



NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 414

COURSE TITLE: PHOTOCHEMISTRY AND PERICYCLIC REACTIONS

CHM 414

PHOTOCHEMISTRY AND PERICYCLIC REACTIONS

Course Guide

Introduction

Most forms of life on the earth exist in the environment in which light is a prominent factor, and thus they must accommodate the light intensities encountered on the earth. The accommodation is expressed by the evaluation of systems that are not permanently harmed by incident light and also by the development of photoactive systems that are beneficial to particular organisms. The conversion of light to chemical processes, ranging from the capture of light energy by the photosynthetic pigments to the photochemical reactions of carbon assimilation. It is of interest to know that, the usual way for the photochemical reaction in living cells result from the activation of photoreceptor by means of absorption of a light quantum, which causes the photoreceptor molecules in the ground state to be elevated to an excited state, which then initiates the reaction that are peculiar to that system. The reaction initiated may be an electron transfer reaction, as in the case of photosynthesis, or it may be lead to other chemical changes and produce a new chemical compound, or change in the configuration such as cis/trans isomerization. In all cases, the chromophores return to the ground state by differing means and at different rates. In this course we have provided the students the necessary background on the basics of photochemistry. A problem often encountered in connection with photochemical reactions is that they are still considered too “exotic” and unpredictable for wide synthetic application. On the other hand, predicting how an organic molecule will behave upon absorption of light, difficult as that may be, is of crucial importance for introducing photochemical reactions into the armory of synthetic methods. Accordingly, the developers of this course have embarked on the ambitious aim of defining the “paradigms for proceeding from the possible to the plausible to the probable photochemical processes”.

Things you will learn in this course

In this course titled “photochemistry and pericyclic reaction”, you will be presented information in a structured way to make learning easier. Each unit is planned in an easy to follow pattern for beginners in this aspect of chemistry. We have adopted a step-by-step approach in order to introduce you to a fascinating world of excited-state reactions. All the units follow the same pattern and so after the first unit the rest will become easy to follow.

Learning Outcomes- Aims and Objectives

This course aims at providing you the necessary background on the basics of photochemistry so as to enable you understand the underlying mechanism for all photochemical processes. On completion of this course you should be able to:

- Distinguish between thermal reactions and photochemical reactions.
- Discuss the role of photochemistry in our everyday living.
- Identify photochemical process in what goes on in your environment.
- Explain simple pericyclic reactions.

Course Materials

In unit 1 the concept of photochemistry is introduced and explained. Interaction of radiation with matter is discussed and difference between thermal and photochemical processes highlighted. Laws of photochemistry were discussed with a view to providing basis for understanding photochemical transformations.

Unit 2 presents a detailed treatment of the overall configurations of excited states, and the construction of the energy diagrams of such states.

Unit 3 is concerned with photochemical processes. These are the main competing paths of a photochemical reaction, and limit the extent to which the absorption of light is productive for a chemical transformation. The chapter includes detailed examples of the deactivation paths (radiative or radiationless transitions) leading back to the ground state, as well as useful generalizations and predictions for identifying the chromophores that are more prone to these processes.

Unit 4 presents detailed learning information on pericyclic reactions.

Each study unit has a set of performance objective with other relevant learners guide. At the end of each unit is listed a set of recommended textbooks and relevant websites.

Unit 1

Photochemistry

1.0 Introduction

Photochemistry is the study of light-induced chemical reactions and physical processes. The pillars of photochemistry are UV/VIS spectroscopy, photochemical reactions in organic chemistry and photosynthesis in biochemistry.

The Photochemistry course is concerned with the interaction of visible and ultraviolet light with molecules, an important aspect of modern chemistry which is relevant to biology (e.g. photosynthesis, vision), lasers, organic synthesis, reaction kinetics and atmospheric science (e.g. the ozone hole). Some familiarity with concepts such as Hund's rules, the Franck Condon principle, basic reaction kinetics and the steady-state approximation is expected.

Photochemical reactions and the properties of excited states are also critical in many commercial processes and devices. Photography and xerography are both based upon photochemical processes, while the manufacture of semiconductor chips or the preparation of masks for printing newspapers relies on UV light to destroy molecules in selected regions of polymer masks.

This unit shall be considered under the following headings:

- Photochemistry.
- Interaction of radiation with matter, difference between thermal and photochemical processes.
- Laws of photochemistry :Grothus-Draper law and Stark-Einstein law

1.1 Objectives

By the end of this unit, you should be able to:

- Define photochemistry
- Explain the fundamental principles and applications of photochemistry
- Differentiate between thermal and photochemical processes
- State the laws of photochemistry

1.2 Photochemistry

1.2.1 What is photochemistry?

Photochemistry is the branch of science which deals with chemical reactions which occurred by the absorption of light waves which are called photons of energy. Only the radiations which fall under the region 800 nm to 200 nm can cause such reactions. Also the photons should contain sufficient amount of energy to raise the atoms from ground to excited state. In excited state atoms or groups of atoms undergo chemical reactions more rapidly as compared to ground state. When an atom goes from ground state to excited state, it essentially get promoted from bonding molecular orbital called BMO to anti bonding molecular orbital called ABMO.

The term photochemistry generally applies to chemical modifications induced by interaction of light (electromagnetic radiation) with matter. Therefore, light is always one of the reactants in a photochemical system. Electromagnetic radiation with the wavelength ranging from ~800 nm (near-IR) to ~150 nm (far UV) is of primary importance for photochemistry and photobiology, but the wavelength regions adjacent to this range are also of interest for certain applications. With the advent of lasers, multiphoton photochemistry, i.e. chemistry initiated by simultaneous absorption of two or more photons, came into wide use. This made IR radiation of particular interests for photochemists. The wavelength range of 150-800 nm corresponds to the photon energy ranging from 800-150 kJ mol⁻¹. These energies are much higher than those associated with thermal motion at ambient temperature and are comparable to the energies of chemical

bonds. That is why photochemistry is often referred to as high-energy chemistry. The fact that the spectral region mentioned above contains electromagnetic radiation detectable by the human eye (visible light) suggests an interrelation of photochemistry and vision mechanisms. Humans can see radiation in this part of the spectrum because visual receptors are organic compounds that absorb light with these wavelengths. Notice that the spectral maximum of the solar radiation reaching the earth surface is located within the visible light range (~500 nm).

Most forms of life on the earth exist in the environment in which light is a prominent factor, and thus they must adapt to light intensities encountered on the earth. The adaptation is expressed by the evolution of systems that are not permanently harmed by incident light and also by the development of photoactive systems that are beneficial to particular organisms. The conversion of light to chemical processes, ranging from the capture of light energy by the photosynthetic pigments to the photochemical reactions of carbon assimilation. It is of interest to know that, the usual way for the photochemical reaction in living cells result from the activation of photoreceptor by means of absorption of a light quantum, which causes the photoreceptor molecules in the ground state to be elevated to an excited state, which then initiates the reaction that are peculiar to that system. The reaction initiated may be an electron transfer reaction, as in the case of photosynthesis, or it may lead to other chemical changes and produce a new chemical compound, or change in the configuration such as cis/trans isomerization. In all cases, the chromophore returns to the ground state by differing means and at different rates.

Damaging Effects of Photochemistry: The most well known damaging effect of photochemistry is the effect of sunlight on the dyes used for coloring of fabrics. Due to this effect colored fabrics fade away.

1.2.2 Differences between thermal and photochemical processes

Many chemical reactions occur only when a molecule is provided the necessary "activation energy". A simple example can be the combustion of gasoline (a hydrocarbon) into carbon dioxide and water. In this reaction, the activation energy is provided in the form of heat or a spark. In case of photochemical reactions light provides the activation energy. Simplistically, light is one mechanism for providing the activation energy required for many reactions. If laser light is employed, it is possible to selectively excite a molecule so as to produce a desired electronic and vibrational state. Equally, the emission from a particular state may be selectively monitored, providing a measure of the population of that state. If the chemical system is at low pressure, this enables scientists to observe the energy distribution of the products of a chemical reaction before the differences in energy have been smeared out and averaged by repeated collisions.

The absorption of a photon of light by a reactant molecule may also permit a reaction to occur not just by bringing the molecule to the necessary activation energy, but also by changing the symmetry of the molecule's electronic configuration, enabling an otherwise inaccessible reaction path, as described by the Woodward-Hoffmann selection rules. A 2+2 cycloaddition reaction is

one example of a pericyclic reaction that can be analyzed using these rules or by the related frontier molecular orbital theory.

Photochemical reactions involve electronic reorganization initiated by electromagnetic radiation. The reactions are several orders of magnitude faster than thermal reactions; reactions as fast as 10^{-9} seconds and associated processes as fast as 10^{-15} seconds are often observed. Difference between photochemical reactions and thermal reactions are summarized below:

Table 1.1 Difference between thermal and photochemical reactions

THERMAL REACTIONS	PHOTOCHEMICAL REACTIONS
These reactions involve absorption or evolution of heat.	These reactions involve absorption of light.
They can take place even in absence of light i.e. dark.	The presence of light is the primary requisite for the reaction to take place.
Temperature has significant effect on the rate of a thermochemical reaction.	Temperature has very little effect on the rate of a photochemical reaction. Instead, the intensity of light has a marked effect on the rate of a photochemical reaction.
The free energy change ΔG of a thermochemical reaction is always negative.	The free energy change ΔG of a photochemical reaction may not be negative.
They are accelerated by the presence of a catalyst.	Some of these are initiated by the presence of a photosensitizer. However a photosensitizer acts in a different way than a catalyst.

1.3. Laws of photochemistry

Two fundamental principles are the foundation for understanding photochemical transformations: Grotthuss-Draper law and Stark-Einstein law.

1.3.1. The Grotthuss-Draper law: (also called the Principle of Photochemical Activation) was first proposed in 1817 by Theodor Grotthuss and in 1842, independently, by John William Draper states that only that light which is absorbed by a system (molecule) can bring about a photochemical change. This law relates photochemical activity to the fact that each chemical substance absorbs only certain wavelengths of light, the set of which is unique to that substance. Therefore, the presence of light alone is not sufficient to induce a photochemical reaction; the light must also be of the correct wavelength to be absorbed by the reactant species. Here and below, the term "molecule" is broadly defined and includes also atoms, radicals, etc. The law emphasizes the importance of light absorption by the molecule involved in the primary photo process, which is a chemical reaction or a physical process involving directly excited species. All aspects and consequences of this law must be considered for quantitative analysis of a photoreaction. Materials such as dyes and phosphors must be able to absorb "light" at optical frequencies. This law provides a basis for fluorescence and phosphorescence.

In the early 1900s the development of the quantum theory of light—the idea that light is absorbed in discrete packets of **energy** called photons—led to the extension of the laws of

photochemistry. The second law of photo-chemistry, developed by Johannes Stark (1874-1957) and Albert Einstein (1879-1955), states that only one quantum, or one **photon**, of light is absorbed by each molecule undergoing a photochemical reaction. In other words, there is a **one-to-one correspondence** between the number of absorbed photons and the number of excited species. The ability to accurately determine the number of photons leading to a reaction enables the efficiency, or quantum yield, of the reaction to be calculated.

1.3.2. The Stark–Einstein law: The second law is the Stark–Einstein law, which says that primary chemical or physical reactions occur with each photon absorbed. The Stark–Einstein law is named after German-born physicists Johannes Stark and Albert Einstein, who independently formulated the law between 1908 and 1913. It is also known as the **photochemical equivalence law** or **photoequivalence law**. In essence it says that every photon that is absorbed will cause a (primary) chemical or physical reaction that is, only one quantum, or one **photon**, of light is absorbed by each molecule undergoing a photochemical reaction. In other words, there is a **one-to-one correspondence** between the number of absorbed photons and the number of excited species. The ability to accurately determine the number of photons leading to a reaction enables the efficiency, or quantum yield, of the reaction to be calculated.

The photon is a quantum of radiation, or one unit of radiation. Therefore, this is a single unit of EM radiation that is equal to Planck's constant (h) times the frequency of light. This quantity is symbolized by γ , $h\nu$, or $h\omega$. The photochemical equivalence law is also restated as follows: *for every mole of a substance that reacts, an equivalent mole of quanta of light are absorbed*. The formula is:

$$\Delta E_{mol} = N_A h\nu$$

Where N_A is Avogadro's number.

The photochemical equivalence law applies to the part of a light-induced reaction that is referred to as the primary process (i.e. absorption or fluorescence). In most photochemical reactions the primary process is usually followed by so-called secondary photochemical processes that are normal interactions between reactants not requiring absorption of light. As a result such reactions do not appear to obey the one quantum–one molecule reactant relationship. The law is further restricted to conventional photochemical processes using light sources with moderate intensities; high-intensity light sources such as those used in flash photolysis and in laser experiments are known to cause so-called biphotonic processes; i.e., the absorption by a molecule of a substance of two photons of light. Typically several competing processes occur in the excited state. In this case, the second law can be reformulated as: the sum of the quantum yields for the primary processes must be unity.

SAS 1: What is another name for Stark–Einstein law?

1.4 Conclusion

Photochemistry is the chemistry of the effects of light on chemical systems. It is concerned with the interaction of visible and ultraviolet light with molecules. Absorption of visible and/or

ultraviolet light by a molecule introduces energy sufficient to break or reorganize most covalent bonds. Photochemistry plays an important role in everyday life such as in vision, photosynthesis, and the manufacture of many inorganic compounds. Also on photography, modern printing technology, in phototeching used in electronic industry and in the manufacture of integrated circuits used in electronic devices.

1.5 Summary

- The concept of photochemistry is introduced and explained.
- Interaction of radiation with matter is discussed and difference between thermal and photochemical processes highlighted.
- Laws of photochemistry: Grothus-Draper law and Stark-Einstein law provide basis for understanding photochemical transformations.
- The presence of light alone is not sufficient to induce a photochemical reaction; it must also be of the correct wavelength to be absorbed by the reactant species.

1.6 Tutor-Marked Assignments

1. (a) Define photochemistry

(b) Give four areas of its application in everyday life.

2. (a) State the laws of photochemistry

(b) What is the role of photochemistry in everyday life? Discuss the damaging effects of photochemistry.

(c) What is the difference between photochemical and thermal reactions?

1.7 References

1. Turro, N. J. (1991). *Modern Molecular Photochemistry*. University Science Books.
2. Wayne, R. P. (1991). *Principles and Applications of Photochemistry*. 2nd ed., OUP.
3. "Photochemical equivalence law". *Encyclopædia Britannica Online*.
<http://www.britannica.com/EBchecked/topic/457732/photochemical-equivalence-law>.

Unit 2

Photochemical Transformations

2.0 Introduction

The first law of photochemistry, the Grotthuss-Draper law, states that light must be absorbed by a compound in order for a photochemical reaction to take place.

The second law of photochemistry, the Stark-Einstein law, states that for each photon of light absorbed by a chemical system, only one molecule is activated for subsequent reaction. This "photoequivalence law" was derived by Albert Einstein during his development of the quantum (photon) theory of light.

To begin a photochemical process, an atom or molecule must absorb a quantum of light energy from a photon. When this occurs, the energy of the atom or molecule increases above its normal level. The atom or molecule is now in an excited (or activated) state. If a quantum of visible or ultraviolet light is absorbed, then an electron in a relatively low energy state of the atom or molecule is excited into a higher energy state. If infrared radiation is absorbed by a molecule, then the excitation energy affects the motions of the nuclei in the molecule. After the initial absorption of a quantum of energy, the excited molecule can undergo a number of primary photochemical processes. A secondary process may occur after the primary step. The absorption step can be represented by $M \rightarrow M^*$ where the molecule M absorbs a quantum of light of appropriate energy to yield the excited M^* molecule.

