

## Lesson 1

### PHOTOCHEMICAL REACTIONS

#### INTRODUCTION TO PHOTO CHEMISTRY AND PHOTO PHYSICAL PROCESSES

##### 3.1.i) Introduction

The subject of photochemistry deals with the reactions that are affected by ultra-violet, a visible radiation, which is a part of electromagnetic radiation. Even though photosynthesis, a photochemical reaction played an important role in the development of life, organic photochemistry received only limited importance until 1940s. Many examples of organic photochemical reactions appeared before that time, but systematic studies were limited to only gas phase reaction. Even though the products of some of the early reactions, studied were not available from other methods of synthesis, solution photochemistry was neglected, largely because the reaction mixture was complex and no useful methods were developed for the isolation of products. The instruments were costly and the scientists were handicapped by the non-availability of artificial sources of visible and ultra-violet light of suitable intensity. The introduction of new spectroscopic and analytical methods reduced the difficulty in characterising the complex mixture of products of photochemical reactions and the development of organic photochemistry.

##### 3.1.ii) Interaction of electromagnetic radiation with matter

In photochemistry a molecule absorbs radiation and promoted to highly energetic state called excited state. Therefore, it is necessary to know about radiation and excited states associated with photochemistry. The regions of electromagnetic spectrum that are important to



photochemist for ultraviolet (1500-4000 Å), the near ultraviolet (2000 to 4000 Å) and the visible region (4000 to 8000 Å).

We know that the absorption of energy by molecules or atoms, which normally exist in a state of minimum electronic energy or ground state, raises them to a less stable state of higher electronic energy or excited state. The absorption process is referred to as excitation. Excited species can lose their energy by a variety of means. The most common of these are the emission of radiation and the loss of surroundings through collisions.

In a photochemical process this energy is in the form of light. Light of any wavelength has associated with it an energy value given by equation  $E = h\gamma$ , where  $\gamma$  is the frequency of the light and  $h$  is Planck's constant whose value is  $6.6 \times 10^{-27}$  erg. sec or  $6.6 \times 10^{-34}$  Joule-sec. It may be seen from the relationship  $E = h\gamma$ ,  $\gamma = C/\lambda$  and  $E = hC/\lambda$  that energy is inversely proportional to wavelength i.e the larger the wavelength the lower the energy of radiation.

Since the energy levels of the molecule are quantized, the amount of energy required to raise an electron in a given molecule from one level to a higher one is a fixed quantity. Only light with exactly the frequency corresponding to this amount of energy will cause the electron to move to a higher level. If the light of another frequency is sent through a sample, it will pass out without a loss in intensity, since the molecules will not absorb it. However, if light of correct frequency is passed in the energy will be used by the molecules for electron promotion and hence the light that leaves the sample will be diminished in intensity or altogether. Therefore each substance is selective in its absorption of radiation depending on the presence of chromophores which are atoms or functional groups which usually contain p electrons or  $\pi$  bonds. The various wavelength

ranges at which absorption takes place are determined from the absorption spectra, which are the plots of the wavelength against the amount of radiation absorbed or passing through a substance.

The total energy of the system consists of 3 components.: rotational, vibrational and electronic energies. The difference between two adjacent vibrational levels is smaller than the difference between adjacent electronic levels, and the difference between adjacent rotational levels is small still than vibrational levels i.e why a molecule at any time is in a given electronic state but also in a given vibrational and rotational state. When electron move from one electronic level to another, it moves from a given vibrational and rotational level within that electronic level to some vibrational and rotational level at the next electronic level. IR spectra involve only transitions between vibrational levels like  $V_0, V_1$  of  $E_1$  and rotational transitions are found in far IR. The largest of the 3 energies is electronic excitation energy and it is about 10 times that of vibrational energy. Visible and UV will cause transitions between electronic levels. The excitation energy is of high magnitude which can be comparable to bond energies of molecules, i.e. many reactions involving breakage of bonds with this energy as feasible.

