

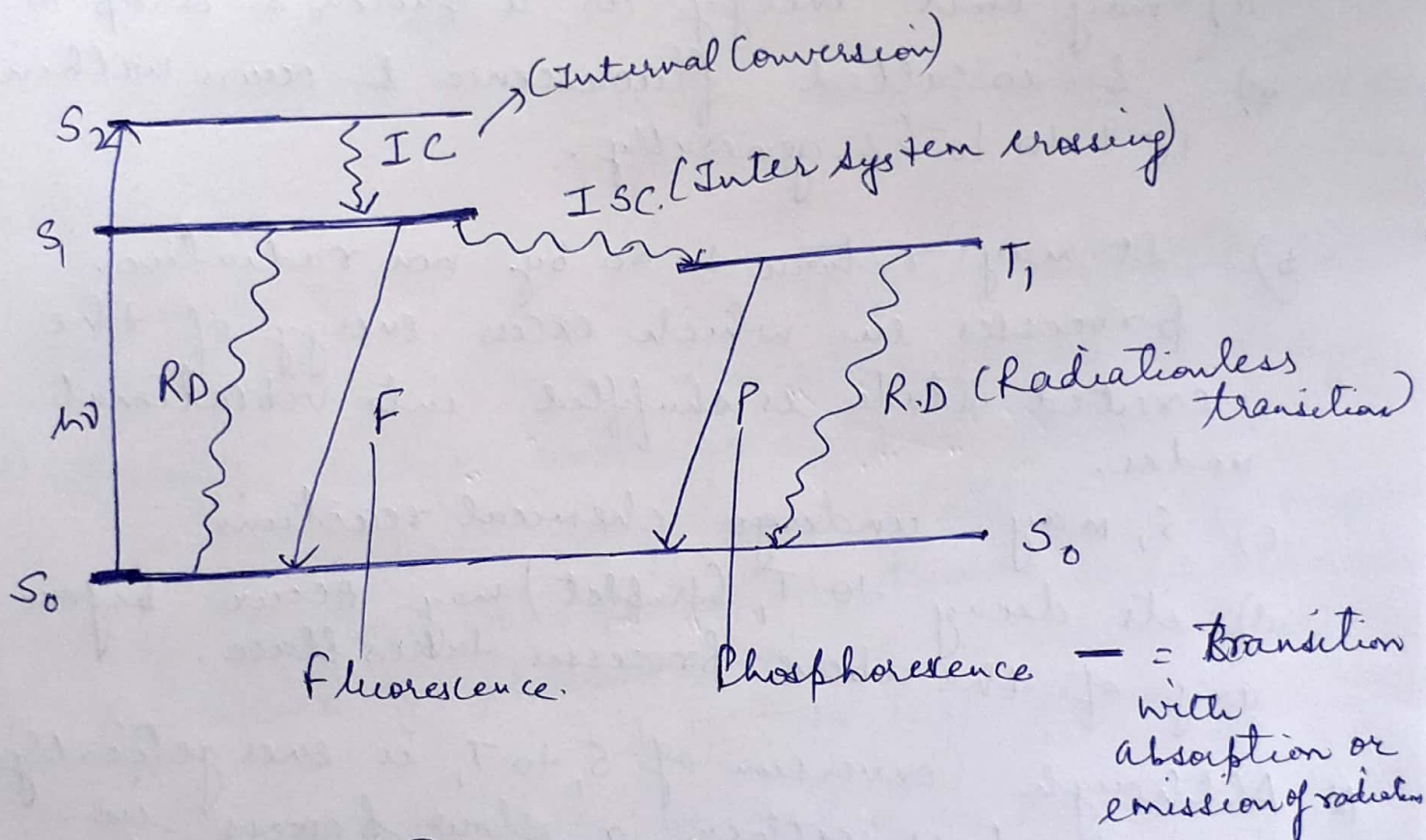
Modes of Dissipation of Energy :- (ऊर्जा क्षय की विधियाँ)

Jablonski Diagram

Spin Allowed Transitions :- (S-S) & (T-T) transitions

Spin forbidden Transitions :- (S-T) & (T-S)

Such transitions are called Inter system crossing (ISC).