2.1 Objectives

At the end of the unit you should be able to:

- Explain the principle of photochemical transformation
- Distinguish between primary and secondary photochemical processes
- Define and write the equation representing quantum yield

- Show the possible decay routes for an electronically excited molecule
- State the difference between fluorescence and phosphorescence
- List and explain the radiative and non-radiative decay routes of an excited molecule

2.2. What happens when light is absorbed by a molecule?

Absorption of visible and/or ultraviolet light by a molecule introduces energy sufficient to break or reorganize most covalent bonds. From the relationship $E = hc / \lambda$, we see that longer wavelength visible light (400 to 800 nm) is less energetic (70 to 40 kcal/mole) than light in the accessible shorter wavelength (200 to 400 nm) near ultraviolet region (150 to 70 kcal/mole). Consequently, ultraviolet light is most often used to effect photochemical change. Care must also be taken to construct lamps and reaction vessels from glass that is transparent to the desired wavelength range. The low wavelength cut-off for some common glass types are given in the table on the right.

Table 2.1: Wavelength Cut-off of Glasses

Type of Glass	Wavelength Cut-off
Pyrex	< 275 nm
Corex	< 260 nm
Vycor	< 220 nm
Quartz	< 170 nm

The electronic configuration changes when light is absorbed by a molecule. The ***Franck-Condon principle*** says that the heavy atom nuclei do not change their positions. This leads to an initial geometry of the excited state which is usually not the energy minimum. During excitation the electron spin remains unchanged. Spin inversion during excitation is forbidden by quantum mechanics and therefore unlikely.

Right after the excitation several things may happen:

- 1) Vibronic relaxation brings the molecule quickly into the new energy minimum structure for the excited state. Energy is released into the solvent. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy.
- 2) Intersystem crossing leads to triplet states by spin inversion. Again, the new energy minimum is reached by vibrational relaxation.
- 3) Emission of light and return to the ground state (luminescence, fluorescence, phosphorescence).
- 4) Quenching of the excited state: Energy is transferred to another molecule. Usually we observe diffusion controlled dynamic quenching by collision. Investigation of this is possible by the Stern-Vollmer plot (1/quantum yield vs concentration of quencher). Gives a straight line for diffusion controlled quenching; large excess of quencher usually needed (1000 times excess).
- 5) Radiationless deactivation. Molecule goes back to ground state by vibrational (thermal) deactivation (no light emission). The energy goes to the solvent/environment of molecule. Alternatively, a photochemical reaction may occur.

SAS 2: Explain the term radiative deactivation.

2.3 Primary photochemical processes

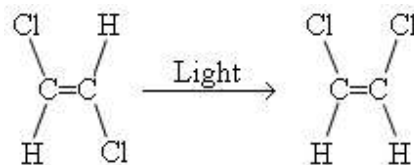
Listed below are the various primary processes that the excited M^* molecule can undergo.

The highly energized—or excited—molecule may return to its initial state according to any of three physical processes: 1) it can release its excitation energy by emitting luminescent radiation through fluorescence or phosphorescence.

2) It may transfer its energy to some other molecule, C, with which it collides, without emitting light. The latter energy transfer process results in a normal molecule, M, and an excited molecule, C^* .

3) As a result of the initial light absorption step, an electron (e^-) in the atom or molecule may absorb so much energy that it may escape from the atom or molecule, leaving behind the positive M^+ ion. This process is called *photoionization*.

If the excited M^* molecule (or atom) does react, then it may undergo any of the following chemical processes: photodissociation, intramolecular (or internal) rearrangement, and reaction with another molecule C. Photodissociation may result when the excited molecule breaks apart into atomic and/or molecular fragments A and B. A rearrangement (or photoisomerization) reaction involves the conversion of molecule M into its isomer N—a molecule with the same numbers and types of atoms but with a different structural arrangement of the atoms. The conversion of *trans*-1,2-dichloroethylene into the *cis* isomer is an example of intramolecular rearrangement. The reaction is shown below:



In the *trans* isomer the chlorine atoms lie on opposite sides of the double bond, whereas in the *cis* isomer they are on the same side of the double bond.

SAS 3: What is photodissociation?

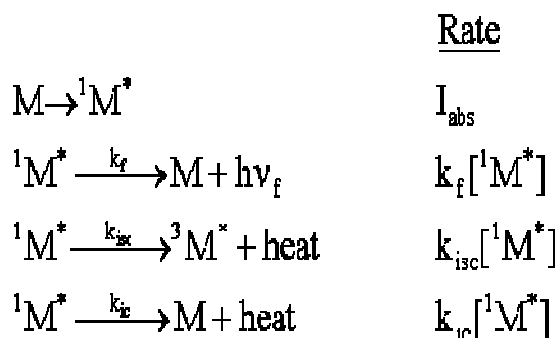
2.4 Quantum Yield and Lifetimes

The energy that a molecule gains when it absorbs light is subsequently lost in one of several ways. As shown graphically in the Jablonski diagram (Figure 2.2), it can lose the energy as heat as it returns to the ground state (internal conversion). Alternately, it can lose the energy as light (fluorescence), usually on a nanosecond time scale. A third pathway is intersystem crossing to a triplet state, from which energy can also be lost as light (phosphorescence), but over much longer

times (microseconds or longer). And finally, the energy can be transferred to another molecule.

The *quantum yield* of a process is the probability that an absorbed photon undergoes one particular process. Thus, one can define a quantum yield for fluorescence, a quantum yield for phosphorescence, or a quantum yield for other pathways. Each quantum yield is typically a number between 0 and 1 (except under unusual circumstances), and the total of all quantum yields for a particular absorption event should sum to one. Note that these processes are competing. If conditions are altered such that the quantum yield for fluorescence is increased, then the quantum yield for some other processes must decrease.

Consider a molecule, M, that is exposed to light, and absorbs photons at the rate, I_{abs} . As shown in the following formulas, the excited singlet state of the molecule, $^1M^*$, can fluoresce emitting a photon, $h\nu_f$. It can lose energy as heat, and move to the triplet excited state, $^3M^*$, by intersystem crossing (*isc*). Finally, it can lose energy as heat, and move to the ground state by internal conversion (*ic*). The rate of each of these loss processes will be proportional to the concentration of the excited singlet state, $^1M^*$, and a rate constant, k , for each process, as given in the second column below.

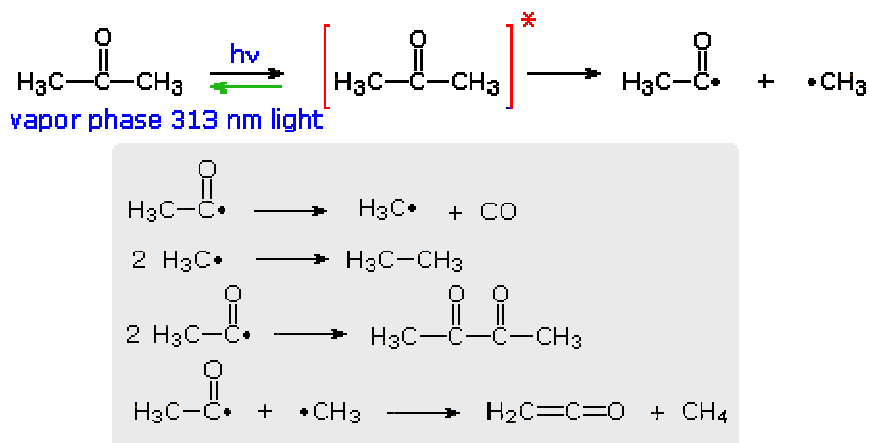


Because the lifetime of the singlet excited state is relatively short, we can assume that the entire excited singlet states that are formed by light absorption will rapidly decay through one of the three means just described. This is the "steady state" approximation. Since the rate of formation of the excited singlet state is I_{abs} , then the sum of the rates of loss, each given above, must be equal to the rate of formation.

$$I_{\text{abs}} = \sum_i k_i [^1M^*]$$

From this relationship, one can determine the quantum yield for each process. It is simply the rate of that process as a fraction of all pathways for the loss of energy.

The efficiency with which a given photochemical process occurs is given by its **Quantum Yield** (Φ). Since many photochemical reactions are complex, and may compete with unproductive energy loss, the quantum yield is usually specified for a particular event. Thus, we may define quantum yield as *"the number of moles of a stated reactant disappearing, or the number of moles of a stated product produced, per Einstein of monochromatic light absorbed."* where an einstein is one mole of photons. For example, irradiations of acetone with 313 nm light (3130 Å) gives a complex mixture of products, as shown in the following diagram. The quantum yield of these products is less than 0.2, indicating there are radiative (fluorescence & phosphorescence) and non-radiative return pathways. The primary photochemical reaction is the homolytic cleavage of a carbon-carbon bond shown in the top equation. Here the asterisk represents an electronic excited state, the nature of which will be defined later.



Several secondary radical reactions then follow (shown in the gray box), making it difficult to assign a quantum yield to the primary reaction. The biacetyl product, formed in the third reaction, may itself be excited by light or accept excitation energy from an excited acetone molecule, further complicating this process. By comparison, the light induced chlorination of methane, or other alkanes, has a large quantum yield, often near 10^6 , because of the secondary chain reactions that follow the primary cleavage of the Cl-Cl bond.

Quantum Yield can also be defined in fluorescence (emission) in which case the quantum yield is a measure of the efficiency with which absorbed light produces some effect and the quantum yield can be defined by the equation:

(1)

$$\phi = \frac{\text{number of molecules undergoing the reaction of interest}}{\text{number of photons absorbed by the photoreactive substance}}$$

Eq. (1) would define the quantum yield of product formation, ϕ_p , if the number of product molecules would be determined. If the two numbers in Eq. (1) are measured per time and volume unit then the quantum yield is expressed in terms of rates.

(2)

$$\phi = \frac{\text{rate of the reaction of interest}}{\text{rate of light absorption by the photoreactive substance}}$$

The latter quantity is also referred to as the differential quantum yield. Notice that these two definitions of the quantum yield agree only if the yield is constant during the course of the reaction. Eqs. (1) and (2) indicate that two separate measurements may be required to determine a quantum yield. In the simplest set-up, a reaction cell is mounted in a fixed position relative to the light source. The cell is charged with the sample of interest and irradiated. Photochemical conversion is determined with a suitable experimental technique (spectroscopy, chemical analysis, etc.).

2.5 Electronic Excitation

We begin by considering the electronic excitation of a simple diatomic molecule such as Cl_2 or Br_2 . Both absorb light, chlorine in the 300 to 380 nm region and bromine in the 360 to 510 nm region. The diagram on the right illustrates the initial electronic excitation. Both the ground (lowest energy electronic state) and excited states are shown as energy profiles populated by vibrational energy states (green lines) as well as rotational states (not shown). The electron reorganization that occurs when the ground electronic state is excited by absorption of a photon takes place much more rapidly than any movement of the atom nuclei that eventually follow. In other words, electron shifts, when viewed from the perspective of the nuclear coordinates, occur as if the heavier nuclei were fixed in place. This consequence of the Born-Oppenheimer approximation led James Franck and R. Condon to formulate the **Franck-Condon Principle**: *Electronic transitions occur much faster than nuclei can respond.*

Overall bonding in an excited state is usually lower than in the ground state. Thus, the X–X bond length is increased in the excited state. At normal temperatures essentially all molecules will exist in the ground vibrational state (zero level). The Franck-Condon principle requires that excitation occur by a vertical transition, shown by the red line, resulting in the population of higher vibrational levels in the excited state. Several events may then take place.

1. The vibrational energy may be lost as heat, relaxing the excited state to its zero vibrational level.
2. The excited state may return to the ground state by emitting a photon (light blue line). If this happens from the zero vibrational level the frequency or energy of the emitted light will be lower than that of the initially absorbed light. This radiative decay is called **fluorescence** if it takes place rapidly from the initial excited state. It is termed **phosphorescence** if it occurs slowly by way of other excited states.

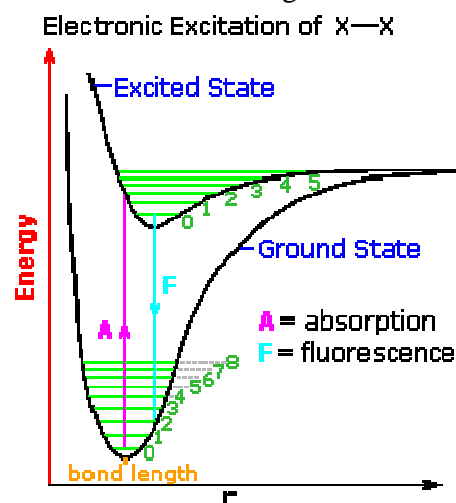


Figure 2.1 Franck-Condon Energy Level Diagram

3. If a higher vibrational level of the excited state is populated, either by the initial Franck-Condon transition or by collisional activation, the molecule may cleave into two $X\bullet$ atoms. Note that vibrational level 5 of the excited state is roughly coincident with bond breaking.

Virtually all organic compounds have more than two atoms, so the potential energy state diagram of X_2 must be adjusted for the increased number of bonding relationships. One way of doing this is to retain the energy coordinate while dispensing with the dimensional (r) coordinate. The **Jablonski diagram** shown below is an example, in which the spatial orientation of the various electronic states is not specified. Nevertheless, Franck-Condon transitions are expected. One important feature conveyed by the diagram is that more than one electronic excited state is likely to exist for a given molecule; six are drawn and labeled in the diagram. Each electronic state will have a group of vibrational (and rotational) states, depicted by light blue lines above each state marker. Transitions between electronic states often occur to higher vibrational levels which then relax to lower levels by collisional loss of heat (translational energy).

2.6 Possible fates of an electronically excited molecule: Jablonski diagram

The energy gained by a molecule when it absorbs a photon causes an electron to be promoted to a higher electronic energy level. The figure below illustrates the principal photophysical radiative and non-radiative processes displayed by organic molecules in solution. The symbols S_0 , S_1 , T_2 , etc., refer to the ground electronic state (S_0), first excited singlet state (S_1), second excited triplet state (T_2), and so on. The horizontal lines represent the vibrational levels of each electronic state. Straight arrows indicate radiative transitions, and curly arrows indicate non-radiative transitions.

Note that all transitions from one electronic state to another originate from the lowest vibrational level of the initial electronic state. For example, fluorescence occurs only from S_1 , because the higher singlet states (S_2 , etc.) decay so rapidly by internal conversion that fluorescence from these states cannot compete.