### 3.1.iii) Quantum yield

The quantitative relationship between the number of molecules which react or are formed and the number of photons absorbed in a unit time is given by quantum yield  $\phi$ .

$$\phi = \frac{\text{Number of molecules undergoing a particular process}}{\text{Number of quanta absorbed by the system}}$$

The number of molecules reacting or formed per unit time is measured by any convenient analytical kinetic technique, and the number of photons absorbed per unit time is measured by actinometer (a chemical or physical device capable of counting photons). Thus if for every photon



absorbed a molecule undergoes a certain photochemical process, the quantum yield for the process is unity. If other processes, such as fluorescence or phosphorescence compete with the one under consideration, the quantum yield will be less than unity. Thus the quantum yield of photochemical reactions, referring specifically to the primary process, is always  $\leq 1$ . The primary process is here defined as starting with the absorption of a photon and ending with the disappearance of the molecule or its deactivation to a non reactive state.

### 3.1.iv) Electronically excited states (Singlet and triplet states and forbidden transitions)

Electronically excited states are obtained by the promotion of an electron from bonding molecular orbital to antibonding molecular orbitals. Bonds are considered to be spaces of higher electron density between adjacent atoms; they are physical representations of molecular orbitals. The latter are wave functions concerned with expressing the probability of finding electrons and they can be expressed in terms of linear combination of atomic orbitals.

In photochemistry we deal mostly with three types of molecular orbitals characterized by their spacial properties (1) " $\sigma$ " orbitals formed by the axial overlap of atomic orbitals, (2)  $\pi$  orbitals formed by parallel overlap of pure p orbitals and (3) n-orbitals which contain non-bonding electron pair on atoms such as oxygen and nitrogen which are localised on those atoms. These three molecular orbitals ( $\sigma$ ,  $\pi$  and n) which are of lower energy are usually populated in the ground state and are called bonding orbitals. The absorption of light energy by organic compounds in the visible and UV region involves promotion of electrons in the  $\sigma$ ,  $\pi$  and n orbitals to higher energy states. These higher energy states are described by molecular orbitals that are vacant in the ground state are commonly called "antibonding orbitals." The antibonding orbitals



associated with  $\sigma$  and  $\pi$  are  $\sigma^*$  and  $\pi^*$ . As the "n" electrons do not form bonds, there are no antibonding orbitals associated with them.

In most organic molecules all electrons in the ground state are paired, each member of a pair possessing opposite spin, as demanded by the Pauli principle. When one of a pair of electrons is promoted to an orbital of higher energy, however, the Pauli principle no longer applies because the two electrons are no longer sharing an orbital, and the promoted electron may in principle have the same spin as its former partner or the opposite spin. When referring to the relative spins of two such electrons, one speaks of the multiplicity of the molecule. The term originally referred to the number of spectral lines in the atomic absorption and emission spectra observed in magnetic fields of appropriate strength. It is defined by  $2S + 1$ , where  $S$  is the total spin – the absolute value of the sum of the spin quantum numbers involved ( $+\frac{1}{2}$  or  $-\frac{1}{2}$ ).

In most photochemical reactions only two half-vacant orbitals are associated with a molecule in the excited state, the orbital from which the transition takes place and the antibonding orbital to which the electron is promoted, and consequently only two values for multiplicity are obtained, 1 and 3. The former in which the spin has been preserved is called the "singlet" state and the latter, in which the spins are parallel, is the "triplet" state. Most organic molecules in the ground state are singlets. Thus a molecule in which two unpaired electrons have the same spin is called a triplet, while one in which all spins are paired is a singlet. Thus at least in principle, for every excited singlet state there is a corresponding triplet state. In most cases the triplet state has a lower energy than the corresponding singlet. Therefore a different amount of energy and hence a different wavelength is required to promote an electron from the ground state (which is almost always a singlet) to an excited singlet than to the corresponding triplet state.

It would thus seem that promotion of a given electron in a molecule, could result either in a singlet or a triplet excited state depending on the amount of energy added. However, this is often not the case because transitions between the energy levels are governed by selection rules which state that certain transitions are "forbidden." There are several types of forbidden transitions, out of which spin-forbidden transitions and symmetry-forbidden transitions are more important.

**a. Spin forbidden transitions**

Transitions in which the spin of an electron changes are not allowed, because a change from one spin to the opposite involves a change in angular momentum, and such a change would violate the law of conservation of angular momentum. Therefore, a singlet-triplet and triplet-singlet transitions are forbidden, whereas singlet-singlet and triplet-triplet transitions are allowed. The presence of heavy atoms, unpaired electrons or a magnetic field results in a breakdown of the selection rules, and singlet-triplet conversions then take place, even though according to the rules of spin conservation they are not "allowed."

