

# REVIEW: PHOTOCHEMICAL REACTION AND APPLICATIONS IN SYNTHESIS

DR SHRADDHA UPADHYAY

Department of Applied Science and Humanities, Subharti Institute of Technology and Engineering  
Swamivivekanand Subharti University, Meerut-250005, India

Email: [dr.shrupa@gmail.com](mailto:dr.shrupa@gmail.com)

## ABSTRACT

*Chemical as well as physical property that may occur under the influence of light is called Photochemistry. Photochemical transformations have two fundamental principles. According to first law photochemical reaction initiated when molecule or compound absorb photon, this law is discovered by Grotthus- Draper. The second law gives a photo equivalence law. This law given by Stark-Einstein. Quantum Yield ( $\Phi$ ) calculates the efficiency of photochemical reaction. Many photochemical reactions are categorized as complex reaction, thus for a particular event the quantum yield is specified. It represented by a formula as "ratios of disappearance of reactant to number of moles of a product appear, on absorption of one mole of light by compound." After that many of secondary reactions proceeded (shown in the gray box). Absorption of light (uv/vis) induces energy sufficient in molecule to break covalent bonds. Since,  $E = hc / \lambda$ , hence, longer wavelength have less energy and vice-versa. Consequently, ultraviolet light is most effect photochemical reactions. In this review we discuss about amongst all some of photochemical reactions collectively which are initiated by ultraviolet light specifically.*

**Keywords:** *Electromagnetic Radiations, Singlet State, Triplet State, Excited State, Photochemical transformations*

## INTRODUCTION

In the early 1900's Giacomo Ciamician from University of Bologna used sunlight for his research hence he is the father of photochemistry. Before that era, many sources used for a photochemical reaction these are bright lamps which have infrared and visible light, mercury lamps, flash sources and lasers. For careful studies regarding specific chromophore, sources of monochromatic light can be desired. In this review we focus on all respective mechanism including electronic excited states which is generated when a photon is absorbed by a chromophoric functional group present in molecule. Ultraviolet radiation belongs to wavelengths less than 200 nm which is sufficient to excite an electron belongs to lower energy state to a higher energy state.

It clearly shown above that all the six possible transitions are achieved. Electronic excitation will be from HOMO to LUMO which is energetically favored transition, and the state generated is called an electronic excited state. Electronic transition in the molecule is occurring only when sufficient light energy absorbed. On excitation electron further goes to a higher energy level from lower one.

The spectrum is drawn in between absorbance and wavelength. Franck-Condon Principle state in his theory that electronic transition of electron is so faster than nuclei can respond. In spite, bonding strength is usually weakens than in the ground state which clear that, bond length on molecules in compound is increased in the excited state. After excitation excited electron return to the ground state during this process they emitting a photon which is appear as light blue line. This is one form of radiative decay which is termed as fluorescence. While when it occurs slowly by way of other excited states it is termed phosphorescence

Excited states are of two types, singlet and triplet. This difference is just because of electron spin angular momentum. Most ground states are singlet, hence excited states which is initially formed is singlet. On relaxation in which energy loss in form of heat energy Internal conversion (IC) takes place. Also, relaxation may occur via emitting a photon. Type of relaxation in between intersystem such singlet state to triplet state termed as intersystem crossing. Intersystem crossing is slower than internal conversion. Phosphorescence phenomenon is also a radiative decay and is quite slow phenomenon.

### Types of electromagnetic radiation

Electromagnetic wave is only wave which is able to travel in empty space. Energy which is related with electromagnetic wave is called as electromagnetic energy. Einstein along with Max Plank collectively said in his theory that Electromagnetic radiation is in form of small packet of energy which is called photons. This energy behaves as waves and energy packets. In other word it may be defined as energy that carries information in the form of waves from one place/material to another. Electromagnetic wave produced from acceleration of charged particles placed in magnetic and electric field which are right angle to each other. Oscillation of the wave particles associated with energy which is called as electromagnetic energy. Electromagnetic wave energy can be in the form of heat, light, radio waves etc and have same speed as speed of light. The main sources of electromagnetic energy are Sun light {table 1}.

**Table 1: Some Electromagnetic Radiations**

Region	Energy, (J)	Wavelength (nm)	Frequency,
(Hz)			
X-rays	$5 \times 10^{-19}$	10 nm	$3 \times 10^{19}$
Vacuum ultraviolet	$2.5 \times 10^{-19}$	10-200nm	$3 \times 10^{16}$
Near ultraviolet	$6.6 \times 10^{-20}$	200-400nm	$1.5 \times 10^{15}$

Visible	$5 \times 10^{-19}$	400-800nm	$7.5 \times 10^{14}$
Near Infrared	$2.5 \times 10^{-19}$	0.8-2.5 $\mu\text{m}$	$3.8 \times 10^{14}$
Infrared	$6.6 \times 10^{-20}$	2.5-50 $\mu\text{m}$	$1 \times 10^{14}$
Far Infrared	$4 \times 10^{-21}$	50-300 $\mu\text{m}$	$6 \times 10^{12}$
Microwaves	$6.6 \times 10^{-22}$	0.3 mm-0.5 m	$1 \times 10^{12}$
Radio wave	$4 \times 10^{-25}$	$0.5-300 \times 10^6$	$6 \times 10^3$

### Some Facts about Electromagnetic Energy

1. According to formulae  $E = hc/\lambda$  it is clear that energy and wavelength are inversely proportional to each other.
2. It can pass in vacuum also.
3. Their speed same as that of light.
4. Interestingly, when it enters into matter, energy decreases but wavelength increases.
5. Heat at the surface of object is generated when electromagnetic radiations hit an object causes the particles of that object to vibrate. While when object is heated, particles undergo acceleration. Due to this acceleration electric and magnetic fields get changed which is responsible to generate electromagnetic wave.