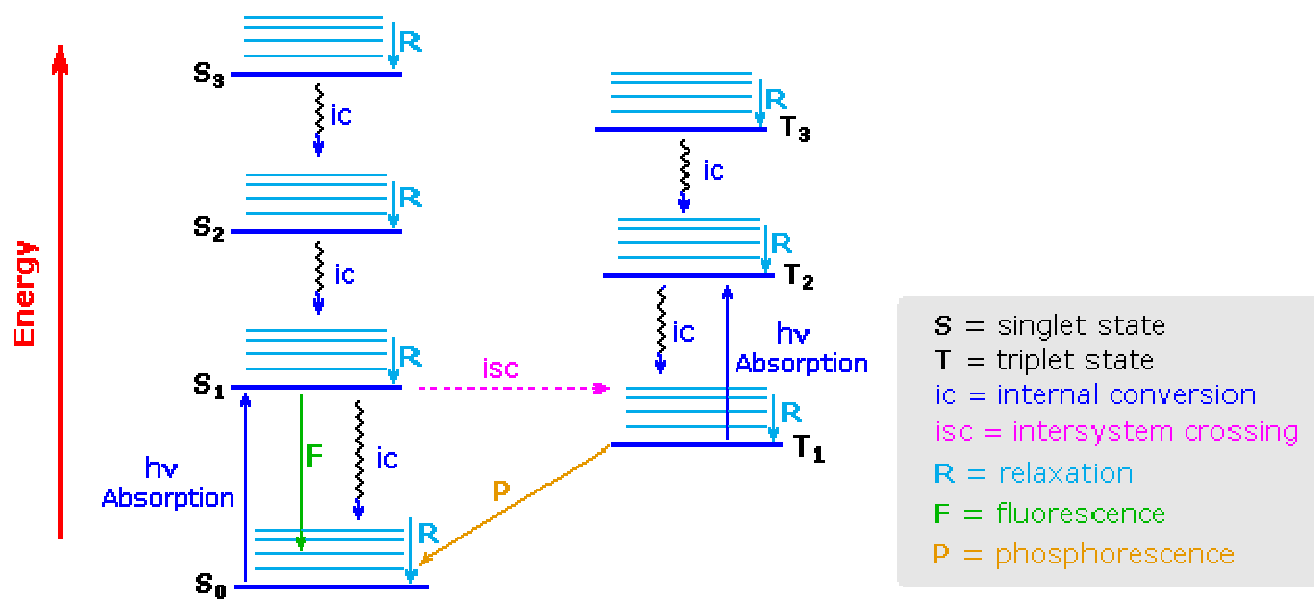


Figure 2.2 A Jablonski diagram

Excited states may be classified as singlet or triplet based upon their electron spin angular momentum. The electrons in most non-metallic organic compounds are paired (opposite spins) in bonding and non-bonding orbitals, resulting in a net zero spin diamagnetic molecule for the ground state. Such states have a single energy state in an applied magnetic field, and are called singlets. Electronic states in which two electrons with identical spin occupy different orbitals (the Pauli Exclusion Principle) have a net spin of 1 ($2 \cdot 1/2$) and are paramagnetic. In a magnetic field such states have three energy levels (+1, 0, -1) and are called triplets. Molecular oxygen is a rare example of a triplet ground electronic state.

The distinction between singlet and triplet states is important because photon induced excitation always leads to a state of the same multiplicity, i.e. singlet to singlet or triplet to triplet. Since most ground states are singlets, this means that the excited states initially formed by absorption of light must also be singlets. Internal conversion of excited states to lower energy states of the same multiplicity takes place rapidly with loss of heat energy (relaxation). Alternatively, an excited state may return to the ground state by emitting a photon (radiative decay). In the study of acetone described above, nearly 80% of the excited singlet states lose energy by internal conversion and about 3% by fluorescence. Conversion of a singlet state to a lower energy triplet state, or vice versa, is termed intersystem crossing and is slower than internal conversion. Radiative decay from a triplet state is called phosphorescence and is generally quite slow. The approximate timescales for these transitions are given in the following table.

Table 2.2 Timescales for Electronic States Transitions

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

The non-radiative decay noted in the last row may take place by intermolecular energy transfer to a different molecule. This collisional process is termed **quenching** if the focus is on the initially excited species or **sensitization** if the newly created excited state is of interest. Photochemical sensitization commonly occurs by a $T_1 + S_0 \rightarrow S_0 + T_1$ reaction, where the bold red-colored species is the sensitizer. The new triplet excited state may then undergo characteristic reactions of its own.

2.7 Possible decay routes for an electronically excited molecule

- Fluorescence
- Phosphorescence
- Internal Conversion
- Intersystem Crossing
- Isomerisation
- Dissociation (Predissociation)
- Collisional Relaxation (Quenching)

All these are traditionally summarised using a *Jablonski diagram*.

S_0 = ground singlet ($S = 0$) state

S_1, \dots, n = singlet states of progressively higher energy

T_1, \dots, n = excited triplet ($S = 1$) states.

SAS 4: List any four possible decay routes for an electronically excited molecule.

Fluorescence: Radiative decay between states of *same* spin multiplicity (*i.e.* $\Delta S=0$). Emission of electromagnetic radiation, usually visible light, caused by excitation of atoms in a material which

then reemit immediately (within about 10^{-8} seconds). The initial excitation is usually caused by the absorption of energy from incident radiation of particles, such as X-Rays or electrons. Because reemission occurs so quickly the fluorescence ceases as soon as the exciting source is removed, unlike phosphorescence, which persists as an afterglow. A fluorescent light bulb is coated on the inside with a powder and contains a gas; electricity causes the gas to emit ultraviolet radiation, which then stimulates the tube coating to emit light.

George Gabriel Stokes named the phenomenon *fluorescence* in 1852. He chose the name “to denote the general appearance of a solution of sulphate of quinine and similar media”. The name was derived from the mineral fluorite (calcium difluoride), some examples of which contain traces of divalent europium, which serves as the fluorescent activator to emit blue light.

Fluorescence has many practical applications, including mineralogy, gemology, chemical sensors, fluorescence labeling, dyes, biological detectors, and, most commonly, fluorescent lamps. The most striking examples of fluorescence occur when the absorbed radiation is in the ultraviolet region of the spectrum, and thus invisible and the emitted light are in the visible region.

Rules: There are further rules that deal with fluorescence. The “Kasha-Vavilov” rule dictates that the quantum yield of luminescence is independent of the wavelength of exciting radiation. The “Jablonski diagram” describes most of the relaxation mechanism for excited state molecules.

Phosphorescence: Radiative decay between states of different spin multiplicity (*i.e.* $\Delta S \neq 0$). The emission of light from a substance exposed to radiation and persisting as an afterglow after the exciting radiation has been removed. Unlike fluorescence, in which the absorbed light is spontaneously emitted about 10^{-8} seconds after excitation, phosphorescence requires additional excitation to produce radiation and may last from about 10^{-3} seconds to days or years depending on the circumstances. The study of phosphorescent materials led to discovery of radioactivity in 1896. Unlike fluorescence, phosphorescence is temperature dependent. In simple term phosphorescence is a process in which energy absorbed by a substance is released relatively slowly in the form of light. This is in some cases the mechanism is used for “Glow- in- the-dark” material which are charged by exposure to light. Unlike the relatively swift reaction in a common fluorescent tube, phosphorescent materials used for these materials absorb the energy and store it for a longer time as the processes required to re-emit the light occur less often.

Phosphorescent Substances: Phosphorescent substances have the ability to store up light and release it gradually. The notion of a metastable state explains this. If the molecules of the substance can get from the ground state to a metastable state, and if the metastable state can slowly decay back to the ground state via photon emission, then we have phosphorescence.

Chemiluminescence: It is the generation of electromagnetic radiation as light by the release of energy from a chemical reaction. While the light can, in principle, be emitted in the ultraviolet, visible or infrared region, those emitting visible lights are most common. Chemiluminescent reactions can be grouped into three types:

1. Chemical reactions using synthetic compounds and usually involving a highly oxidized species such as peroxide are commonly termed chemiluminescent reactions.
2. Light-emitting reactions arising from a living organism, such as the firefly or jellyfish, are commonly termed bioluminescent reactions.
3. Light-emitting reactions which take place by the use of electrical current are designated electrochemiluminescent reactions.

Chemiluminescence differs from fluorescence in that the electronic excited state is derived from the product of a chemical reaction rather than the more typical way of creating electronic excited states, namely absorption. It is the antithesis of a photochemical reaction, in which light is used to drive an endothermic chemical reaction. Here, light is *generated* from a chemically exothermic reaction.

A standard example of chemiluminescence in the laboratory setting is found in the luminol test, where evidence of blood is taken when the sample glows upon contact with iron. When light chemiluminescence takes place in living organisms, the phenomenon is called bioluminescence. A light stick emits by chemiluminescence.

Photosensitization: This is a process of initiating a reaction through the use of a substance capable of absorbing light and transferring the energy to the desired reactant. The technique is commonly employed in photochemical work, particularly the reactions requiring light source of certain wavelength that are not readily available.

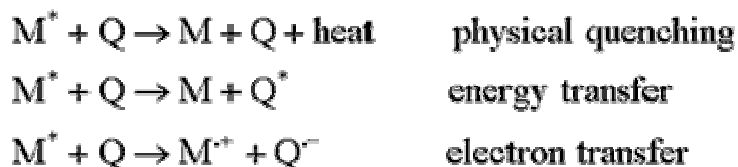
Example: A commonly used sensitizer is Mercury which absorbs radiation at 1849 and 2537 angstroms; these are the wavelength of light produced in high intensity Mercury lamps. Another used sensitizer is Cadmium, some of the Noble Gases particularly Xenon, Zinc and a large number of Organic Dyes.

Internal Conversion: Radiationless transition between states of same spin multiplicity (e.g. $S_n \rightsquigarrow S_m <n \text{ or } T_n \rightsquigarrow T_m <n$). Internal conversion is a transition from a higher to a lower electronic state in a molecule or atom. It is sometimes called "radiationless de-excitation", because no photons are emitted. It differs from intersystem crossing in that, while both are radiationless methods of de-excitation, the molecular spin state for internal conversion remains the same, whereas it changes for intersystem crossing. The energy of the electronically excited state is given off to vibrational modes of the molecule or phonons. The excitation energy is transformed into heat.

A classic example of this process is the quinine sulfate fluorescence, which can be quenched by the use of various halide salts. What happens is that the excited molecule can de-excite by increasing the thermal energy of the surrounding solvated ions

Intersystem Crossing: Radiationless transition between states of differing spin multiplicity (e.g. $S_n \rightsquigarrow T_n$). This process, intersystem crossing is the non-radiative conversion of a singlet state to a lower energy triplet state, or vice versa and is slower than internal conversion.

Excited State Quenching: When a second molecule interacts with a molecule in an excited state, new ways may be created for the excited state species to lose its energy of excitation. Such interactions (collisions) can induce the loss of energy in the form of heat, which is called physical quenching, or it can cause the energy to be transferred to the second molecule with or without the transfer of an electron. The former is called simply energy transfer, and the latter electron transfer. Formally, one can write:



When this kind of quenching occurs it reduces the concentration of the excited state more rapidly than if the quencher were not present. This means that fluorescence, which is proportional to the concentration of the excited state, will also be reduced.

SAS 5: Mention two radiationless or non-radiative deactivation processes.

2.8 Conclusion

In this unit you learnt about possible processes after the initial absorption of a quantum of energy. You should have learned that the excited molecule can undergo a number of radiative and non-radiative photochemical processes. Most of these processes are unproductive energy-loss events competing with the complex photochemical reactions thereby reducing the quantum yield of the products.

2.9 Summary

- Statement of laws of photochemistry are recalled and applied to the efficiency of photochemical reactions.
- Quantum yield is a measure of the efficiency with which absorbed light produces some effects.
- A molecule in the excited state may rapidly deactivate via fluorescence or radiationless decay, it may undergo intersystem crossing into the triplet manifold.
- The Jablonski diagram summarizes the possible fates of an excited molecule.
- phosphorescence is a process in which energy absorbed by a substance is released relatively slowly in the form of light

2.10 Tutor-Marked Assignments

1 (a) Differentiate between: (i) fluorescence and phosphorescence (ii) internal conversion and intersystem crossing.

(b) What the possible deactivation routes for an electronically excited molecule?

(c) Define quantum yield and give the mathematical representation.

2.11 References

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2. Turro, N.J. (1991). *Modern Molecular Photochemistry*. University Science Books, Mill-Valley, California.
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Unit 3

Photochemical Reactions

3.0 Introduction

A photochemical reaction is a chemical reaction that is induced by light. Photochemical reactions are valuable in organic and inorganic chemistry because they proceed differently from thermal reactions. Photochemical reactions involve electronic reorganization initiated by electromagnetic radiation. The reactions are several orders of magnitude faster than thermal reactions; reactions as fast as 10^{-9} seconds and associated processes as fast as 10^{-15} seconds are often observed. The light required for a photochemical reaction may come from many sources. Giacomo Ciamician, regarded as the "father of organic photochemistry", used sunlight for much of his research at the University of Bologna in the early 1900's. Depending on the compounds being studied and the information being sought, bright incandescent lamps (chiefly infrared and visible light), low, medium and high pressure mercury lamps (185 - 255 nm, 255 -1000 nm & 220 -1400 nm respectively), high intensity flash sources and lasers have all been used. In careful studies of specific chromophores, sources of monochromatic light may be desired.

In this unit we shall focus chiefly on the nature and behavior of the electronic excited states formed when a photon is absorbed by a chromophoric functional group. As a rule, such excitation results in a change in molecular orbital occupancy, an increase in energy, and changes in local bonding and charge distribution. (A revision on the principles of the UV-Visible spectroscopy will provide a helpful foundation).

3.1 Objectives

By the end of this unit you should be able to:

- Define a photochemical reaction
- Explain photochemical reaction pathway
- List the features of photochemical reactions
- Classify photochemical reactions with examples

3.2. Features of photochemical reactions:

1. photochemical reactions do not take place in dark but take place in the presence of light by absorbing it.

2. Since different colored radiations in the range of visible light have different frequencies and hence different energies, therefore all radiations may not be able to initiate a particular reaction. For example, a photon of violet light has highest frequency and hence the highest energy. Hence a reaction which is initiated by violet light may not be initiated by other colored radiations of visible light. On the other hand, a photon of red light has lowest frequency and energy. Therefore a reaction that can be initiated by red light can be initiated by all other radiations as well.

3. Temperature has very little effect on the rate of a photochemical reaction. Instead, the intensity of light has marked effect on the rate of photochemical reaction.

4. The free energy change of a photochemical reaction may not be negative.

5. There are many substances which do not react directly when exposed to light. However, if another substance is added, the photochemical reaction starts

3.2.1. Why are photochemical reactions interesting?

1) The excited states are rich in energy. Therefore reactions may occur that are highly endothermic in the ground state. Using the equation $E = h \times \nu$ we can correlate light of a wavelength of 350 nm with an energy of 343 kJ/mol!

2) In the excited state antibonding orbitals are occupied. This may allow reactions which are not possible for electronic reasons in the ground state.

3) Photochemical reaction can include singlet and triplet states; thermal reactions usually only show singlet states. In photochemical reaction intermediates may be formed which are not accessible at thermal

3.2.2 Essential criteria for all photochemical reactions:

- Molecule must absorb light
- Radiation energy must match energy difference of ground and excited state

Typical absorption range of some important classes of organic compounds:

Simple alkene	190 - 200 nm
Acylic diene	220 - 250 nm
Cyclic diene	250 - 270 nm
Styrene	270 - 300 nm
Saturated ketones	270 - 280 nm
α,β -Unsaturated ketones	310 - 330 nm
Aromatic ketones/aldehydes	280 - 300 nm
Aromatic compounds	250 - 280 nm

3.2.3 When light is absorbed by a molecule what happens?

1) Vibronic relaxation brings the molecule quickly into the The electronic configuration changes at the absorption of light by a molecule. The *Franck-Condon principle* says that the heavy atom nuclei do not change their positions. This leads to an initial geometry of the excited state which is usually not the energy minimum. During excitation the electron spin remains un-changed. Spin inversion during excitation is forbidden by quantum mechanics and therefore unlikely.

Right after the excitation several things may happen.

new energy minimum structure for the excited state. Energy is released into the solvent.

2) Intersystem crossing leads to triplet states by spin inversion Again, the new energy minimum is reached by vibrational relaxation.

3) Emission of light and return to the ground state (luminescence, fluorescence, phosphorescence).

4) Quenching of the excited state: Energy is transferred to another molecule. Usually we observe diffusion controlled dynamic quenching by collision. Investigation of this is possible by the Stern-Vollmer plot ($1/\text{quantum yield}$ vs concentration of quencher). Gives a straight line for diffusion controlled quenching; large excess of quencher usually needed (1000 times excess).

5) Radiationless deactivation. Molecule goes back to ground state by vibrational (thermal) deactivation (no light emission). The energy goes to the solvent/environment of molecule.

Alternatively: A photochemical reaction may occur.

