PHOTOSENSITIZED REACTIONS: AN IMPORTANT ROUTE OF REACTION IN PHOTOCHEMISTRY

Ankur H. Dwivedi[1], Shibu G. Pillai[2]

[1]*Department of Chemical Engineering, Nirma University, Ahmedabad (India)*

ABSTRACT

Today, photosensitized reactions are of much more importance in the field of photochemistry. The photochemistry of different compounds by the route of photosensitization technique is being studied extensively with considerable interest in recent years due to the interesting aspects of photosensitization of different compounds. In this paper, different types of photosensitized reactions, mechanism and their applications in different fields are discussed in brief.

***Keywords*: Photosensitized Reactions, Photo sensitizer, Photochemistry.**

I. INTRODUCTION

In photochemistry, photosensitized reactions have attracted the chemists from different areas of chemistry as the route is simple as well as low-cost in comparison to the other photochemical techniques. Due to this fact, the field of the photosensitized reactions is now growing field today for all chemists. Its application is not limited to any specific branch of chemistry but the technique can be applied in different area of chemistry. The most important feature of these reactions is the very less amount of the photosensitizer is required for the completion of the reaction. This can also help us to protect our environment against the chemical pollution; which is again fulfilling the condition of one of the twelve green chemistry principles (Lancaster, 2002 and Clark, 2002). Certain reactions, though not sensitive to light, are made sensitive by the presence of small quantity of substance. The foreign substance can absorb light and stimulate the reaction without taking part in it. The substance which after absorbing light induces a photochemical reaction without undergoing any chemical reaction is known as sensitizer and this phenomenon is known as photosensitization. Photosensitized reactions are the reactions in which; the light-absorbing molecule transfers its energy to another molecule and itself comes to the ground state. The energy-accepting molecule goes to excited state and gives chemical reaction (Dwivedi, Pande, 2012).

Every year number of papers are published in national and international journals on photosensitized reactions. Different compounds are used as photosensitizer such as ketones, aliphatic and aromatic amines, methylene blue, eosin, eosin yellow, rose bengal, acridin orange, chlorophyll, hematoporphyrin, carbazole, naphthalene and its derivatives, anthracene, riboflavin, dienes, hydroquinones, borohydride, mercury, ozone, H_2O_2, UV/H_2O_2, UV/O_3, UV/Fenton's reagent, organometallic complexes and many more compounds are reported as photosensitizer in different applications. A wide range of chemicals, including some that are fungal and bacterial

in origin, may act as photosensitizing agents (Quintero et al., 2000, Dwivedi, 2012, and Powet et al., 1987). In this paper, mechanisms, types and applications of photosensitized reactions have been discussed in brief.

II. MECHANISM OF PHOTOSENSITIZED REACTION

This type of reaction is known as indirect photochemical reaction in which the photons of visible light are not directly absorbed by the substrate molecule but the energy for performing photochemical reaction is received from the sensitizer. As these reactions can be performed with the help of visible light which is available freely, cost of the reaction can be reduced. In this reaction, the photosensitizer molecule (Donor) will first absorb the visible light frequency and it will get into the singlet excited state. By inter system crossing (ISC), it will get into the triplet excited state; where the life time of the excited species is very less and by transferring the energy from triplet state to the substrate molecule (Acceptor), the photosensitizer will come back to the ground state. By this energy transfer process, substrate molecule will get into the singlet excited state and from there and ultimately result in chemical alteration of the other molecule in the system (Fig. 1) (Dwivedi, Pande, 2012 and Dwivedi, 2012).

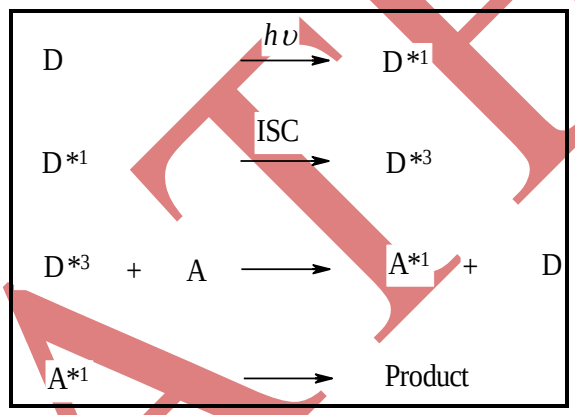

Fig. 1: General mechanism of photosensitized reaction

III. TYPES OF PHOTOSENSITIZED REACTIONS

Mainly there are two types of photosensitized reactions. First type is by electron transfer and second is by energy transfer. Generally these types of reactions are oxidation reactions which are also known as photo-oxidation reactions. For type one, there is either hydrogen atom abstraction or electron transfer and radical will be formed and then radical will react with oxygen to give oxidation product while for type two, energy transfer occurs between excited sensitizer and oxygen giving excited singlet oxygen from which; the oxidation product will be formed. Singlet oxygen has special physical properties; which allow characterization of it and the photosensitized mechanism can be derived for a particular reaction (Powet et al., 1987).