Jablonski Diagram

Let us study major events that occur in a molecule from S_0 to S_2 (S_2 represents higher vibrational level of upper excited singlet state) in detail.

→ Life time of S_2 is very less < (less than 10^{-11} sec) and rapidly decay to lowest level(s) by a process called interconversion.

- Decay of S_1 to S_0 may also occur but it is usually a slower process than decay from (S_2 to S_1) ⁽¹⁰⁾
- S_1 has longest life ($\sim 10^{-8}$ s) of all excited singlet state.

S_1 may undergo one of the four energy degrading processes:

a) may emit energy as a photon & drop to S_0 .
* & is called fluorescence & occurs within 10^{-9} to 10^{-6} s, generally.

b) It may return to S_0 by non radiative processes in which excess energy of the excited state is shuffled into vibrational modes.

c) S_1 may undergo chemical reactions

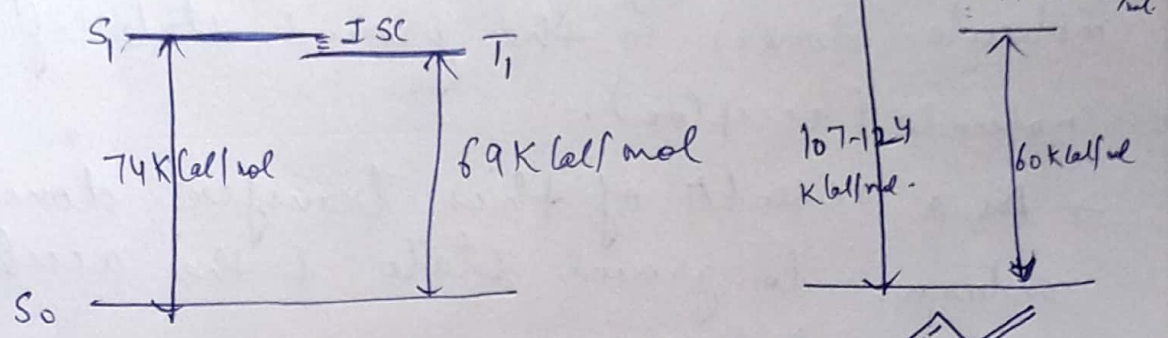
d) its decay to T_1 (triplet) may occur before any of the above processes takes place.

* Although conversion of S_1 to T_1 is energetically gainful, it is rather a slow process in accordance with spectroscopic rule (spin forbidden process)

However, if singlet state is sufficiently long lived, as in aromatic & $>C=O$ compounds, the $S_1 \rightarrow T_1$ change (called ISC) with a high degree of efficiency.

* ISC is very important process as T_1 exists for much longer period of time (10^{-3} to 1 s) than a singlet state.

* ISC is more efficient in the molecules where energy gap b'n S_1 & T_1 is rather small. (11)
 eg. Benzophenone (small energy gap 5Kcal/mol)



ISC in benzophenone
 (High tendency of ISC due to low energy gap)

1,3 butadiene
 (Lower tendency of ISC due to high energy gap)

Probable paths for $T_1 \rightarrow T_1$ state may not be converted to S_1 again since T_1 is of lower energy.

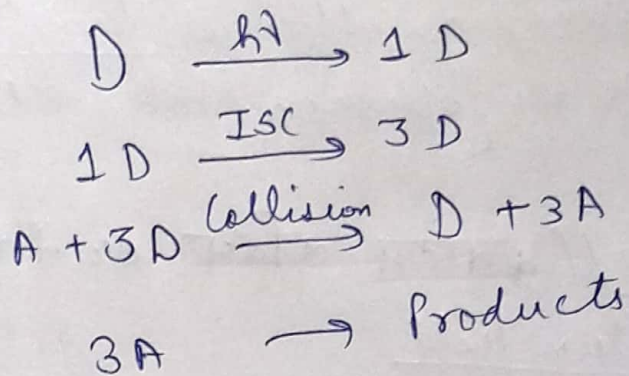
- a) It may either undergo a chemical rx or
- b) may return to ground state (S_0) by emission of photon. This process is known as phosphorescence. Life time of phosphorescence is in the range of $(10^{-3}$ to 10^5) generally.
- c) may return to S_0 by radiation less decay.