3.3 Factors Determining Outcome of a Photochemical Reaction

The wide variety of molecular mechanisms of photochemical reactions makes a general discussion of such factors very difficult. The chemical nature of the reactant(s) is definitely among the most important factors determining chemical reactivity initiated by light. However, a better understanding of this aspect may be gained from a closer examination of the individual groups of chemical compounds. The nature of excited states involved in a photoreaction is directly related to the electronic structure of the reactant(s).

Environmental variables, i.e., parameters that are not directly related to the chemical nature of the reacting systems, may also strongly affect photochemical reactivity. It is useful to distinguish between variables that are common for thermal and photochemical reactions, and those that are specific for the reactions of excited species. The first group includes reaction medium, reaction mixture composition, temperature, isotope effects to name the most important. The distinctive feature of photochemical reactions is that these parameters almost always operate under conditions when one or more photophysical processes compete with a photoreaction. The result of a photoinduced transformation can only be understood as the interplay of several processes corresponding to passages on and between at least two potential energy surfaces.

Reaction medium may directly modify the potential energy surfaces of the ground and excited states and hence affect the photoreactivity. The outcome of some reactions changes dramatically when solvent polarity and hydrogen bonding capacity are changed. The protolytic photodissociation of 1-naphthol is completely suppressed in aprotic solvents because of unfavorable solvation energies both for the anion and proton. Under such conditions, proton transfer reaction cannot compete with the deactivation.

Solvent viscosity will strongly affect photoreactions where the encounter of two reactants or a substantial structural change is required. In highly viscous or solid solutions the loss of excitation via light emission or unimolecular non-radiative deactivation is more probable than a chemical modification of the excited species. On the other hand, slow diffusion in viscous solutions may prevent self-deactivation of the triplet state via a bimolecular process called triplet-triplet annihilation and enhance the efficiency of a photoreaction from this state. Triplet-triplet annihilation belongs to electronic-energy transfer processes, which may be classified as quenching of excited states. Quenching rate is a very important factor in discussing effects of

3.4 Types of Photoreactions

There exists a plethora of photoreactions practically for each class of chemical compounds. These reactions may be categorized according to chemical composition and structure. They may also be classified under different types by using theoretical models for the description of the excited state(s) or structure of the potential energy surface. However, for our introductory discussion it seems to be more appropriate just to consider some examples classified by general reaction types (Figure 3.1).

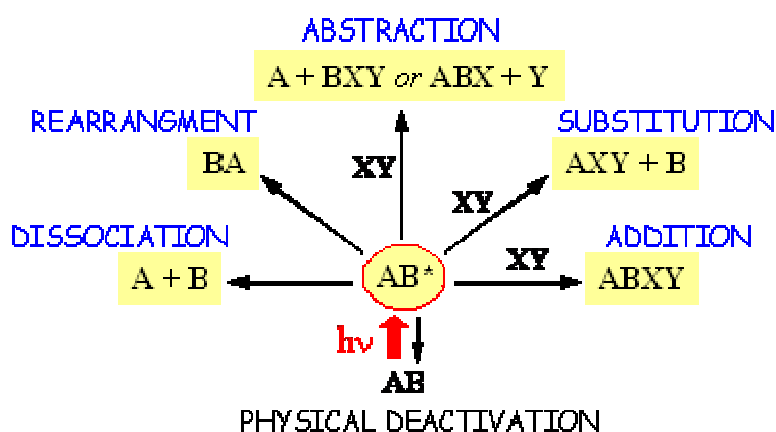
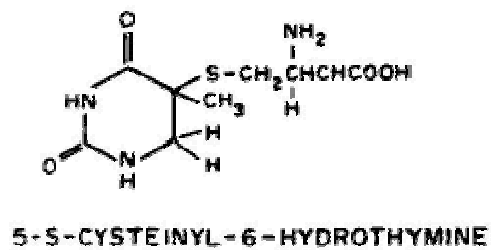
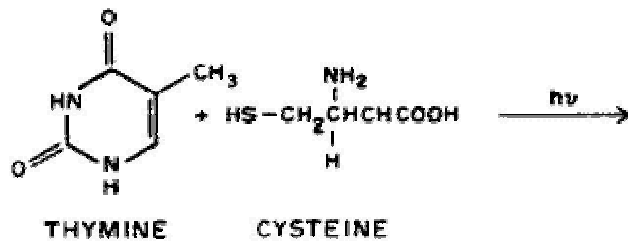
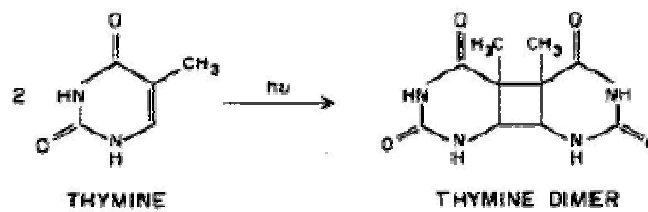


Figure 3.1. Multiple reaction pathways for electronically excited species.

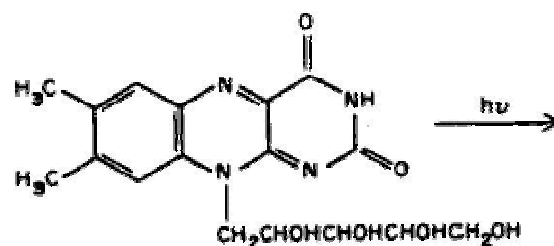
3.4.1. *Linear addition to an unsaturated molecule*, e.g., the pyrimidine base, thymine, in DNA can combine with the amino acid residue, cysteine, in proteins. This is a model for the photochemical crosslinking of DNA and proteins by UV radiation.



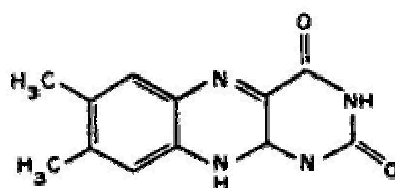
3.4.2. *Cycloaddition of unsaturated molecules*, e.g., two thymines can react to form a ring product, the thymine dimer, an important class of products formed in DNA by UV radiation (see the section on Ultraviolet Radiation Photobiology).



3.4.3. *Photofragmentation*, e.g., the side chain of riboflavin can split off to form lumiflavin.



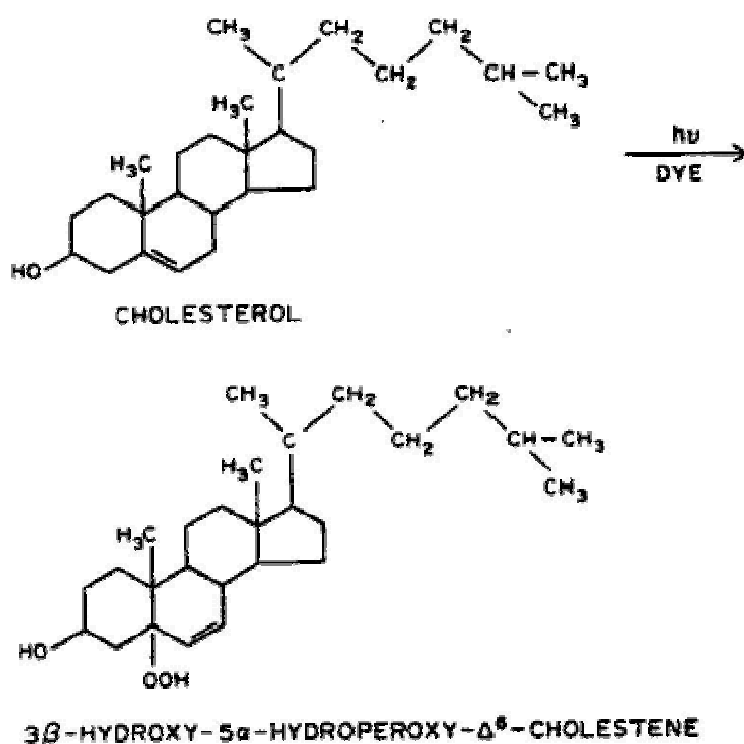
RIBOFLAVIN



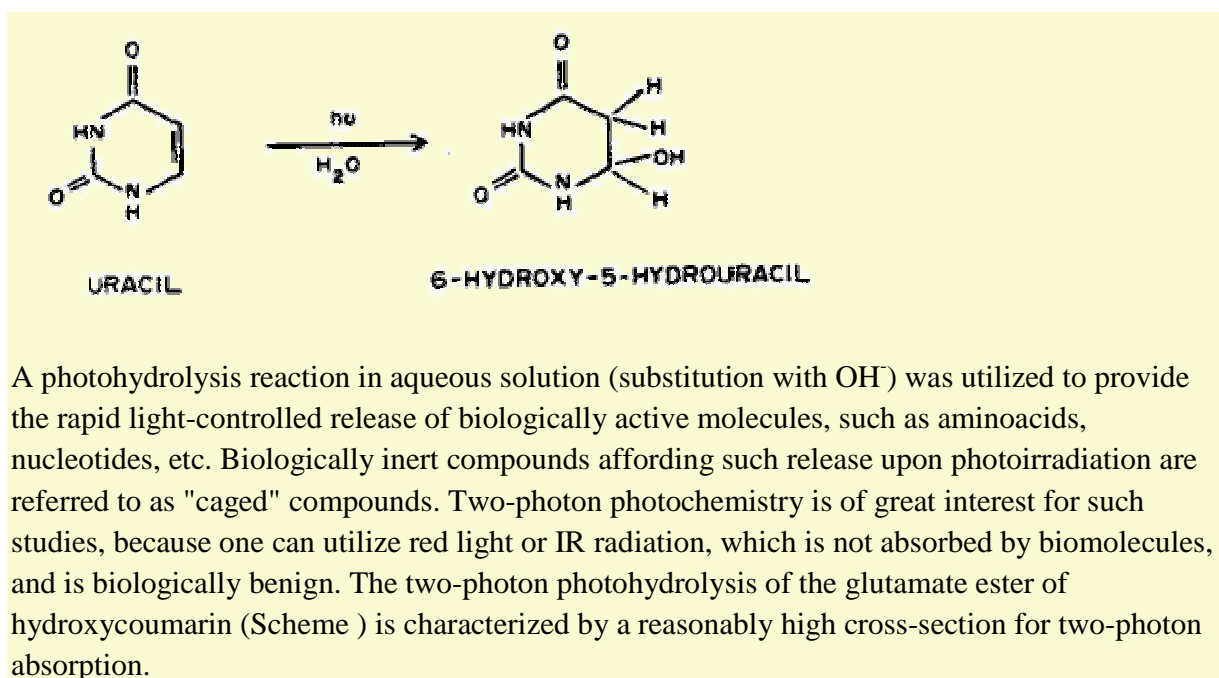
LUMIFLAVIN



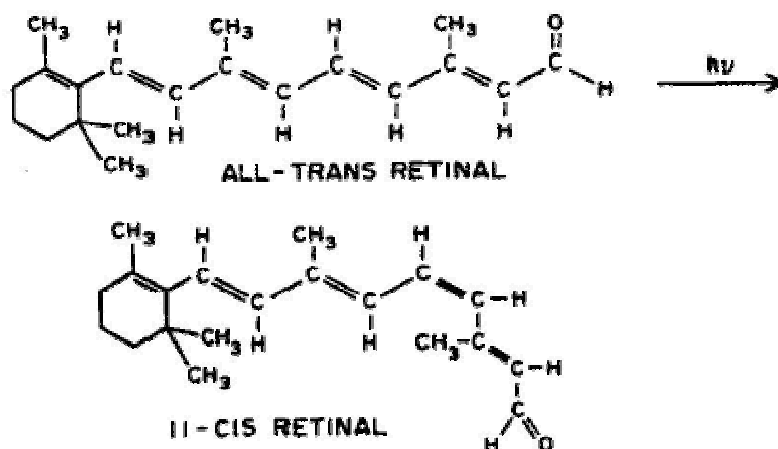
3.4.4. *Photooxidation*, Singlet oxygen is an easily available reagent. It can be generated from triplet oxygen in many solvents by a broad variety of sensitizers. The reaction of organic compounds with singlet oxygen can lead to reactive molecules, such as hydroperoxides, 1, 2-dioxetanes and endoperoxides. These compounds are useful for subsequent transformations. e.g., the ring structure of cholesterol can add a peroxy group.



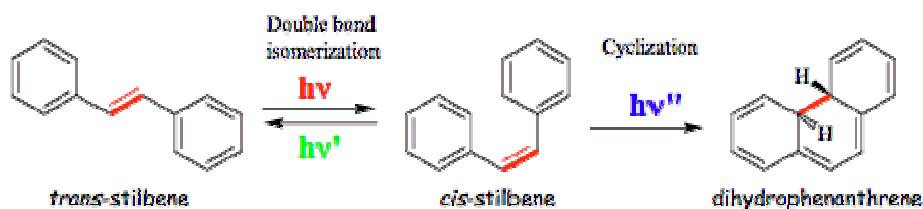
3.4.5. *Photohydration*, e.g., uracil can add a molecule of water to its 5-6 double bond when UV irradiated.



3.4.6. *Cis-Trans Isomerization*, e.g., all-*trans* retinal can be converted to 11-*cis* retinal.

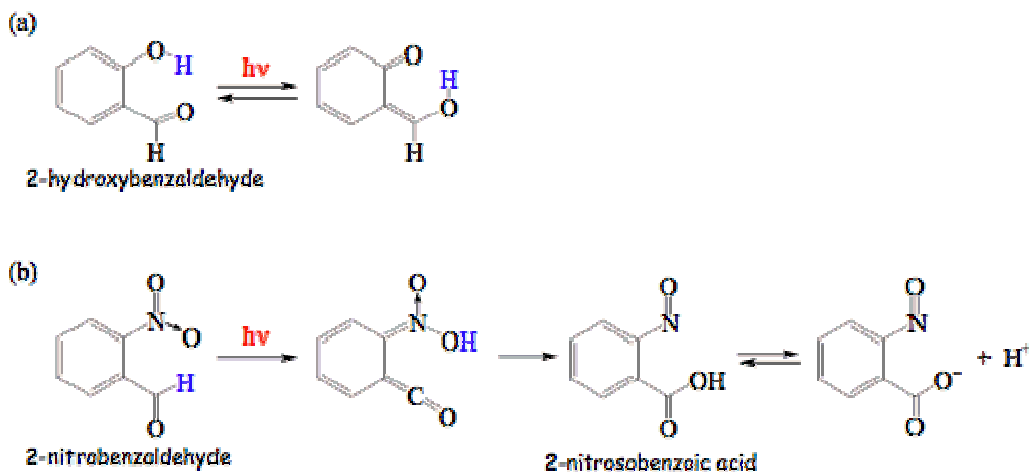


Rearrangements of electronically excited molecules present one of the most exciting chapters in photochemistry in the sense that they follow reaction pathways that are usually inaccessible for the ground state (activation barriers in the ground state are very high). The *cis-trans* isomerization of double bonds belongs to such reactions. The azobenzene reaction provides an instructive example. Scheme 1 shows photoinduced rearrangements of stilbene that has been extensively studied. In addition to double bond isomerization, *cis*-stilbene undergoes also cyclization with a lower quantum yield to form dihydrophenanthrene. The *cis-trans* isomerization of stilbene occurs through rotation around the double bond. In the ground state this rotation encounters a large barrier, i.e., there is a maximum on the ground-state potential energy surface at the geometry corresponding to a twist angle of about 90° . In contrast, both the first singlet excited state and triplet state have a minimum approximately at the same geometry. The close proximity of the minimum and maximum facilitates a jump to the ground state. The *cis-trans* isomerization of azobenzene may proceed not only through rotation, but also through nitrogen inversion, i.e. in-plane motion of the phenyl ring.



