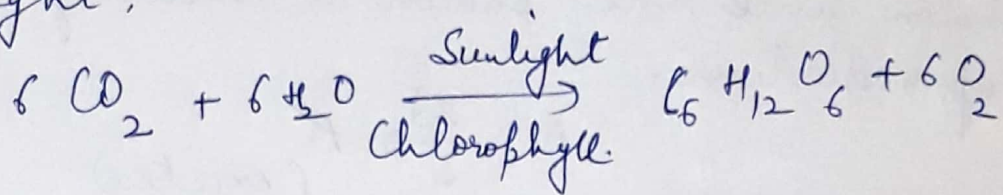


Unit II Photochemistry (प्रकाश रसायन)

It is the study of reactions that are brought about by the action of visible (दृश्य) or ultraviolet light (पराबैंगनी प्रकाश).

→ Most common example of photochemical rx. is Photosynthesis in plants by means of sunlight.



Principles of Photochemistry:

1) Grothuss Draper's Law (1818) :- (Principle of Photochemical Activation)

It states that only that light which is absorbed by a system can bring about a photochemical change.

→ Not all the light falling on the substances will necessarily bring about chemical change, since some of it can be re-emitted in the form of heat or light. The ^{maximum}

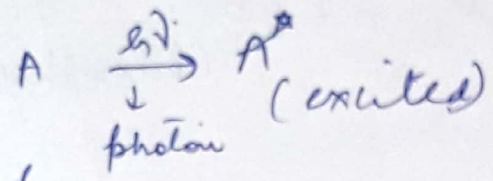
→ Every substance absorbs^{max} at a specific λ & is called λ_{max} and the substance absorbs radiation of λ_{max} and this light radiation absorbed will perform the rx.

→ This law is a qualitative law, this does not tell us the relationship between quantity of absorbed light and no. of reacting molecules.

2) Law of Photochemical Actuality Equivalence or Stark - Einstein's Law - (1912)

It states that for every quantum of radiation that is absorbed, one molecule of the substance reacts.

One unit of radiation is basically termed as photon since the photon is basically a quantum of radiation.



I stage \rightarrow Mol. ^{comes} in excited state but it is not necessary that it ^{will} give product because A^* undergoes modifications by several photophysical processes & desired product not obtained.

\therefore One molecule get excited by absorbing one photon ^{it is not necessary that} and every activated molecules give product.

This law is also called Principle of Quantum Activation.

\rightarrow Basic relationship of energy of radiation to frequency and wave length is given:

$$E = nh\nu$$

$n =$ Avogadro No. (6.023×10^{23})

$h =$ Planck's constant $(6.625 \times 10^{-27} \text{ erg sec})$

$\nu =$ freq. of absorbed radiation

$$\nu = \frac{c}{\lambda}$$

$$\therefore E = \frac{nhc}{\lambda} \text{ erg}$$

$$E = \frac{6.023 \times 10^{23} \times 6.625 \times 10^{-27} \times 3 \times 10^{10}}{\lambda} \div 4.185 \times 10^7 \text{ Calorie}$$

$$E = \frac{2.859}{\lambda} \text{ Calorie per mole}$$

$$= \frac{2.859 \times 10^8}{\lambda (\text{A}^\circ)} \text{ Cal per mol.}$$

Energy of photons of avogadro no. is c/a
One einstein.

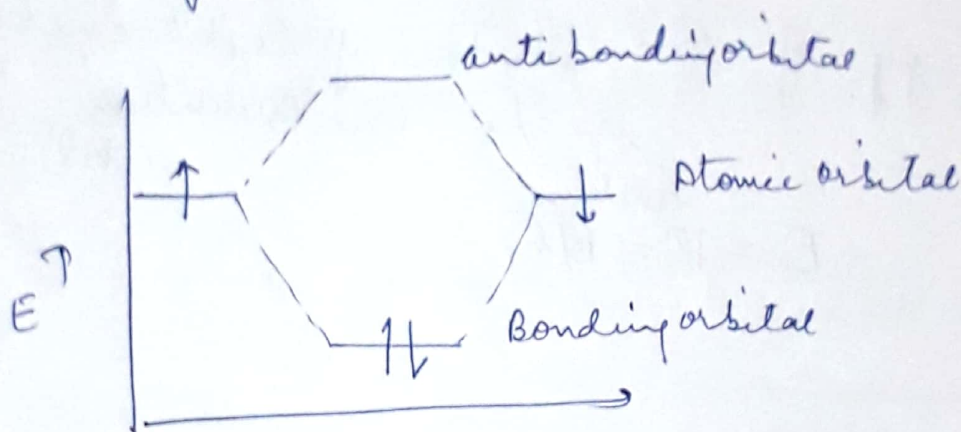
Energy of one photon of light energy
is c/a One Quantum
($h\nu$).

