equivalence, the basic principle of photo processes, each reactant molecule is capable of absorbing only one photon of radiant energy. The absorption of photon by a reactant molecule may lead to any of the photo process.



*The chemical reactions, which are initiated as a result of absorption of light, are known as**photochemical reactions***. In such cases, the absorbed energy is sufficient to activate the reactant molecules to cross the energy barrier existing between the reactants and products or in other words, energy associated with each photon supplies activation energy to reactant molecule required for the change.

(1) **Characteristics of photochemical reactions**

(i) Each molecule taking part in a photo process absorbs only one photon of radiant energy thereby increasing its energy level by $h\nu$ or $\frac{hc}{\lambda}$

(ii) Photochemical reactions do not occur in ***dark***.

(iii) Each photochemical reaction requires a definite amount of energy which is characteristic of a particular wavelength of photon. For example, reactions needing more energy are carried out in presence of UV light (lower λ, more E/Photon). A reaction-taking place in UV light may not occur on exposure to yellow light (lower λ and lesser E/Photon)

(iv) The rate of photochemical reactions depend upon the intensity of radiation's absorbed.

(v) The ΔG values for light initiated reactions may or may not be ***negative***.

(vi) The temperature does not have marked effect on the rate of light initiated reactions.

(2) **Mechanism of some photochemical reactions**

(i) ***Photochemical combination of H_2 and Cl_2*** : A mixture of H_2 and Cl_2 on exposure to light give rise to the formation of *HCl*, showing a chain reaction and thereby producing 10^6 *to* 10^8 molecules of HCl per photon absorbed.

$$H_2 + Cl_2 \xrightarrow{sunlight} 2HCl$$

The mechanism leading to very high yield of *HCl* as a result of chemical change can be as follows. Chlorine molecules absorb radiant energy to form an excited molecule which decomposes to chlorine free radicals (*Cl*) to give chain initiation step.

Light absorption step: $Cl_2 \xrightarrow{hv} Cl_2^*$ (*Excited molecule*) ....(i)

Chain initiation step: $Cl_2^* \rightarrow Cl^\bullet + Cl^\bullet$ ....(ii)

The chlorine free radical then combines with H_2 molecule to form *HCl* and $H^\bullet$ free radical. The $H^\bullet$ free radical so formed again combines with another Cl_2 molecule to give *HCl* and $Cl^\bullet$ free radical back resulting into chain propagation step.

Chain propagation step: $Cl^\bullet + H_2 \rightarrow HCl + H^\bullet$ ....(iii)

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

The combination of two $Cl^\bullet$ free radicals leads to chain terminating step.

Chain terminating step: $Cl^\bullet + Cl^\bullet \rightarrow Cl_2$ ....(iv)

(ii) ***Photochemical combination of H_2 and Br_2*** : The combination of H_2 and Br_2 to form *HBr* in presence of light is also an example of chain reaction like photochemical combination of H_2 and Cl_2 Here two Br_2 molecules absorb photon, however, inspite of chain reaction only one molecule of *HBr* is formed for each 100 photon absorbed by 100 molecules of Br_2. The mechanism of reaction is given below.

$$H_2 + Br_2 \xrightarrow{light} 2HBr$$

Mechanism:

Light absorption step: $Br_2 + h\nu \rightarrow Br_2^*$ ....(i)

Chain initiation step: $Br_2^* \rightarrow Br^\bullet + Br^\bullet$ ....(ii)

Chain propagation step: $Br^* + H_2 \rightarrow HBr + H^\bullet$ ....(iii)

$H^* + Br_2 \rightarrow HBr + Br^\bullet$ .... (iv)

Chain termination step: $Br^\bullet + Br^\bullet \rightarrow Br_2$ ....(v)

The lower values of *HBr* formation per photon of light absorbed has been attributed to the fact that step (III) is highly endothermic and thus before step (III) can take place most of the bromine free radicals recombine as per step (V) to give Br_2 molecule and thus providing less feasibility for step (IV) *i.e.* steps regenerating free radicals. Also the decomposition of *HBr* increases with increase in temperature.

(3) **Quantum yield** (or quantum efficiency)**:**The quantum efficiency or yield (ϕ) of a photochemical reaction may be expressed as, $\phi = \frac{\text{No. of molecules reacted or product formed}}{\text{No. of photon absorbed}}$

(4) **Application of photochemistry:**Photochemistry has significant role in our daily life. Some of the photochemical reactions commonly known as cited below.

(i) Photosynthesis in plants

(ii) Photography

(iii) The formation and destruction of ozone layer

(iv) Photo etching in electronic industry

(v) Many polymerization reactions.

(vi) Modern printing technology

(vii) Free radical combinations to obtain many compounds.

(5) **Damaging effect of photochemistry:** As already discussed, the destruction of ozone layer by chloro-fluorocarbon is due to photochemical decomposition of these compounds. The fading away of colors in colored fabrics is due to the photochemical decomposition of coloring material (i.e. dyes) used in printing technology.

Note: Generally ultraviolet or visible radiations are used for carrying out such type of reactions because their photons possess energies approximately of the order of 420 kJ per mol which is comparable to mole of the bond energy.

Thus UV radiation energy is capable of breaking the bonds. On the other hand IR radiations are generally not used because their photons possess energy of the order of 60 kJ per mole which is quite less for breaking the bonds.

Destruction of ozone layer: The formation and dissociation of ozone keeps a balance of ozone and oxygen in the ozone layer. However the diffusion of chloro-fluorocarbon such as $CFCl_3$ *and* CF_2Cl_2 *into the ozone layer are* destroying the ozone. $Cl_2 + h\nu \rightarrow CF_2\dot{C}l + \dot{C}l$; $\dot{C}l + O_3 \rightarrow \dot{C}lO + O_2$; $\dot{C}l\,O + O_3 \rightarrow \dot{C}l + 2O_2$. Chloro-fluorocarbons are used as aerosol repellents and as refrigerants.

Hence, ozone layer which acts as an umbrella for earth is being continuously destroying by the harmful UV radiation's coming from the sun.