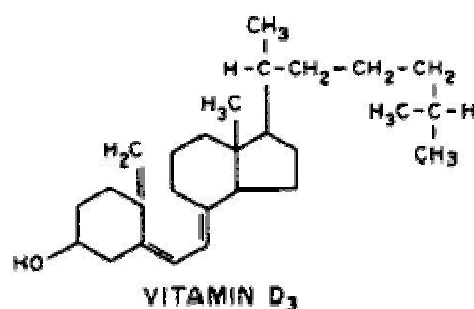
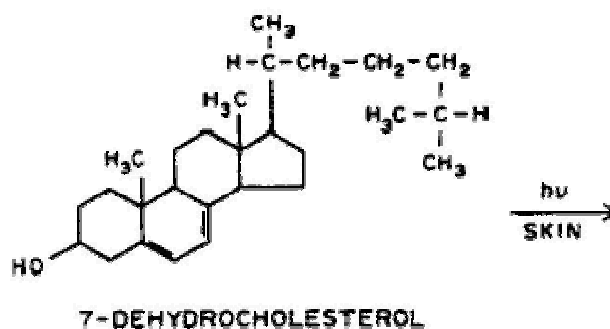
Scheme 1

3.4.7. *Photorearrangement*, Two illuminating examples of photoinduced rearrangements of substituted benzaldehydes are presented in Scheme 2. Intramolecular hydrogen transfer in 2-hydroxybenzaldehyde is an extremely fast reaction in the singlet excited state. However, the process is completely reversed upon a jump to the ground state. Overall, no chemical conversion is observed and excitation energy is either dissipated as heat or emitted as light, but with a longer wavelength. This behavior is typical for aromatic carbonyl compounds with *ortho*-hydroxy groups, and they found application as UV protectors, in sunscreens for example. Molecules acting as UV protectors absorb light that is harmful for biological molecules, and convert light into heat or radiation that is biologically benign. In contrast, an intramolecular hydrogen transfer in 2-nitrobenzaldehyde initiates a sequence of the ground-state reactions that leads to 2-nitrosobenzoic acid. The latter molecule is a moderately strong acid, and dissociates in aqueous solutions so that the photochemistry of 2-nitrobenzaldehyde can be used to create a rapid pH-jump in solution. Many biological macromolecules, such as proteins and nucleic acids, show pH-dependent conformational changes. Those changes can be monitored in real time by using the light-induced pH-jump.



Scheme 2

Another important example is the conversion of 7-dehydrocholesterol to vitamin D₃.



3.4.8. *Energy Transfer*, e.g., all photosensitized reactions (Photosensitization).

When a second molecule is located near an electronically excited molecule, the excitation can be transferred from one to the other through space. If the second molecule is chemically different, there can be a substantial change in the luminescence. For example, the chemiluminescence of a jellyfish is actually blue, but, because the energy is transferred to GFP, the observed fluorescence is green.

Photosensitized molecular oxygen is a powerfully oxidative species that severely hampers the photosynthetic efficiency of plants and causes health problems such as cataracts in humans. The ground state of molecular oxygen is very unusual in that it is a triplet; hence, it can accept electronic energy from more-energetic triplet states of other molecules in a process called quenching (as in the case of the space shuttle wing described above). When this occurs, the donor molecule begins in its triplet state and undergoes a change in spin to its singlet ground state. The molecular oxygen begins in its triplet ground state and also changes spin to a singlet excited state. Because the total spin between the two molecules is unchanged, the transfer of energy can occur rapidly and efficiently. The resulting molecular oxygen singlet state phosphoresces in the far red and the near infrared. Moreover, it is both a strong oxidant and peroxidant and, if formed, may chemically attack (oxidize) a nearby molecule, often the same molecule that sensitized the molecular oxygen. The oxidation reaction often changes the molecule to a form without colour. This light-induced bleaching (one kind of photodamage) can be observed in nearly any coloured material left in sunlight. In fact, the photosynthetic systems in plants must be continuously dismantled, repaired, and rebuilt because of photodamage (primarily from singlet molecular oxygen).

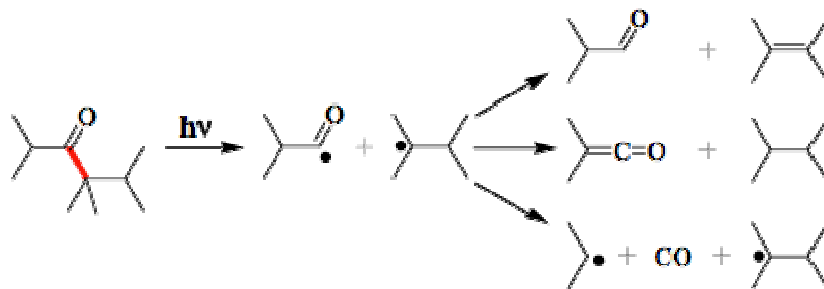
Some organisms use photodamage to their advantage. A remarkably effective plant-pathogenic fungus, *Cercospora*, produces a pigment that efficiently sensitizes singlet molecular oxygen. Peroxidation of the plant cell membrane causes the cells of the infected plants to burst, giving nutrients to the fungus.

3.4.9. Carbonyl compounds

The $n \rightarrow \pi^*$ excited states of carbonyl compounds display a rich chemistry in their own right. Since the oxygen has an unpaired electron, it behaves in much the same way as an alkoxy radical. Hydrogen abstraction and addition to double bonds are typical reactions. Cleavage of neighboring carbon-carbon bonds may also occur, the two most common of these being designated **Type I** and **Type II**.

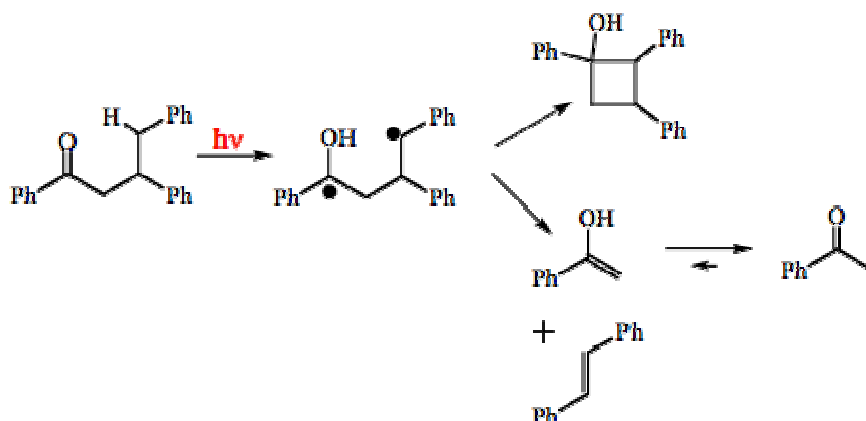


An important primary photoprocess of carbonyl compounds is α cleavage, also known as a Norrish Type I reaction (Scheme 3). Besides recombination, the acyl and the alkyl radicals formed in the primary reaction can undergo numerous secondary reactions that are responsible for the multitude of final products.



Scheme 3

Intramolecular hydrogen abstraction is a common photoreaction of carbonyl compounds with a hydrogen atom attached to the fourth carbon atom (Scheme 17). The resulting diradical can form cycloalkanol or undergo C-C bond fission to give an alkene and enol. The latter is usually thermodynamically unfavorable and converts to a ketone. Intramolecular abstraction of a γ -hydrogen is known as a Norrish Type II process.



Scheme 4

SAS 6: Which of the following is not a photochemical reaction: (a). photoisomerization (b). photooxidation (c). photohydration (d). phototropism

3.5. Conclusion

In this unit you have learnt that photochemical reactions are chemical reactions initiated by the absorption of energy in the form of light. They involve electronic reorganization initiated by electromagnetic radiation. The consequence of molecules absorbing light is the creation of transient excited states whose chemical and physical properties differ greatly from the original molecules. These new chemical species can fall apart, change to new structures, combine with each other or other molecules, or transfer electrons, hydrogen atoms, protons, or their electronic excitation energy to other molecules. Excited states are stronger acids and stronger reductants than the original ground states. It is this last property that is crucial in the most important of all photochemical processes, photosynthesis, upon which almost all life on earth depends.

3.6. Summary

What you have learned in this unit concerns the chemistry that distinguishes photochemical reactions from other reactions. It has served to introduce you to the peculiar types of photochemical reactions such as photo-isomerization, photo-oxidation, photo-fragmentation, photo-rearrangement and photosensitization.

3.7. Tutor-Marked Assignments

- (1). A photochemical reaction occurs when internal conversion and relaxation of an excited state leads to a ground state isomer of the initial substrate molecule. Illustrate this with stilbene.
- (2). Explain how solvent viscosity affects the outcome of a photochemical reaction.
- (3). Write short notes on photofragmentation and its applications

3.8 References

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Unit 4

Pericyclic Reaction

4.0 Introduction

For the synthetic organic chemist, the development of a general procedure that leads to the formation of carbon-carbon bonds is considered a laudable achievement. A general method that results in the simultaneous formation of two carbon-carbon bonds is worthy of a Nobel Prize. In 1950, two chemists, Otto Diels and Kurt Alder, received that accolade for their discovery of a general method of preparing cyclohexene derivatives that is now known as the Diels-Alder reaction. The Diels-Alder reaction is one type of a broader class of reactions that are known as pericyclic reactions. Pericyclic reactions are the *concerted* reactions involving reorganization of electrons which occur by the way of a single *cyclic transition state*. Pericyclic reactions represent an important class of concerted (single step) processes involving π -systems. The fact that the reactions are concerted gives fine stereochemical control of the product, however, this page is more concerned with the general types of pericyclic reaction, than with regio and stereochemical control. In 1965 two other Nobel laureates, Robert B. Woodward and Roald Hoffmann, published a series of short communications in which they presented a theoretical basis for these well known, but poorly understood pericyclic reactions. Their theory is called orbital symmetry theory. Subsequently other chemists published alternative interpretations of pericyclic reactions, one called frontier orbital theory, and another named aromatic transition state theory. All of these theories are based upon MO theory. In this topic we will use the Diels-Alder reaction to illustrate aspects of each of these theories.

Pericyclic reactions that involve a redistribution of bonding and non-bonding electrons in a cyclic, concerted manner is an important class of organic reactions. Since the publications of the Woodward-Hoffmann rules on the conservation of orbital symmetry and the frontier molecular orbital theory (FMO) by Fukui first described in the late 1960s, the underlying principles of these processes at the molecular level have become fully understood. Many modern organic chemistry textbooks include pericyclic reactions as a major topic. They are usually covered in detail in a typical introductory organic chemistry course. Among the two fundamental approaches to pericyclic reactions, the FMO approach has gained some popularity at the undergraduate teaching level. It is simpler and can be based on a pictorial approach. A detailed understanding of molecular orbital theories and symmetry is not required. When learning the mechanisms of organic reactions, our students have often expressed a wish that they could see how the electrons “jump” and the orbitals “move” in the microscopic world. Pericyclic Reactions: FMO Approach has partially fulfilled the students’ request.

- Pericyclic reactions have a *cyclic* transition state.
- While in this transition state, a concerted rearrangement of the electrons takes place that causes σ and π -bonds to simultaneously break and form.

- Pericyclic reactivity can be understood in terms of frontier molecular orbital (FMO) theory and the outcome of reactions can be predicted using the Woodward-Hoffmann rules.

Pericyclic reactions are popular with synthetic chemists because the reagents and conditions are mild and the reactions are usually very "clean" unlike so many organic chemical reactions that result in the formation of large quantities of brown-black, smelly by-product of unknown composition.

4.1 Objectives

By the end of this unit, you should be able to:

- Give a concise definition of pericyclic reactions
- Explain the mechanisms of pericyclic reactions and its associated terminology
- Give various approaches to analyzing pericyclic reactions
- Discuss the Frontier molecular orbital theory
- Draw an orbital correlation diagram
- Classify an orbital as symmetric or antisymmetric
- State and explain the generalized and Woodward-Hoffmann orbital symmetry rules

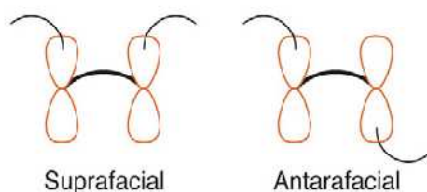
4.2 Mechanism of pericyclic reactions and associated terminology (Theory)

Pericyclic reaction involves several simultaneous bond-making and bond-breaking processes with a cyclic transition state involving delocalized electrons. The combination of steps is called a *concerted process* where intermediates are skipped. We distinguish between *concerted* and *stepwise* reaction mechanisms on the basis of absence and presence of intermediate(s).

Historically, pericyclic reactions were unusual in that they were clearly important in practice but seemed to have "no mechanism"; i.e., no intermediates could be identified. A concerted reaction mechanism may be *synchronous* or *asynchronous*. The term "synchronous" is used when multiple bond-making or bond-breaking events occur to the same extent at the transition state. Of course, perfect synchronicity is rarely achieved. The HOMO is the "highest occupied molecular orbital". The LUMO is the "lowest unoccupied molecular orbital". Together, these are the *frontier molecular orbitals (FMO)*. If there is an orbital at the same energy level as a p orbital, this is an NBMO (nonbonding molecular orbital). In compounds for which a MO has just one electron, the orbital occupied by that electron is a SOMO (singly occupied molecular orbital).

Suprafacial and antarafacial These terms define the topology of interaction in a pericyclic transition state. For π systems and lone pairs, suprafacial interactions involve same face; antarafacial interactions involve opposite faces. For σ systems, the terms are defined as shown.

A. π Systems



B. σ Systems



Figure 4.1 Suprafacial and Antarafacial Interactions

Forbidden reactions and allowed reactions A “forbidden” reaction is expected to have an electronic barrier on the reaction pathway due to unfavorable orbital properties. An “allowed” reaction is not expected to have such a barrier. These terms are perhaps overly dramatic, but they indicate accurately the tendencies of certain reactions to occur or not to occur.

4.2.1 Orbital symmetry diagram (Orbital correlation diagram)

Consider the [2+2] cycloaddition of two ethylene molecules. Let us assume that the two molecules approach each other with their π systems arranged symmetrically (i.e., a symmetric pericyclic transition state). If so, then we can identify two symmetry elements: two mirror planes, as shown. Each pair of interacting p orbitals in the reactant combination leads to one σ bond in the cyclobutane product.

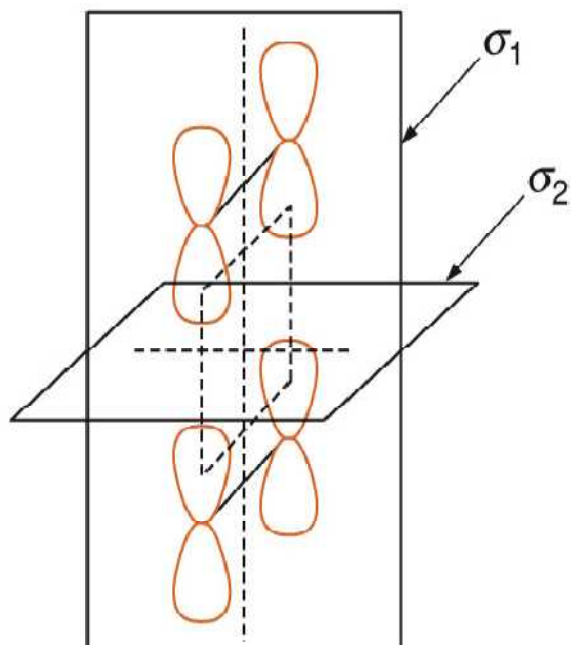


Figure 4.2 Transition state geometry with two mirror planes of symmetry

The fundamental feature of the orbital symmetry analysis is to draw the MOs of the reactant(s) and the MOs of the product(s). One then considers how the symmetries of the orbitals relate to each other. Orbitals of reactants are transformed smoothly into orbitals of products, with **conservation of orbital symmetry**.