$$E = \overset{\text{einstein}}{1} \nu = N h \nu$$

Electronic Excitation

We know that an orbital can accommodate a maximum of two e⁻s and that a combination of two atomic orbitals (to form a bond) produces two molecular orbitals.

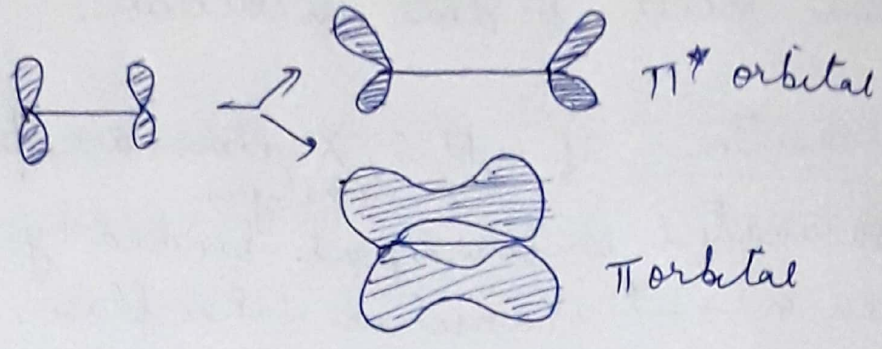
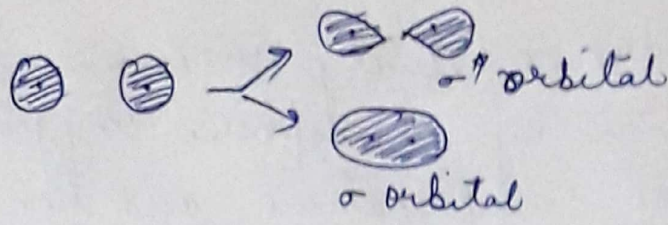
- One of them is a low energy orbital (Bonding orbital) as it accommodates both electrons in the ground state of the molecule.
- Other orbital called antibonding orbital, has higher energy than either of the ~~atomic~~ atomic orbitals & it remains vacant in the ground state.



- Non-bonding orbitals may be present in molecules, but nonbonding electrons are not involved in the bond formation.
- Excitation promotes a nonbonding electron either to a σ^* or a π^* .

→ Following types of electronic transitions involved in the visible & ultraviolet regions