### PHOTOCHEMICAL REACTION

Chemical reactions initiated by light are called as photochemical reactions. Energy in form of photon is absorbed or emitted by matter.

On absorption of light an electronic excitation takes place which is from ground state to excited state. This leads to promote an electron. The types of excitation are like  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  etc. Most of photochemical reactions take place during excitation from S1 and T1 excited states.

There are two possibilities that occur when a molecule undergoes electronic excitation. The first possibility is after excitation the molecule undergoes photochemical reactions and the second possibility is that they lose their extra energy via radiative processes and non-radiative processes. The first one involves emission of a photon, e.g., phosphorescence is the best example of a radiative phenomenon in which electron relaxation occurs. While when relaxation occurs from  $S1 \rightarrow S0$  another example of a radiative phenomenon is called as fluorescence. Alternatively, the non-radiative processes, as the name shows, deal with no emission of a photon. In this non-radiative process the only internal conversion occurs which does not involve a change in spin, such as  $S1 \rightarrow S0$  and  $T1 \rightarrow T0$ . While intersystem crossing  $T1 \rightarrow S0$  involves a change in spin multiplicity. When excitations occur by energy transfer, it is called as sensitization phenomenon, and when deactivation occurs by energy transfer, it is called a quenching process. There are many photochemical reactions. Some of these are discussed in this review.

1. **Photo induced Geometrical Isomerism: in this case** photochemical cis/trans (E / Z) isomerism takes place, in which mostly thermodynamically less stable cis-isomer form [1].
2. **Electrocyclizations**, Photochemical electrocyclization occur via  $4n + 2$  – conrotatory [2].
3. **DeMayoReaction** is retro-aldol type reaction which is initiated by light [3].
4. **Paterno buchi** reaction is also came into category of photochemical cycloaddition their resultant product obtained is called as oxetane which is cyclooxobutane [4].
5. **Arene-Olefin Cycloadditions is type of photochemical reaction**, in this case a photocatalyzed cycloadditions reaction between olefin and arenes takes place [5].
6. **Photo induced Electron Transfer** which is also called as Wit kop Cyclization, in which radical ions responsible for further subsequent chemical reactions [6].
7. **Photolysis of butanone derivative** resulted into five major reaction products these are acetone, acetic acid, formaldehyde, CO and methanol [7].
8. **Di-pi methane rearrangement** reaction involves photolysis of molecule which carries two pi-bonds bonded to single  $sp^3$  hybridized carbon atom undergoes intramolecular cyclization reaction resulted into synthesis of cyclopropane [8].
9. **Photolysis of carbonyl compound** with alkene in presence of light resulted in trimethylene oxide [9].
10. **Photoinduced isomerization** of azobenzene is the simplest photoinduced isomerisation is seen in azobenzene [10].
11. **Norrish type II reaction** is a type of photochemical reaction when photo-excited ketone abstract intramolecularly Hydrogen-radical from their  $\gamma$ -position resulted into corresponding biradicals, which is further converted into cyclobutane is called Norrish type II reaction [11].
12. **Photolysis of 2-formyl phenylalkene** or their derivatives in presence of UV light and benzene solution undergoes novel photochemical rearrangement afforded the polysubstituted isochromanones [12].
13. **Photo-Fries rearrangement** is an interesting photochemical reaction which involves the heterolytic cleavage of bond exist between Carbon, oxygen, sulphur, nitrogen etc [13].
14. **Nitro-nitrite rearrangement** involves photochemical initiated rearrangement nitro aromatic species in which nitro group converted into nitrite group [14].

**15. Photolysis of ethyl di-azo-trifluoropropanoate** in presence of light resulted into simultaneously intramolecular rearrangement and insertion of  $\text{OCH}_3$  reaction [15].

**16. Photochemical rearrangements of isoxazoles** affords acyl azirines, which resulted into the corresponding oxazoles [16].

**17. Photo catalytic rearrangements of 4, 4-Diphenylcyclohexenone** leads to migration of phenyl group present at C-4, to C-3 position of cyclohexenone takes place via photolytic cleavage of alkene bond present in cyclohexenone [17].

**18.** The best result of **photochemical rearrangements of Natural Product** is found in santonin which in presence of light converted into lumisantonin [18].

**19. Photochemical Curtius rearrangement** regarding migration of alkyl group takes place along with full retention of configuration at R-group [19].