**b. Symmetry forbidden transitions**

Orbitals are frequently designated by their symmetry properties. The  $\sigma$  orbital of  $H_2$  is often written  $\phi_g$ . The g stands for grade. A gerade orbital is one in which the sign of the orbital does not change when it is reflected through its center of symmetry. The  $\sigma^*$  orbital is ungerade (designated  $\phi_u$ ). The ungerade orbital changes sign when reflected through its center of symmetry.

Selection rules state that  $g \rightarrow u$  and  $u \rightarrow g$  transitions are allowed and that  $g \rightarrow g$  and  $u \rightarrow u$  transitions are forbidden.



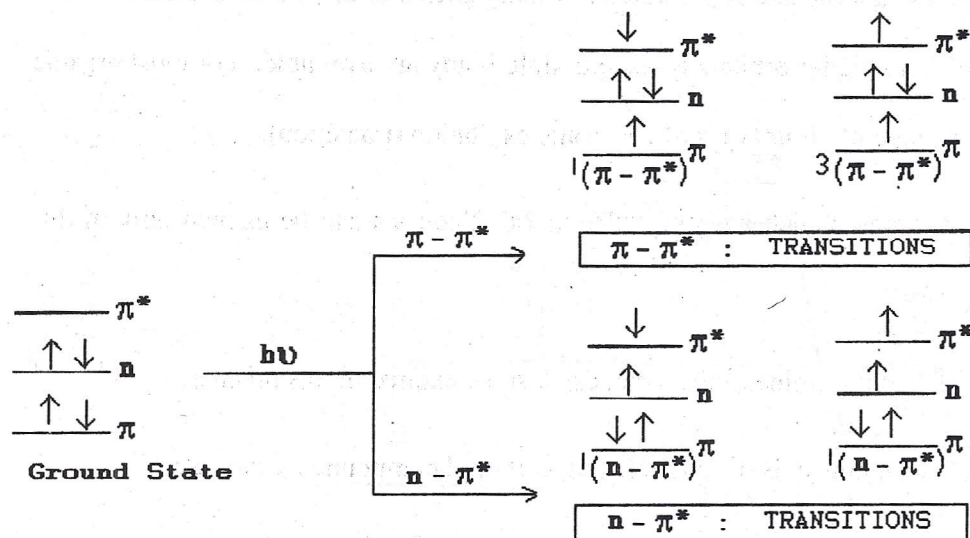
### 3.1.v) Types of transitions and carbonyl chromophore

When an electron in a molecule is promoted it usually goes into the lowest available vacant orbital, though promotion to higher orbitals is also possible if any are available. For most organic molecules there are consequently four types of electronic excitation (transition).

1.  $\sigma - \sigma^*$  : Alkanes, which have no "n" and " $\pi$ " electrons can be excited only in this way.
2.  $n - \sigma^*$  : Alcohols, amines, ethers etc. can also be excited in this manner.
3.  $\pi - \pi^*$  : This pathway is open to alkenes, carbonyl compounds, esters etc.
4.  $n - \pi^*$  : Aldehydes, ketones, esters etc. can undergo this transition in addition to the above three. :

The four excitation types listed above are in the order of decreasing energy. Thus the light of highest energy is necessary for  $\sigma - \sigma^*$  excitation, whereas  $n - \pi^*$  transitions are caused by light of lowest energy. Of the four excitation types listed above the  $\pi - \pi^*$  and  $n - \pi^*$  are more important in organic photochemistry than the other two.

### Transitions and their multiplicity in carbonyl compounds



$S_1$  state always has  $n - \pi^*$  configuration but  $T_1$  state need not have  $n - \pi^*$  configuration.