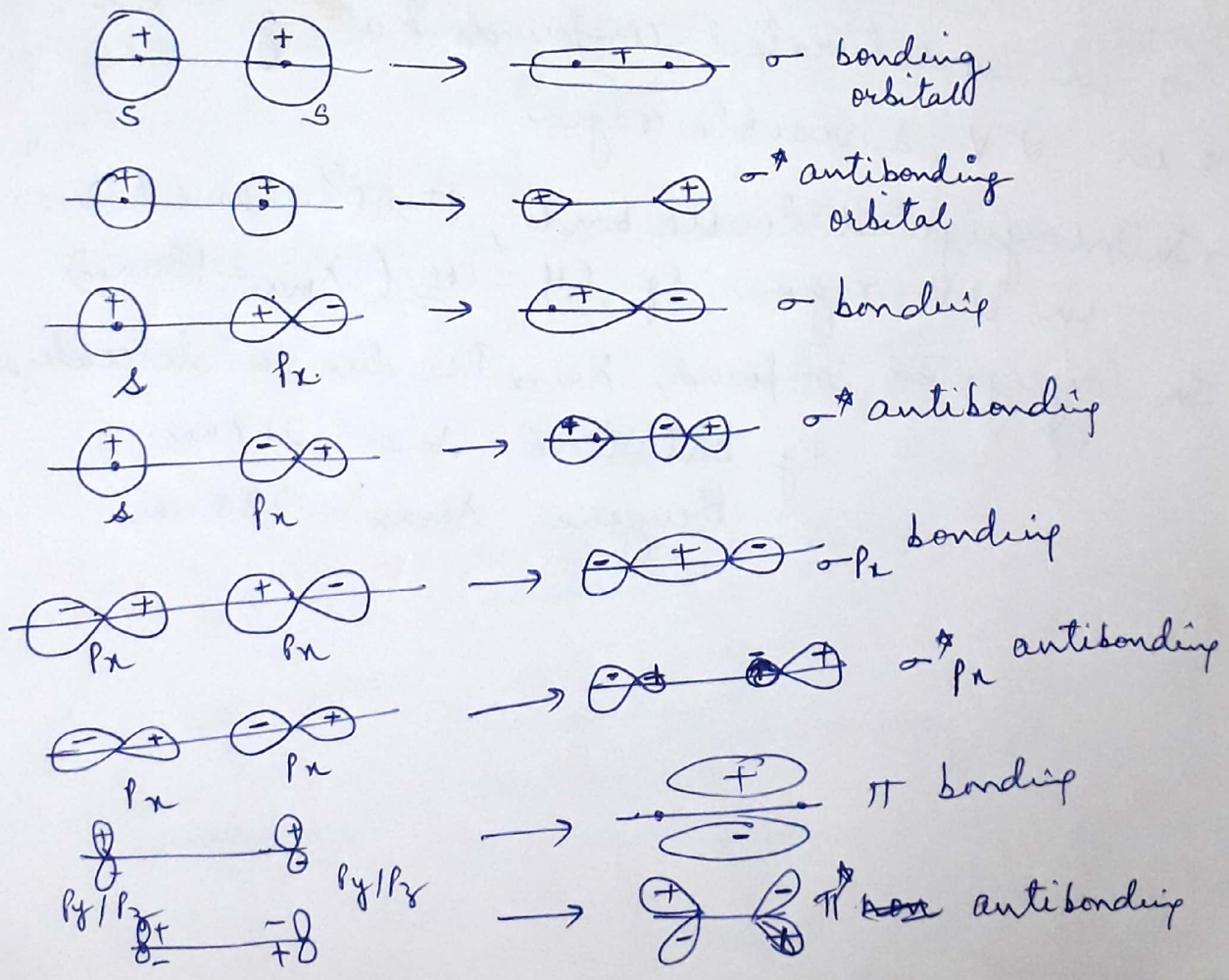
- 1) $\sigma \rightarrow \sigma^*$
- 2) $n \rightarrow \sigma^*$
- 3) $\pi \rightarrow \pi^*$
- 4) $n \rightarrow \pi^*$



Energies required for σ , π & σ^* are usually very high & require λ of far less than 200 nm

1) $\sigma \rightarrow \sigma^*$ transition (सक्रमण)

- takes place in compounds having σ electrons.
- need more energy for transition, \therefore takes place of vacuum-ultraviolet region.
- in saturated hydrocarbons, eg. CH_4 (at 125 nm)



σ, σ^* & n, σ^* are relatively uncommon because strong absorption by atmospheric oxygen below 200 nm creates complications and hence irradiation must be done in vacuum. (6)

2) $n \rightarrow \sigma^*$ transition: If O, N, S, X (halogen) atoms are present in any saturated compound and bonded by single bond, then $n \rightarrow \sigma^*$ transition takes place.

→ less energy required as compared to $\sigma \rightarrow \sigma^*$.

→ absorption in V.V. region.

eg. Trimethyl amine, Methyl alcohol, Methyl Iodide
 $n \rightarrow \sigma^*$ at 227 nm, 153 nm, 258 nm

3) $\pi - \pi^*$ transition:-

→ in unsaturated compounds having π e's.

→ in V.V. & visible region.