**20.** In **Photochemical Harger rearrangement** the phosphinic azide forms a metaphosphonimide in presence of light followed by methanol. This is actually R-groups which migrate [20].

## CONCLUSION

Photochemistry itself came under mature science category. In this review, we have discussed about the some important photochemical reactions. Unique feature of all these photochemical reactions is described above. Overview of photochemical reaction also discusses about the significance of such photo induced chemical reactions and is simultaneously also focused on implications for the main product which is formed at the end of reactions. To understand the underlying processes and mechanisms at the molecular level ubiquity of these photochemical reactions also implies the importance. Now there is more need for new theory in this area. Which is surely expected to be discovered in the near future and it also seems as a promising field for coming future research.

## CONFLICT OF INTERESTS

There is no any possibility of conflict of interest.

## REFERENCES

1. Zhan K, Li Yi, Visible-Light Photocatalytic E to Z Isomerization of Activated Olefins and Its Application for the Syntheses of Coumarins. *Catalysts* 2017; 7: 337.
2. Woodward RB, Hoffmann R. Stereochemistry of Electrocyclic Reaction. *J. Am. Chem. Soc* 1965; 87: 395.
3. Challand BD, Hikino H, Kornis G, Lange G, de Mayo P. de Mayo P reaction. *J. Org. Chem* 1969; 34: 794-806.

4. Mihailovic M, Lorenc L, Paulovic V, Kalvoda J. vitamin D<sub>3</sub> analogs. *Tetrahedron* 1977; 33: 441.
5. Wilzbach KE, Kaplan LA, Photochemical 1,3 Cycloaddition of Olefins to Benzene. *J. Am. Chem Soc* 1966; 88: 2066–2067.
6. Yonemitsu O, Cerutti P, Witkop B, Photoreductions and photocyclizations of tryptophan. *J.Am.Chem.Soc* 1966; 88: 3941.
7. Bouzidi H, Laversin H, Tomas A. Reactivity of 3-hydroxy-3-methyl-2-butanone: Photolysis and OH Reaction kinetics. *Atmospheric Environment* 2014; 98: 540-548.
8. Hixson SS, Mariano SS, Zimmerman EH. Di- $\pi$ -methane and oxa-di- $\pi$ -methane rearrangements. *Chem. Rev* 1973; 73: 531-551.
9. Büchi G, Charles Inman GC, Lipinsky ES, Light-catalyzed Organic Reactions. The Reaction of Carbonyl Compounds with 2-Methyl-2-butene in the Presence of Ultraviolet Light. *J. Am. Chem. Soc* 1954; 76: 4327-4331.
10. Chatani S, Kloxin JC, Bowman NC. The power of light in polymer science: photochemical processes to manipulate polymer formation, structure, and properties. *Polym. Chem* 2014; 5: 2187-2201.
11. Chiba S, Chen H, sp<sup>3</sup> C–H oxidation by remote H-radical shift with oxygen- and nitrogen-radicals: a recent update. *Org. Biomol. Chem* 2014; 12: 4051-4060.
12. Xia W, Shao Y, Gui W, Yang C. Efficient synthesis of polysubstituted isochromanones *via* a novel photochemical rearrangement. *Chem. Commun* 2011; 47: 11098-11100.
13. Iguchi D, Balsells RE, Bonesi SM. Photo-Fries rearrangement of aryl acetamides: regioselectivity induced by the aqueous micellar green environment. *Photochem. Photobiol. Sci* 2016; 15: 105-116.
14. Saito I, Takami H, Matsuura T. Nitro-nitrite rearrangement and intramolecular cycloaddition in the photochemistry of nitro-olefins. *Tetrahedron Letters* 1975; 16: 3155-3158.
15. i) Ge SS, Chen B, Wu YY et al, Current advances of carbene-mediated photoaffinity labeling in medicinal chemistry. *RSC Adv* 2018, 8: 29428-29454. ii) Chowdhry V, Vaughan R, and Westheimer F H, 2-diazo-3,3,3-trifluoropropionyl chloride: reagent for photoaffinity labeling. *PNAS* 1976, 73: 1406-1408
16. Beccalli EM, Majori L, Marchesini A. Torricelli, *Science of Synthesis: Oxazoles*. C. Chem. Lett. 1980; 659.
17. Zimmerman HE, Wilson JW, Mechanistic and Exploratory Organic Photochemistry, IX. Phenyl Migration in the Irradiation of 4,4-Diphenylcyclohexenone. *J. Am. Chem. Soc* 1964; 86: 4036-4042.
18. Barton DH, R, De Mayo P, Shafiq M, Photochemical transformations Part II. The constitution of lumisantonin. *J. Chem. Soc* 1958; 140-145.
19. Scriven, EFV, Turnbull K. Azides: their preparation and synthetic uses. *Chemical Reviews* 1988; 88: 297-368.
20. i) Smith PAS. The Curtius reaction *Organic Reactions*. 1946; 3: 337-449. ii) Warren JD, Press JB. Formation and Curtius rearrangement of acyl azides from unreactive acid chlorides. *Synth. Commun* 1980; 10: 107-110.