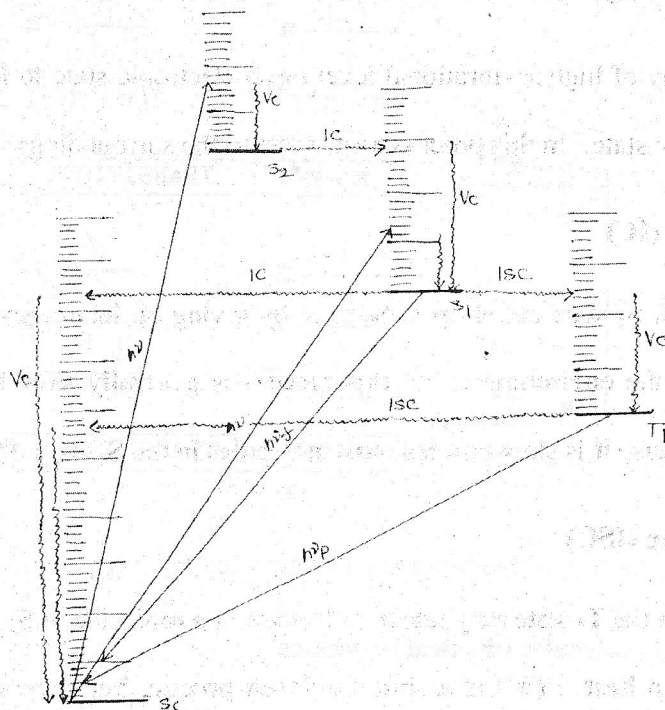
#### 3.1.vi) The fate of excited molecule: Physical processes

##### (Deactivation of excited states)

When a molecule has been photochemically promoted to an excited state, it does not remain there for long time. Most promotions are from  $S_0$  to the  $S_1$  state. As we have seen promotions from  $S_0$  to triplet states are forbidden, promotions to  $S_2$  and higher excited states take place, but in liquids and solids these higher states usually drop very rapidly to  $S_1$  state. The energy which is lost when  $S_2$  or  $S_3$  molecules drops to  $S_1$  is given up in small increments to the environment by collisions with neighbouring molecules. Such a process is called energy cascade. In a similar manner, the initial excitation and decay from higher singlet states initially populate many of the vibrational levels of  $S_1$ , but these also cascade down to the lowest vibrational level of  $S_1$ . Therefore in most cases the lowest vibrational level of the  $S_1$  state is the only important



excited singlet state. This state can undergo various physical and chemical processes. The physical processes are best represented by a diagram called Jablonski diagram.



**Modified Jablonski Diagram Showing transitions between excited states and ground state. Radiative processes are shown by straight lines; radiation less processes by wavy lines. IC= Internal conversion; ISC = Intersysten. crossing; VC=Vibrational cascade;  $h\nu_f$  = fluorescence,  $h\nu_p$  = phosphorescence.**

Photo physical process is of two types – (1) unimolecular photo physical processes and (2) bimolecular photo physical processes. The bimolecular photo physical process is also called photo sensitization or triplet energy transfer. Uni molecular photo physical processes involve loss of energy by an excited states with excess energy leading to deactivation or decay of excited states. This deactivation or decay of an excited state is of two types – (1) Thermal decay which include

vibrational cascade, internal conversion and inter-system crossing and (2) Radiative decay which include fluorescence and phosphorescence.

### **Vibrational cascade (VC)**

Thermal decay of higher vibrational level of an electronic state to lowest vibrational level of the same electronic state. In this process heat is lost to the surroundings including solvent.

### **Internal conversion (IC)**

A molecule in  $S_1$  state can drop to  $S_0$  state by giving up its energy in the form of heat in small increments to the environment, but this process is generally slow because the amount of energy is large. Because it is slow process most molecules in the  $S_1$  state adopt other pathways.

### **Inter-system crossing (ISC)**

A molecule in the  $T_1$  state may return to  $S_0$  state or a molecule in  $S_2$  state may cross over to  $T_1$  state by giving up heat. This is a spin forbidden process but occurs to different extent in different compounds. For example, carbonyl compounds have high inter-system crossing efficiency whereas olefins and conjugated dienes have minimum or zero inter-system crossing efficiency.

### **Fluorescence ( $h\nu_f$ )**

Change over of higher electronic state by emission of radiation to the lower electronic state of same multiplicity is called fluorescence.

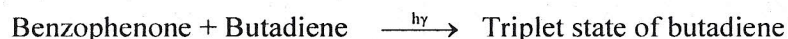


**Fluorescence ( $h\nu_f$ )**

Change over of higher electronic state by emission of radiation to the lower electronic state of different multiplicity is called phosphorescence.