4.2.2 Frontier Molecular Orbital Theory

Frontier Molecular Orbital Theory was developed in the 1960s by Kenichi Fukui who recognized that chemical reactivity can often be explained in terms of interacting Highest Occupied MOs (HOMOs), Lowest Unoccupied MOs (LUMOs) and Singly Occupied MOs (SOMOs).

- HOMO + LUMO -> bonding MO
- HOMO + HOMO -> antibonding MO
- LUMO + LUMO -> null interaction (no electrons)
- SOMO + SOMO -> bonding MO

The FMO approach was developed by Woodward & Hoffmann in the late nineteen sixties who used it to explain an apparently diverse set of reactions involving π -systems, including Diels-Alder cycloaddition. Hoffmann used the approach to explore transition metal complexes.

According to Frontier Orbital Theory it is possible to determine if a pericyclic reaction is allowed or forbidden by simply considering the symmetry relationship of the frontier orbitals of the reactants. The frontier orbitals are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The interaction between these orbitals, a so-called HOMO-LUMO interaction, is a concept that is similar to Lewis acid-Lewis base chemistry which involves the interaction of a filled orbital of the base with an empty orbital of the acid. According to Frontier Orbital Theory, a pericyclic reaction is allowed when the HOMO of one reactant has the same symmetry as the LUMO of the other. The bonding or antibonding interactions of the frontier molecular orbital(s) determine whether the reactions are thermally or photochemically allowed or forbidden.

Cycloaddition can be explained using frontier molecular orbital (FMO) theory. The alkene (dienophile) component has two electrons in a "single" π -bond. FMO theory, here, identifies the HOMO and LUMO components of this system:

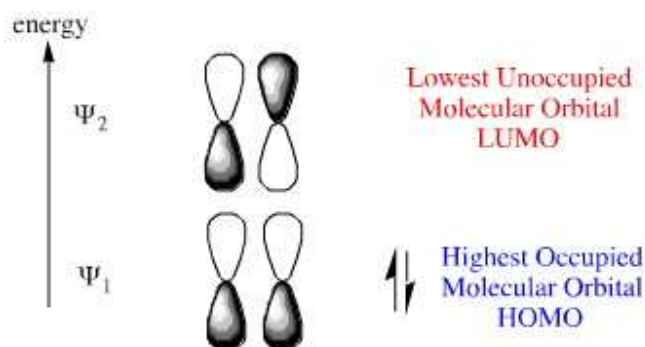


Figure 4.3 HOMO/LUMO components of a dienophile

Likewise, the diene which has four electrons in its conjugated π -system can have its HOMO and LUMO identified within FMO theory:

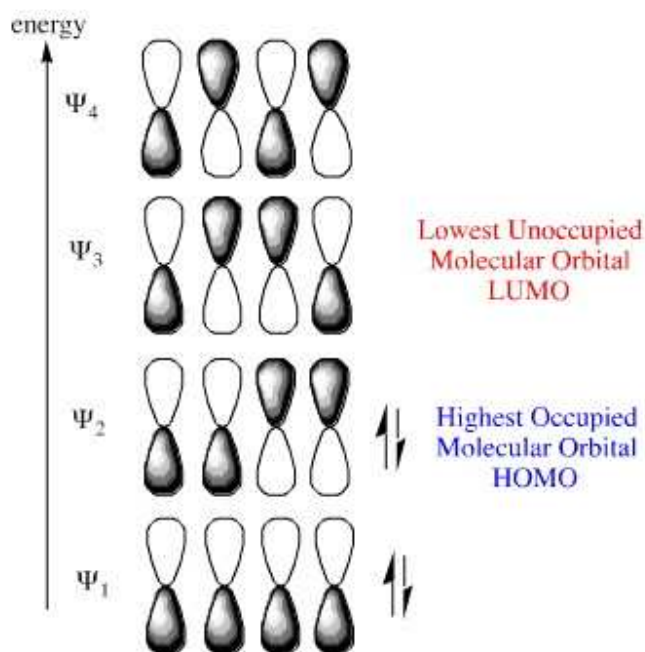


Figure 4.4 HOMO/LUMO components of a diene

If we examine the phases at the ends (termini) of the diene and dienophile we find that the LUMO/HOMO interactions are phase matched:

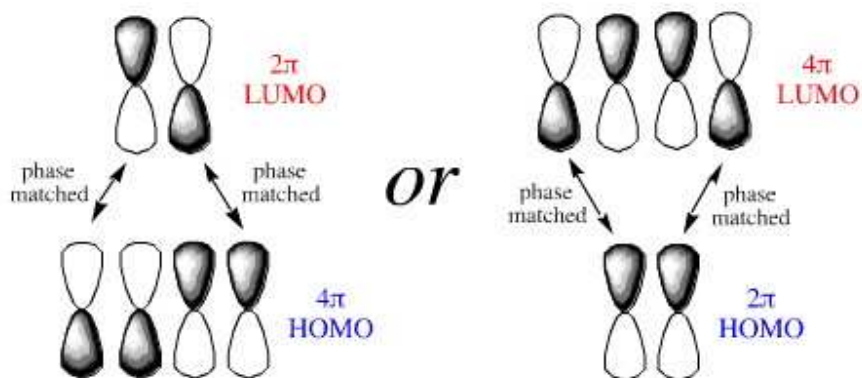


Figure 4.5 LUMO/HOMO interactions of diene and dienophile

Notice that the phases match whichever species is defined as the HOMO or LUMO. In reality, the electron rich species reacts via its HOMO and the electron poor species via its LUMO.

In the FMO diagrams above, the sizes or *coefficients* are all the same size, but usually they are of different sizes. The rule is that the coefficients match as well: small with small and large with large:

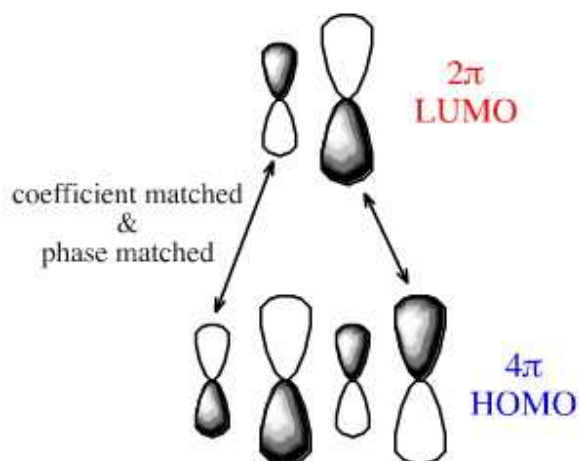


Figure 4.6 Coefficient and phase matched HOMO/LUMO

We can use Hückel MO theory to calculate the sizes of the coefficients at each of the atoms. (There is a web based HMO calculator, here, although at *meta-synthesis* we use a stand alone package: HMO by Allan Wissner.)

If the coefficients are calculated for 1-methoxy-1,3-butadiene the termini are +0.3 and -0.58 (or -0.3 and +0.58). For acrylonitrile the coefficients are +0.2 and -0.66 (or -0.2 and +0.66).

The cycloaddition reaction proceeds so the coefficients "match", both in terms of phase (*essential*) and in terms of coefficient magnitude: +0.3 with +0.2 and -0.58 with -0.66.

Thus, the regioselectivity of the cycloaddition can be explained:

Fukui realized that a good approximation for reactivity could be found by looking at the frontier orbitals (HOMO/LUMO). This was based on three main observations of molecular orbital theory as two molecules interact:

1. The occupied orbitals of different molecules repel each other.
2. Positive charges of one molecule attract the negative charges of the other.
3. The occupied orbitals of one molecule and the unoccupied orbitals of the other (especially the HOMO and LUMO) interact with each other causing attraction.

From these observations, frontier molecular orbital (FMO) theory simplifies reactivity to interactions between the HOMO of one species and the LUMO of the other. This helps to explain the predictions of the Woodward-Hoffmann rules for thermal pericyclic reactions, which are summarized in the following statement:

"A ground-state pericyclic change is symmetry-allowed when the total number of $(4q+2)_s$ and $(4r)_a$ components is odd"

$(4q+2)_s$ refers to the number of aromatic, suprafacial electron systems; likewise, $(4r)_a$ refers to antiaromatic, antarafacial systems. It can be shown that if the total number of these systems is odd then the reaction is thermally allowed.

4.2.1 Characteristics of pericyclic reactions

- The pericyclic reactions occur in single step and hence there is no intermediate formed during the reaction.
- The breaking and making of bonds (both σ & π) occur simultaneously in a cyclic transition state.
- The configuration of the product depends on:
 - 1) The configuration of reactants.
 - 2) The number of electron pairs undergoing reorganization and
 - 3) The reaction conditions (like thermal or photochemical).

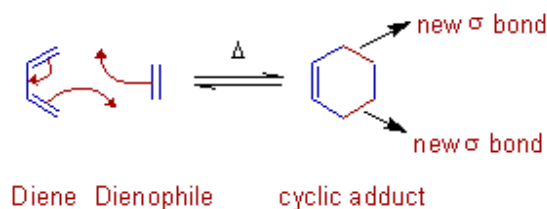
4.3 Types of pericyclic reactions

The pericyclic reactions are further classified into following types:

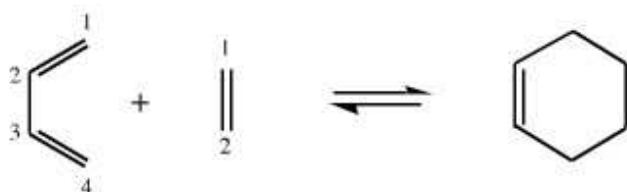
- | | |
|-------------------------------|-----------------------------|
| 1) Cycloaddition reactions | 2) Electrocyclic reactions |
| 3) Sigmatropic rearrangements | 4) Group transfer reactions |
| 5) Cheletropic reactions | 6) Dyotropic rearrangements |

Within each subclass, it is common that reactions can *either* be induced to occur under thermal conditions with simple heating, or under photochemical conditions. The two methodologies are complementary.

4.3.1 Cycloaddition reactions involve the formation of a cyclic product due to addition of two different π bond containing components, which are joined by newly formed two σ bonds at their ends at the expense of two π bonds. It is usually reversible and the backward reaction is also referred to as retro-cycloaddition or a cycloreversion. The classic example of cycloaddition is Diels-Alder reaction between a Diene and a Dienophile to give a cyclic adduct. Cycloaddition, and the reverse process retrocycloaddition, can be observed in the reaction between 1,3-butadiene and ethene to give cyclohexene.



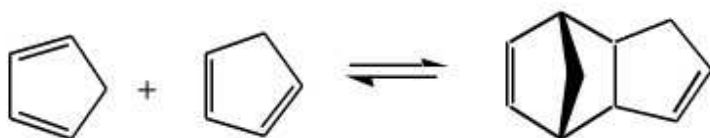
The 1,3-butadiene is a conjugated π -system with 4 π -electrons and the ethene is a conjugated π -system with 2 π -electrons. The reaction between 1,3-butadiene and ethene to give cyclohexene is described as a [4+2] cycloaddition reaction. This type of cycloaddition is also called a Diels-Alder reaction.



In a Diels-Alder reaction the 4 π -electron system is referred to as "the diene" and the 2 π -electron system as the "dienophile". These terms are used in related [4+2] reaction systems even when the functional groups are not actually dienes or alkenes.

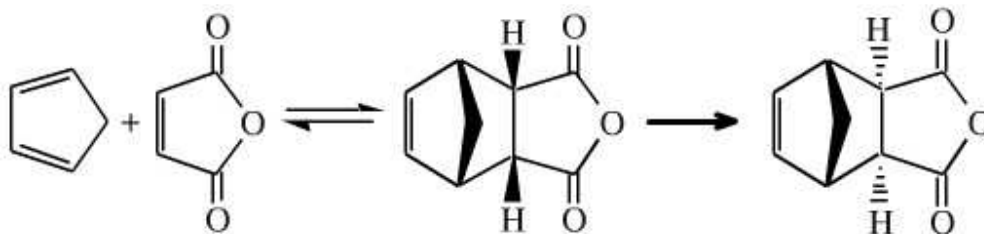
Cycloaddition is a type of $X + Y \longrightarrow X-Y$ complexation, and it follows the usual thermochemistry rules. The formation of the *Diels-Alder adduct* is an exothermic reaction. It follows that high temperatures favour retrocycloaddition and low temperatures favour adduct formation.

However, many cycloaddition reactions require moderate heating to overcome the activation energy. So a cycloaddition may require heating to make the reaction "go", but if it is heated too much the equilibrium will favour retrocycloaddition. The compound cyclopentadiene slowly undergoes cycloaddition with itself: one molecule of cyclopentadiene acts as a 4 π -electron diene and the other as a 2 π -electron dienophile. The product is a Diels-Alder "adduct", often called dicyclopentadiene. This dimeric material can be *cracked* back to cyclopentadiene by heating at 150°C for an hour and then distilling off the diene monomer.

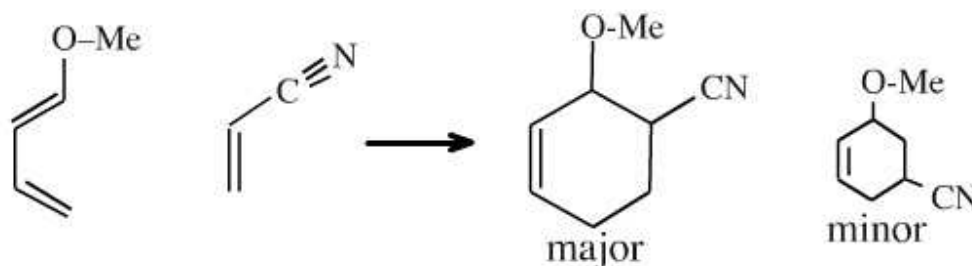


Diels-Alder cycloaddition reactions proceed more efficiently if the diene is electron rich and the dienophile is electron poor. Cyclopentadiene is electron rich. The way to make the dienophile electron poor is to add electron withdrawing groups, such as carbonyl functions. Maleic

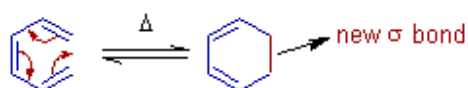
anhydride is an electron poor dieneophile which reacts with cyclopentadiene to give an endo Diels-Alder adduct. Upon heating at 190°C, the endo conformation adduct adopts the more stable exo-adduct conformation.



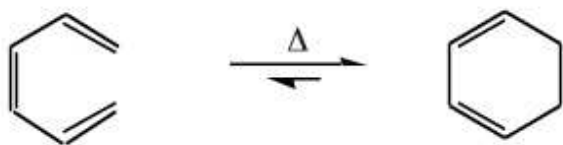
1-Methoxy-1,3-butadiene reacts with acrylonitrile to give 3-methoxy-4-cyanocyclohexene rather than the 3-methoxy-5-cyanocyclohexene isomer. This "ortho" regioselectivity of this reaction can be rationalised using FMO theory.



4.3.2 Electrocyclic reactions are intramolecular pericyclic reactions which involve the rearrangement of π -electrons in an open conjugated system leading to formation of a cyclic product with a new σ bond at the expense of a π -bond. However the electrocyclic reactions not only involve ring-closure but also ring opening, which are referred to as retro-electrocyclic reactions. E.g. The formation of Cyclohexa-1,3-diene by heating Hexa-1,3,5-triene is an example of ring-closure electrocyclic reaction.

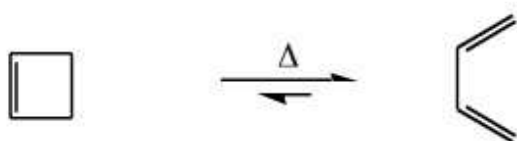


Electrocyclic reactions are unimolecular processes which involve the exchange of π -bonds for ring-closing sigma-bonds. This is best illustrated by an example: Upon heating, 1,3,5-hexatriene will undergo an electrocyclic ring closure to give 1,3-cyclohexadiene:



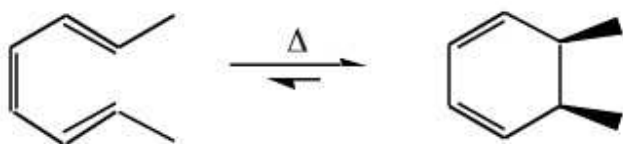
Note that the 3-alkene must be *cis* for the reaction to occur.