→ Subconjugated double bonds, $\pi \rightarrow \pi^*$ transition in V.V. region, eg. $CH_2=CH_2$ ($\lambda_{max} = 180$ nm)

In conjugated compound, λ_{max} ↑ due to delocalization

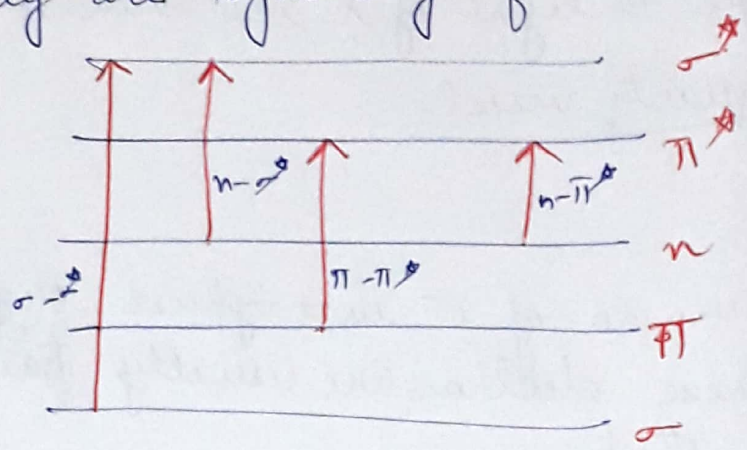
eg. butadiene $\lambda_{max} = 217$ nm

Benzene $\lambda_{max} = 225$ nm

iv) $n \rightarrow \pi^*$ transition:-

\rightarrow takes place in compounds having hetero atoms form ~~along~~ with unsaturated ~~and~~ other atom.
 π bond

\rightarrow These bands are of less intensity because they are symmetry forbidden.



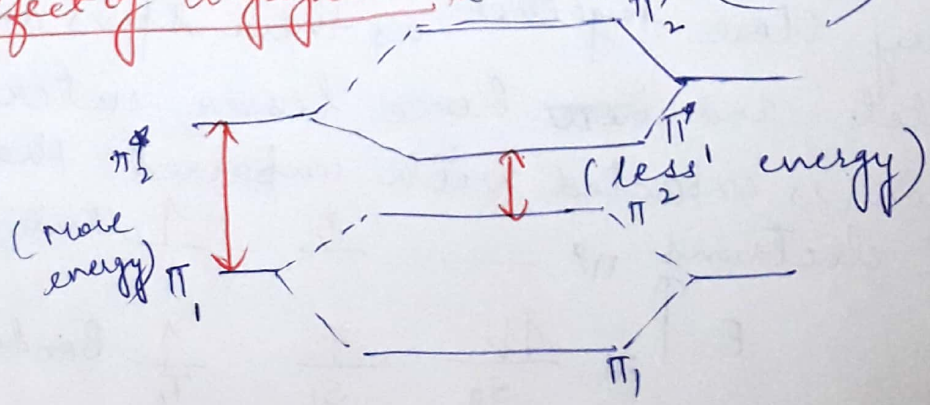
The most interesting types of electronic excitation in organic molecules are n, π^* & π, π^* transitions.

\rightarrow They have lower energy requirements & occur at longer λ s usually ~~to~~ within the region of commercial U.V. lamps.

eg. aldehyde / ketone ($RCHO, RCO R$)

285 nm	180 nm
($n - \pi^*$)	($\pi - \pi^*$)
(less energy high λ)	(More energy less λ)

Effect of Conjugation: (2 π bonds) (diene)



Similarly Benzophenone
 $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
345 nm , 245 nm

* Irradiation with 313.0 nm & 366.0 nm lines are conveniently performed in pyrex vessels (\because pyrex glass is opaque to light of λ less than 300 nm) for 253.7 nm, quartz vessel.

Excited States:

There are an even no. of e^- in a typical organic molecules and these electrons are usually paired in the ground state

Two possibilities:

a) If no spin inversion during transition and the e^- remain paired in excited state, this state is called an excited singlet state (S_1).

b) However, in many cases, electronic excitation is followed by spin inversion thus giving rise to a new excited state with two unpaired e^- . This state is called an excited triplet state (T_1).

T_1 more stable than S_1 , because in T_1 , two e^- do not get very close together as their spins are parallel and hence lesser inter electronic repulsion is expected with unpaired than with paired electrons.