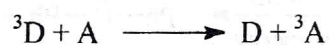
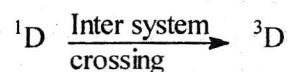
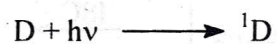
**3.1.vii) Transfer of excitation energy**

This is a secondary means of producing electronically excited states. The method involves transfer of excitation energy from an electronically excited molecule to the ground state of another molecule, and is generally used for producing triplet states. This energy transfer is also called as photosensitization and is intended for the generation of triplet states of compounds with low inter-system crossing efficiency. In this process excess of a compound with very high inter-system crossing (ISC) efficiency (eg: benzophenone) is mixed with a compound with a very low inter-system crossing efficiency (example: butadiene) and irradiated at  $\lambda_{\max}$  of compound with high ISC efficiency. The triplet energy transfer occurs from benzophenone to butadiene at every collision between molecules. In this process the compound with high ISC efficiency is called Donar and the compound with low ISC efficiency is called acceptor and the Donar is also called photo sensitizer.



The important requirements for a good sensitizer is that (1) the energy of sensitizer must be at least 3 K cal more than that of acceptor and (2) for a good sensitizer the triplet energy ( $E_{T1}$ ) and singlet energy ( $E_{S1}$ ) of Donar should be in between those of acceptor. Imagine a donar-acceptor system such that only the donar absorbs the incident light, and the triplet energy of the donar is at least 3 K cal/mole greater than the triplet energy of the acceptor. Light absorption by the donar

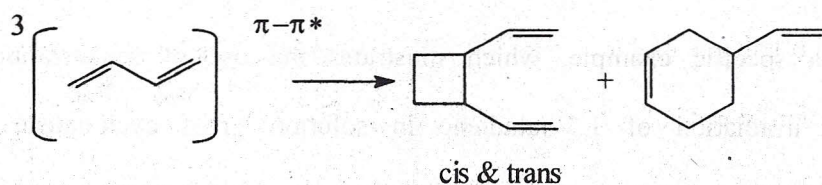
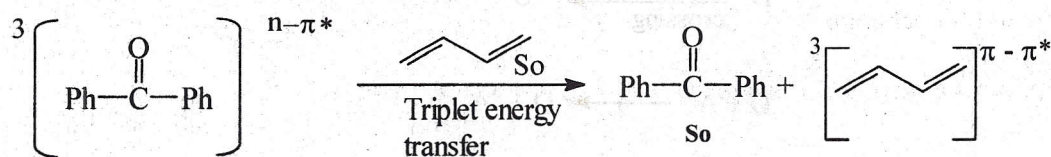
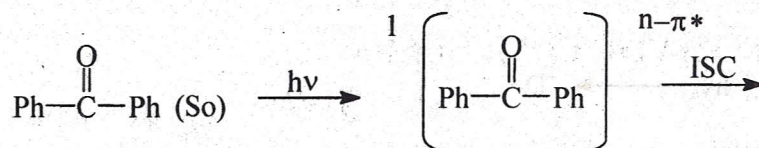
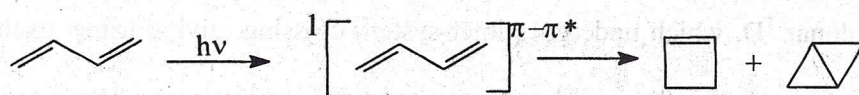
produces singlet excited donar  $^1D$ , which undergoes inter-system crossing, giving triplet excited donar  $^3D$ . Triplet excited donar then collides with acceptor, producing triplet excited acceptor  $^3A$  and ground state donar D.



where D = donar and A = acceptor

Let us consider a specific example, which illustrates the use of sensitization in photochemistry. Direct irradiation of 1,3-butadiene in solution gives cyclobutene and bicyclobutane with minor amounts of dimers. As the inter-system crossing efficiency in 1,3-butadiene is zero triplet derived products are not formed. Triplet excited 1,3-butadiene produced by energy transfer from triplet excited benzophenone gives only dimers.





### Model Question:

1. Write a note on quantum yield.
2. What are electronically excited states? Explain their nomenclature and difference in stability and reactivity.
3. Explain the types of transitions we can expect in carbonyl compounds.
4. Describe different photo physical processes involved in deactivation of excited states and draw the Jablonski diagram incorporating different photo physical processes.
5. Explain the process of photo sensitization

### Recommended books:

1. Importance of antibonding orbitals by Jaffe and Orchin.
2. Molecular reactions and photo chemistry, by Charles Dupey and O.L. Chapman.
3. Molecular photo chemistry, by Turro