The reverse, or *retroelectrocyclic*, reaction can also occur. This is seen with the ring opening of cyclobutene to 1,3-butadiene:

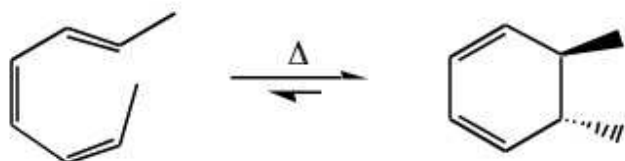


Electrocyclic reactions, like all pericyclic processes, exhibit great stereoselectivity. Consider two 1,3,5-hexatriene systems embedded into longer hydrocarbon chains.

trans-cis-trans-2,4,6-Octatriene will ring close to give a *cis* ring:



trans-cis-cis-2,4,6-Octatriene will ring close to give a *trans* ring:



As with cycloaddition, this selectivity can be explained by examining the FMOs, specifically the HOMO:

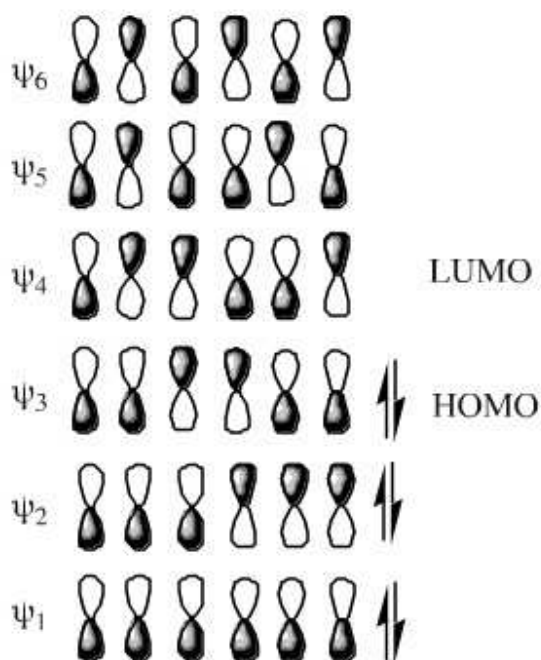


Figure 4.7 Superimposition of HOMO upon triene system

If the termini of the HOMO is superimposed upon the triene system, it can be seen that the end groups must rotate in a disrotatory manner (twist in opposite directions, when viewed front-on) to form the bond:

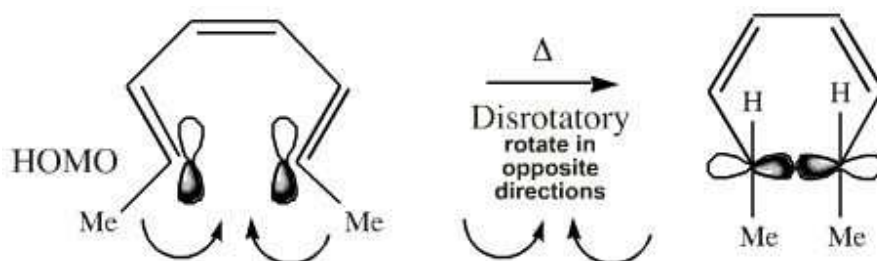


Figure 4.8 Disrotatory twist of HOMO

However, electrocyclic reactions can also occur photochemically. When photoactivated, an electron moves from the HOMO to the next orbital, the LUMO. (Now this orbital contains an electron it is no longer unoccupied, it is either a SOMO or an excited state HOMO).

The photoexcited system will ring close in the opposite manner to the thermal system and the groups conrotate (twist the same way) to form the sigma bond:

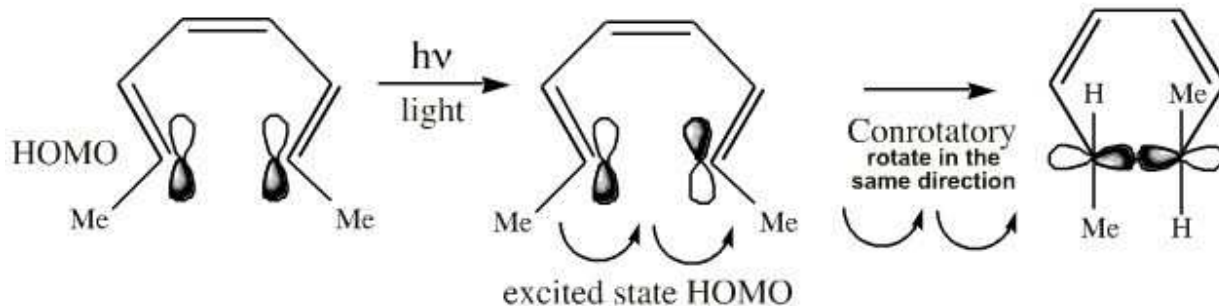


Figure 4.9 Conrotation of photoexcited System

The two products have different stereochemistry and are diastereomers.

This thermal and photo selectivity can be exploited in the reaction sequence below in which 1,3,5-cyclononatriene is converted into bicyclic systems, first with *cis* and then *trans* ring junctions.

The initial 1,3,5-cyclononatriene is all *cis*. This is thermally ring closed in a disrotatory manner and then photo-ring opened at -20°C in a conrotatory manner. The 1,3,5-cyclononatriene now has two *cis* and one *trans* double bonds, however, the nine membered ring is able to accommodate the strain of a *trans* alkene. Thermal ring closure gives the *trans*-ring junction.

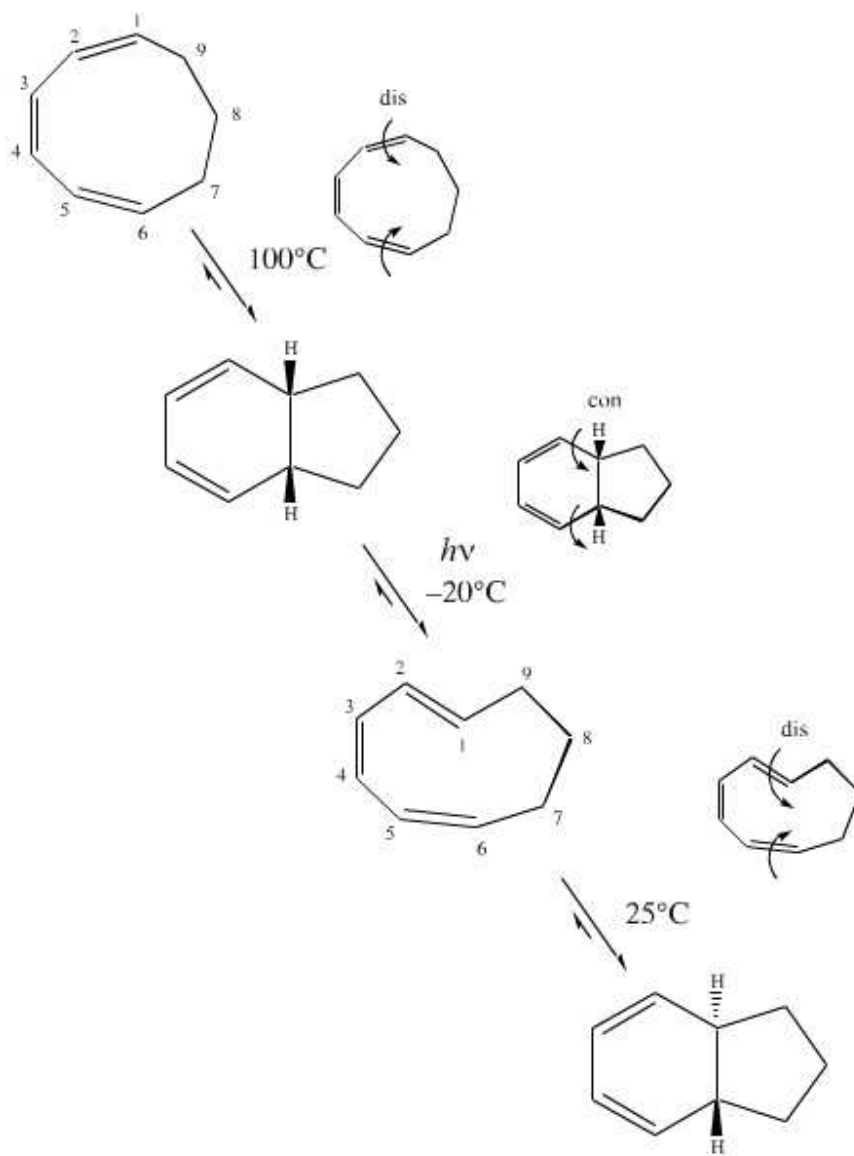
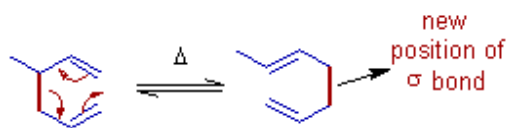


Figure 4.10 Conrotatory twist of 1,3,5-cyclononatriene

4.3.3 Sigmatropic rearrangements are concerted unimolecular isomerization reactions characterized by the overall movement of a σ -bond from one position to another with an accompanying rearrangement of π -electrons of conjugated system so as to accommodate the new σ -bond. For example, the [3,3] Cope rearrangement. The σ -bond undergoing movement is shown as red thick line.

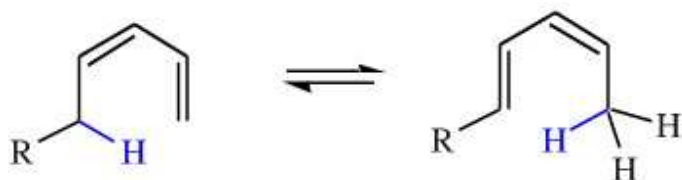


Note: Though looking like electrocyclic reactions, there is no reduction in the number of π -bonds in sigmatropic reactions.

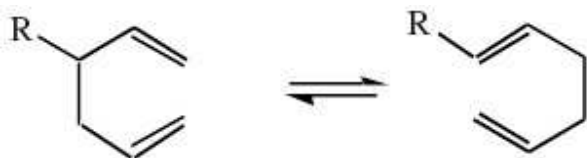
Like electrocyclic reactions, sigmatropic rearrangements are unimolecular processes. Sigmatropic reactions involve the movement of a sigma-bond with the simultaneous rearrangement of the π -system.

Two examples illustrate this:

The [1,5] shift of hydrogen in a 1,3-pentadiene system:



The [3,3] Cope rearrangement:



Note that the generic "R" functions have been added so that the product can be distinguished from the starting materials.

The biosynthesis of vitamin D has photochemical step, and the reaction takes place in skin cells.

A 1,3-cyclohexadiene system associated with the b ring of a steroid undergoes a photoactivated, retroelectrocyclisation to give 1,3,5-hexatriene system.

The thermal reaction is not allowed because it would be necessary to form a six membered ring with a *trans*-alkene, a sterically impossible structure.

1,3,5-hexatriene system then undergoes a thermal [1,7] sigmatropic rearrangement to give vitamin D3. This is further processed in the liver.

Vitamin D Biosynthesis

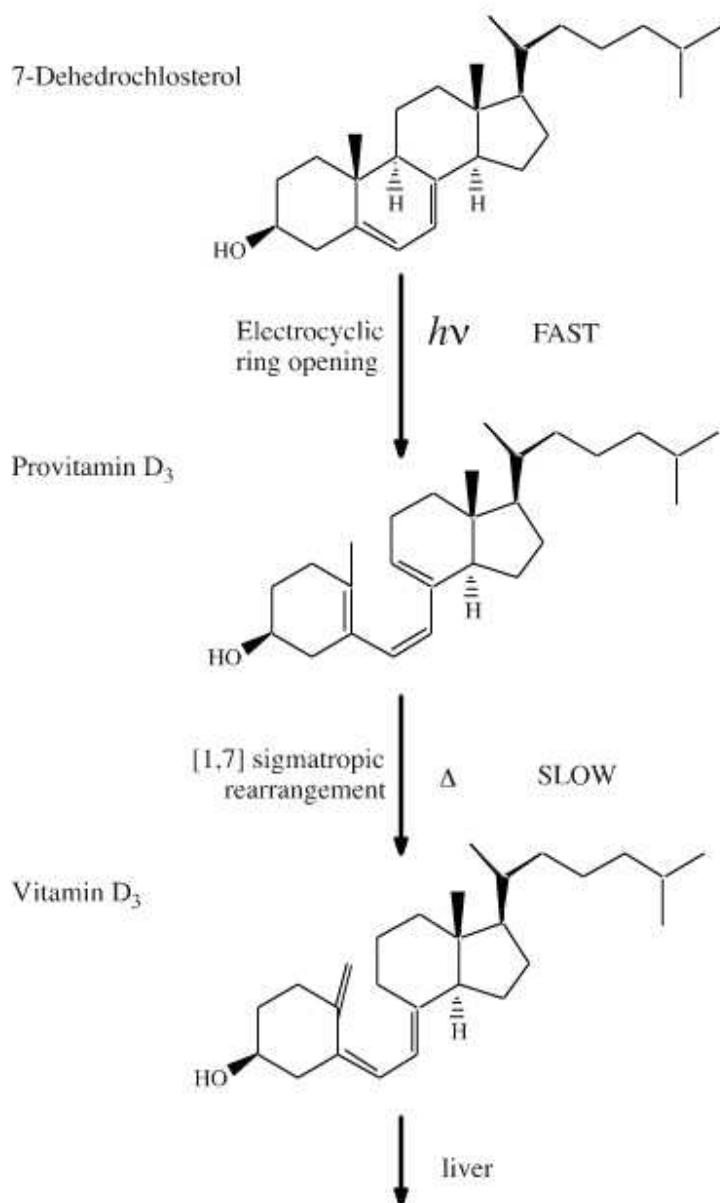
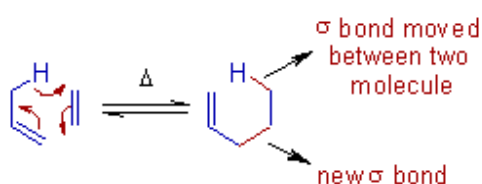


Figure 4.11 Sigmatropic rearrangement in biosynthesis of vitamin D

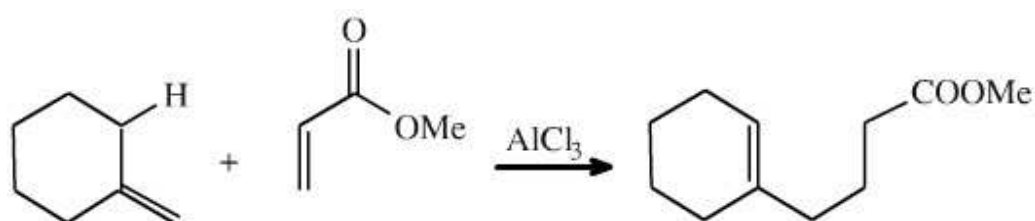
4.3.4 Group transfer pericyclic reaction

The concerted transfer of a group from one molecule to another due to concomitant movement of a σ -bond (from one molecule to another) and formation of a new σ -bond (between two molecules) at the expense of a π -bond is generally referred to as **group transfer** pericyclic reaction. For example, the ene reaction between propene and ethene to give 1-pentene is a classic example of group transfer reaction.