* Since S_1 & T_1 states differ in energy contents and electronic distribution, they are expected to possess different chemical & photochemical properties.

Energy Transfer ∴ (ऊर्जा स्थानांतरण)

(12)

- It refers to one step radiationless transfer of excitation energy from an electronically excited molecule (donor) to the ground state of another molecule (acceptor).
- As a result of this transfer, donor molecule returns to ground state & the acceptor molecule gets excited.
- Depending upon the multiplicity (singlet or triplet state) of the donor molecule, there may be a triplet-triplet or a singlet-singlet energy transfer.
- ∴ the life time of S_1 is short compared to that of T_1 , & hence there is greater possibility probability of energy transfer through triplet state.
- * Basic requirement for energy transfer is that the donor molecule should have at least 5 KJ/mol more energy than energy required to excite the acceptor molecule to its lowest excited state. & energy transfer does take place on every collision between excited donor molecule & ground state acceptor molecule.

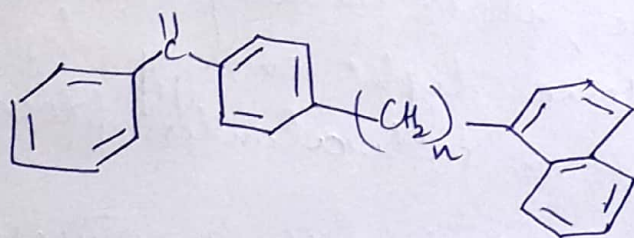


A = Acceptor
 (अर्थात्)
 D = Donor
 (दाता)
 3 = त्रिक
 1 = एक

Intramolecular Energy Transfer :-

It has been observed that certain substituted aromatic ketones and aldehydes are capable of transferring excitation energy from one part of molecule to other.

eg. 4-(1-naphthylalkyl)-benzophenones display two bands for benzophenone & naphthalene compounds



Irradiation of this compound with λ absorbed by benzophenone showed that there is an efficient energy transfer of triplet excitation from benzophenone moiety to naphthalene moiety (supported by study of emission spectrum of the system). Again, there is no possibility of a singlet-singlet energy transfer as S_1 of naphthalene is at a much higher energy level than that of benzophenone. In addition, when

the compound is irradiated with light of λ absorbed by naphthalene, an efficient singlet-singlet energy transfer to benzophenone takes place. (19)

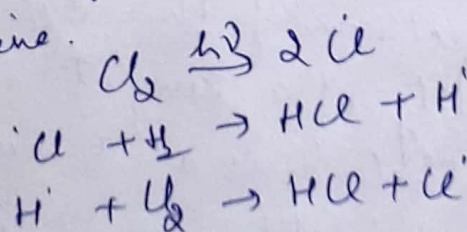
Quantum efficiency (प्रवाह लक्ष्य or प्रवाह दक्षता) = Quantum Yield

$$\phi = \frac{\text{No. of molecules reacting or formed in unit time}}{\text{No. of quanta absorbed in unit time}}$$

Quantum yields may be measured using a ferrioxalate actinometer which permits calculation of the amount of light falling on the compound undergoing a photochemical reaction.

→ If each quantum of light absorbed leads to the formation of product molecule, then ϕ will be 1.0, but in practice, it is usually less than 1 because of decay of some light energy by fluorescence, phosphorescence or radiationless process.

→ In the case of chain rxns, quantum yields may have values as high as several thousands. for eg. HCl formation, Quantum yields may be $10^6 - 10^7$ at room temperature. As over a million molecules of HCl are formed for every one quantum of light absorbed by chlorine.



High Quantum yields due to free radical rx mechanisms