VI. APPLICATIONS OF PHOTOSENSITIZED REACTIONS

Due to the practicality and versatility of the reaction, photosensitized reactions are in high demand in the chemical research field. Today almost in each and every field photochemical reactions are being studied. Furthermore, the cost effectiveness of the reaction adds more value in today's research. These reactions which

involve UV/Vis radiation and biological systems are particularly interesting because of their wide field of applications such as environmental, energetic, biological, medical, polymer etc. (Quintero et al., 2000).

In pharmaceutical field, photosensitized reactions are used for the discovery and synthesis of new drug molecules at bigger scale which; definitely leads the industries towards the green chemistry and eco-friendly approach. Even some of the drug molecules shows the photosensitizer's properties and reactions are being carried out using drug molecules too in pharmaceutical industries (Moore, 1977). In polymer industries, number of photosensitized reactions are performed to get new polymers which reduces the cost of production (Chinmayanandam et al., 1954). Today the whole world is struggling against the problem created due to the pollution of soil, water and air, and photochemical reactions have demonstrated high level of satisfaction for the treatment of polluted soil, water and air samples. Thus in water treatment process, photosensitized reactions are proven as one of the best and economic techniques (Dwivedi, 2012). In biology, photosensitized reactions are popular in aerobic and anaerobic conditions in the presence of different bacteria. In medical field, nowadays therapeutic approach for the treatment of some of the incurable cancer cells is possible due to the photosensitized reactions. In other medical fields like photodynamic therapy, blood purification and in the process of inactivation of viruses, photosensitized reactions are proved very useful. In one of the international journal paper, authors have reported a list of 174 currently used clinical drugs inducing photosensitization is provided in addition to some others from which phototoxic effects are suspected (Quintero et al., 2000 and Ismail et al., 1998). Today, in the development of industries like polymer, agrochemical, pesticides, rubber, fine chemicals, solvents, dyes and intermediates, textile, etc., the applications of photosensitized reaction have played an important and dynamic role. Different photosensitizers work differently and it is not possible to give the mechanism of all those sensitizers here. But in general they follow the same basic mechanism as discussed above.

V. CONCLUSION

The importance of the photosensitization processes can be understood easily taking into account the increasing number of reports, articles and journal papers every year worldwide. The biggest advantage of photosensitized reaction is, with this technique, the molecules which cannot absorb the visible light can also undergo photochemical reaction with the help of visible light radiation through indirect photochemical reactions. As these reaction can be performed with the help of visible light; which is freely available from the universal visible light source sun or economic sun simulated light sources; which is comparatively much cheaper than that of the UV light sources, cost of the reaction can be reduced and we can save our environment from the pollution too.

NOMENCLATURE

A	Acceptor
D	Donor
ISC	Inter system crossing
UV	Ultraviolet

Vis Visible

REFERENCES

[1] Lancaster M., "*Green chemistry: An introductory text*" (Royal Society of Chemistry, London, UK, 2002).

[2] Clark J., and Macquarrie D., "*Handbook of green chemistry and technology*" (Wiley-Blackwell, New York, USA, 2002).

[3] Dwivedi A. H. and Pande U. C., "Photochemical degradation of halogenated compounds: A review", Scientific Reviews & Chemical Communications, 2(1), 2012, 41-65.

[4] Quintero B. and Miranda M. A., Mechanisms of photosensitization induced by drugs: A general survey, Ars Pharmaceutica, 41(1), 2000, 27-46.

[5] Dwivedi A. H., Photochemical degradation of halo-organic compounds: An economical solution for water pollution (Lambert Academic Publishing, GmbH & Co. KG, Germany, 2012).

[6] Powet B. and Chapelon R., Photochemical mechanism in photosensitization, Journal De Physique, 12(48), 1987, C7:247-C7:251.

[7] Moore D. E., Photosensitization by drugs, Journal of Pharmaceutical Sciences, 66, 1977, 1282-1284.

[8] Chinmayanandam B. R. and Melville H. W., Photosensitization of polymerization reactions, Transactions of the Faraday Society, 50, 1954, 73-82

[9] Ismail M. S., Weitzel H. and Berlien H.-P., "*Laser in medicine: Applied photosensitizers' classification for clinical photodynamic therapy*" (Springer Link, Germany, 1998).

Biographical Notes

Dr. Ankur H. Dwivedi is working as an Assistant Professor in Chemical Engineering Department, Nirma University, Ahmedabad, India.

Dr. Shibu G. Pillai is working as an Assistant Professor in Chemical Engineering Department, Nirma University, Ahmedabad, India.