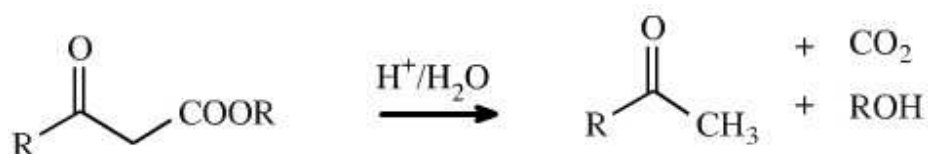
These reactions resemble sigmatropic rearrangements, since a σ -bond moves. However sigmatropic reactions are unimolecular reactions whereas the group transfer reactions are bimolecular. They also resemble cycloadditions, since a new σ -bond is formed at the expense of a π -bond. However, in group transfer reactions, no ring is formed.

Another example of an ene reaction is seen with the reaction of methylenecyclohexene and methyl acrylate. (An aluminium chloride catalyst is required to "activate" the enone system.)

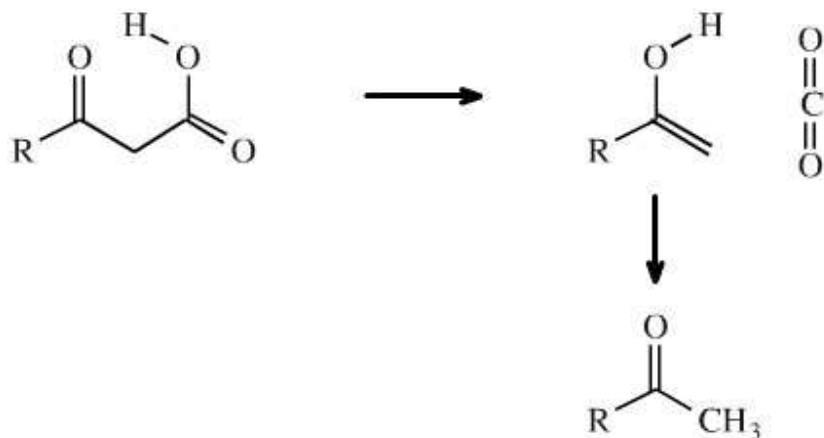


A common reaction in organic synthesis is the acid catalysed decarboxylation of a β -ketoester.

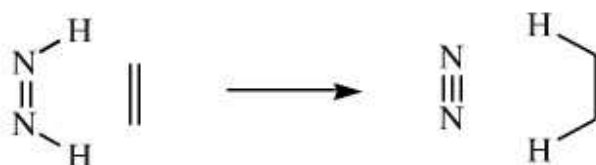
The ester is hydrolysed to the β -ketoacid by the aqueous acid this rapidly loses carbon dioxide.



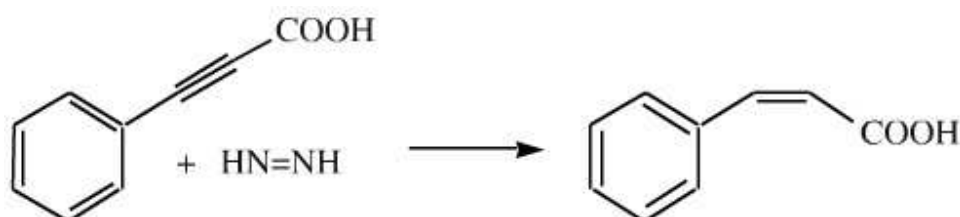
The reaction proceeds as a retroene reaction to give carbon dioxide and an enol system. The loss of CO₂ drives the reaction to the right hand side. The enol rapidly tautomerises to the methyl ketone:



Diimide is used as a reducing agent, it adds H₂ to C=C and N=N bonds and leaves other functions untouched:



For example, 3-phenylpropynoic acid is reduced to *cis*-3-phenylpropenic acid (*cis*-cinnamic acid) by diimide:



4.3.4 Cheletropic reactions are a special class of cycloadditions or retro-cycloadditions in which the two σ -bonds are either made or broken to the same atom. For example, the reversible

addition of sulfur dioxide to 1,3-butadiene is an example of cheletropic reaction, in which the two new σ -bonds (shown in red) are made to the sulfur atom.

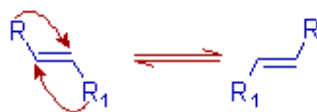


Note: In this reaction, a lone pair on sulfur atom is equivalent a π -bond and is reorganized. One π -bond and a lone pair are disappeared, whereas two σ -bonds are formed. Also note that sulfur atom is oxidized from +4 to +6 state.

4.3.5 Dyotropic rearrangements

The pericyclic reactions which involve concerted intramolecular migration of two σ -bonds simultaneously are known as **dyotropic rearrangements**. However dyotropic reactions can also occur stepwise. There are two types of dyotropic rearrangements:

Type-I: Two migrating groups interchange their relative positions



Type-II: The σ -bonds are migrated to new bonding sites without any positional interchange for groups.



All types of pericyclic reactions are concerted and involve cyclic transition state without any intermediate formed during the reaction. The characteristics which differentiate them from each other are tabulated below.

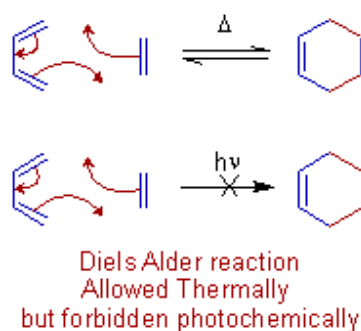
SAS 7: Define pericyclic reactions.

Table 4.1 Comparison of different types of pericyclic reactions

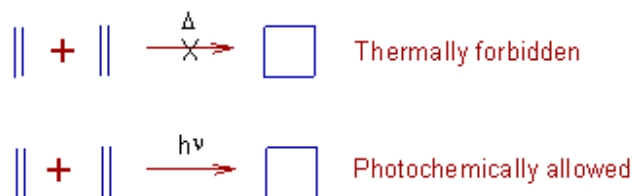
S.no	Type of pericyclic reaction	change in no. of σ bonds	change in no. of π bonds	comments
1)	Cycloaddition reactions	+2	-2	A cyclic product is formed; may be intermolecular or intramolecular.
2)	Electrocyclic reactions	+1	-1	Intramolecular.
3)	Sigmatropic reactions	0	0	Intramolecular; migration of a σ -bond; rearrangement of π -electrons
4)	Group transfer reactions	+1	-1	Intermolecular transfer of a group; migration of a σ -bond from one molecule to another; formation of new σ -bond at the expense of one π -bond.
5)	Cheletropic reactions	+2	-1 (π -bond) -1 (lone pair)	A cyclic product is formed; two σ -bonds are formed to same atom; A lone pair is disappeared.
6)	Dyotropic reactions	0	0	Simultaneous migration of two σ -bonds.

4.4.1 Reaction conditions for pericyclic reactions

It is observed that some of the pericyclic reactions occur only upon heating, whereas others are possible only under photochemical conditions e.g. the Diels-Alder reaction, a [4+2] cycloaddition occurs under thermochemical conditions and is not possible under photochemical conditions.



Whereas the following [2+2] cycloaddition is forbidden under thermal conditions. But the reaction is possible under photochemical conditions.



SAS 7: Name three pericyclic reactions.

4.4.2 Woodward-Hoffmann rules

To predict whether a pericyclic reaction is allowed or not under given condition, Woodward and Hoffmann proposed following set of rules Woodward-Hoffmann rules concept.

A thermal pericyclic reaction is allowed in the ground state, when the total number of $(4q + 2)_s$ and $(4r)_a$ components is odd. Otherwise, if the total of $(4q + 2)_s$ and $(4r)_a$ components is even, the pericyclic reaction is allowed in the excited state i.e., under photochemical conditions.

Table 4.2 Woodward-Hoffmann rules for predicting allowed pericyclic reaction

Number of $(4q + 2)_s$ and $(4r)_a$ components	The condition under which the reaction is allowed
odd	Thermal
even	Photochemical

Component: A bond(s) or an orbital(s) taking part in the pericyclic reaction as a single unit can be considered as a component. It can have any number of electrons but may not have mixtures of π and σ electrons. E.g. A double bond is considered as a π_2 component, since there are two π electrons. A conjugated diene can be considered as π_4 component, since there are four π electrons. 's' represents suprafacial. A suprafacial component forms new bonds on the same face at its both ends. 'a' represents antarafacial. An antarafacial component forms new bonds on the opposite faces of its both ends. E.g. π_{2s} represents a component containing two π electrons and forming new bonds in suprafacial manner. π_{4a} represents a component containing four π electrons and is going to form new bonds in antarafacial manner.

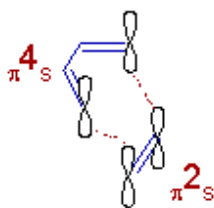
q & r: These are integers.

$(4q + 2)_s$ component: The suprafacial component which may have either 2 or 6 or 10 or _ _ _ electrons of same type. These numbers are obtained by substituting 'q' by 0 or 1 or 2 or _ _ _.

$(4r)_a$ component: The antarafacial component which may have either 4 or 8 or 12 or _ _ _ electrons of same type. These numbers are obtained by substituting 'r' by 1 or 2 or 3 or _ _ _.

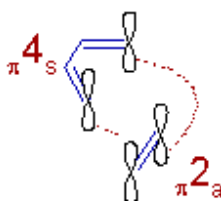
Likewise the meanings of $(4q + 2)_a$ & $(4r)_s$ can be understood.

Application: Let us assume the diene and dienophile in Diels-Alder reaction are approaching suprafacially as shown below.



thermally allowed
suprafacial addition

Since there are 4 π electrons in diene, which is making bonds in suprafacial manner it is a $(4q + 2)_s$ component. i.e, there is one $(4q + 2)_s$ component. And the alkene is a $(4r)_s$ component, since it has 2 π electrons and is approaching the diene suprafacially i.e., there are **no** $(4r)_a$ components. Hence, the total number of $(4q + 2)_s$ and $(4r)_a$ components = $1 + 0 = 1$, an odd number. Therefore Diels-Alder reaction is thermally allowed in ground state when both the components are approaching suprafacially. Hence it is termed as $\pi^4_s + \pi^2_s$ cycloaddition. Antarafacial addition is not allowed under thermal conditions but is theoretically allowed under photochemical conditions in the excited state. However, the strain in the transition state while doing so forbids to do so.



photochemically allowed
antarafacial addition
but never takes place
under these conditions

Note: The orbitals shown in above diagrams are simple 'p' orbitals and are not the frontier molecular orbitals. Do not mix descriptions of FMO theory with Woodward-Hoffmann rules.

4.4.3 Simplified Woodward-Hoffmann rules

Application of above Woodward-Hoffmann rules to pericyclic reactions is tedious and cumbersome; following simplified rules can be used to predict theoretically allowed modes of pericyclic reactions under given conditions.

Table 4.3 Simplified Woodward-Hoffmann rules

No. of π electrons	Reaction conditions	Allowed mode
(4n+2) A Huckel number	Thermal	Supra (or) Dis
	Photochemical	Antara (or) Con
(4n) A non Huckel number	Thermal	Antara (or) Con
	Photochemical	Supra (or) Dis

Remember that even though the pericyclic reactions are allowed theoretically under both the conditions in either of the modes, sometimes the factors like steric hindrance and strain in the transition state may forbid the reaction to occur.

Table 4.4 Pericyclic Reaction Rules

Designation	Thermal	Photochemical
$\pi 2s + \pi 2s$	forbidden	allowed
$\pi 2s + \pi 4s$	allowed	forbidden
$\pi 2s + \pi 2a$	allowed	forbidden
$\pi 2s + \pi 4a$	forbidden	allowed
$\pi 2a + \pi 2a$	forbidden	allowed
$\pi 2a + \pi 4a$	allowed	forbidden

Before we move on, it is worthwhile to clarify the implications of the words allowed and forbidden. An allowed reaction is simply one with a low activation relative to some other pathway, while a forbidden reaction is a process for which there is significant activation energy.

In terms of transition states, an allowed reaction proceeds via an aromatic transition state, while a forbidden reaction does not occur because the transition state would be "anti-aromatic."

4.5 Conclusion

In this unit you have learnt the various rules of pericyclic reactions. All of the theories just described involve two basic assumptions

1. The orbitals overlap suprafacially on both π systems.
2. The reaction is thermally induced.

Given these assumptions, we can state the following:

- A thermally induced $\pi 2s + \pi 4s$ cycloaddition reaction is allowed.
- A thermally induced $\pi 2s + \pi 2s$ cycloaddition reaction is forbidden.

The rules are reversed when the reaction is photochemically induced:

- A photochemically induced $\pi 2s + \pi 4s$ cycloaddition reaction is forbidden.
- A photochemically induced $\pi 2s + \pi 2s$ reaction is allowed.

These rules are summarized in Table 4.4. Note that changing just one of the variables, i.e. faciality, energy source, or number of electrons (two electrons at a time), changes an allowed reaction to a forbidden one and vice versa.

4.6 Summary

- *Pericyclic Reaction* : reaction that occurs by a concerted process through a cyclic transition state
- concerted means that all bonding changes occur at the same time and in a single step (no intermediates)
- A *cycloaddition reaction* is a reaction in which two unsaturated molecules add to one another, yielding a cyclic product
- It is controlled by orbital symmetry; it takes place when a bonding interaction occurs between the HOMO of one reactant and the LUMO of the other.
- Major examples: 1) Diels-Alder reaction (thermal); 2) [2+2] cycloaddition (photochemical)
- *Woodward-Hoffman Rules*: pericyclic reactions can only take place if the symmetries of the reactant molecular orbitals are the same symmetries as the product molecular orbitals (*lobes of reactant MO's must be of the correct algebraic sign for bonding to occur in the transition state leading to the product*)
- *Frontier Orbital Theory*: we need to consider only *two* molecular orbitals, the HOMO and LUMO, to predict the structure of the product; called frontier MO's
- *Three types of pericyclic reactions*: 1) electrocyclic, 2) cycloaddition, 3) sigmatropic rearrangement
- An electrocyclic reaction is a pericyclic process that involves the cyclization of a conjugated polyene

- *Suprafacial*: when a bonding interaction occurs between lobes on the *same* face of one reactant and lobes on the *same* face of the other reactant
- *Antarafacial*: when a bonding interaction occurs between lobes on the *same* face of one reactant and lobes on the *opposite* face of the other reactant

4.7 Tutor-Marked Assignments

- 1 (a). Distinguish between (i) concerted and stepwise processes (ii) synchronous and asynchronous systems.
 (b). List four types of pericyclic reactions and give an example of each.
- 2 (a). What do the following acronyms stand for (i) HOMO (ii) LUMO (iii) SOMO?
 (b) Show the formation of Cyclohexa-1,3-diene from Hexa-1,3,5-triene in an electrocyclic reaction.
- 3(a). State the Woodward-Hoffmann's rule for pericyclic reactions
 (b) Explain the terms allowed and forbidden reactions.

4.8 References

- (1). Woodward, R. B., Hoffmann, R. (1971). *The Conservation of Orbital Symmetry*; Academic Press: New York
 (2). Barltrop, J.A., Coyl, J.D. (1975) *Excited states in organic chemistry*. London ; New York: Wiley.

Solutions to self assessment exercises

- 1). Photochemical equivalence law or photoequivalence law.
- 2). Return of an excited molecule to the ground state by emission of light (luminescence, fluorescence, phosphorescence).
- 3). Photodissociation results when the excited molecule breaks apart into atomic and/or molecular fragments A and B.
- 4). Fluorescence, phosphorescence, internal conversion and intersystem crossing.
- 5). Internal conversion and intersystem crossing.
- 6). Phototropism.
- 7). Pericyclic reactions are concerted and involve cyclic transition state without any intermediate formed during the reaction.
- 8). Three types of pericyclic reactions: 1) electrocyclic, 2) cycloaddition, 3) sigmatropic rearrangement.

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