Review Article

The Application of Light-still on the Run

Raghad Haddad, Atheel Alwash, Mehdi Shihab, Majid Khalaf, Dheaa Zageer, Jawad Shneine, Ahmed Ahmed, Wedad Al-Dahhan, Emad Yousif

Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq

Abstract The role of light in effecting chemical change has been recognized for many years. Photochemical reactions are the study of chemical reactions, isomerizations and physical behavior that may occur under the influence of visible and/or ultraviolet light (UV). During the past century, the role of light in the fields of physics, chemistry, and biology has expanded to include emerging fields such as environmental engineering, agriculture, materials science, and biomedicine. Many of the technological advances that society has enjoyed since the industrial revolution are the result of light-based phenomena

Introduction

UNESCO (the United Nations Educational, Scientific, and Cultural Organization) has declared 2015 the "International Year of Light and Light-Based Technologies". In this celebration, this Outlook provides a general history of light and its applications, from the earliest moments of the Big Bang through its present impact on all forms of life on the planet. It is no exaggeration to say that light has played a crucial role in every aspect of human history, leading to amazing advances in science and technology, but also strongly influencing art, religion, and politics. Even before human existence, there was a period of time (from roughly 10 s after the Big Bang to 380,000 years later) when our universe consisted of nothing but photons1.The energy from our Sun is a faint remnant of these early events, without which we would not exist at all today. During the past century, the role of light in the fields of physics, chemistry, and biology has expanded to include emerging fields such as environmental engineering, agriculture, materials science, and biomedicine. Many of the technological advances that society has enjoyed since the industrial revolution are the result of light-based phenomena [1-2].

1. What is Photochemistry mean?

The role of light in effecting chemical change has been recognized for many years. Photochemical reactions are the study of chemical reactions, isomerizations and physical behavior that may occur under the influence of visible and/or ultraviolet light (UV). Generally, this term is used to describe a chemical reaction caused by absorption of (UV) wavelength from (100-400 nm), visible light (400-750 nm) or infrared radiation (750-2500 nm) [3].Ultraviolet radiation (UV) can cause degradation of certain materials if exposed. Photochemical reactions require a light source that emits wavelengths corresponding to an electronic transition in the reactant. In the early experiments (and in everyday life), sunlight was the light source, although it is polychromatic. Mercury-vapor lamps are more common in the laboratory. Low pressure mercury vapor lamps mainly emit at 254 nm. For polychromatic sources, wavelength ranges can be selected using filters. Alternatively, laser beams are usually monochromatic (using nonlinear optics you can get e.g. two wavelengths) and LEDs have a relatively narrowband that can be efficiently used, as well as Rayonet lamps, to get approximately monochromatic beams. Light provides the activation energy. Simplistically light is one mechanism for providing the activation energy required for many reactions. The connection between light and quantized states in matter led other research breakthroughs over the

next few decades, the maser in the 1950s and the laser in the early 1960s being the most important. The visible light laser was revolutionary for both fundamental and applied science [4].

## 2. Photophysical and Photochemical Processes [5]:

Absorption of a photon by a species (A), leads to the formation of short - lived electronically excited molecule, (A*)

A + hv →A*   **(1)**

The electronic energy can be dissipated physically or chemically.

2.1. Photophysical Processes

Chemists desire to understand the mechanisms of bond breaking and bond forming processes, or about the movement of fundamental particles such as protons and electrons and sometimes both. In terms of light-driven reactions, chemists turn to the well-known Jablonski diagram to understand the photophysical processes leading to reactive excited states [6]. The terms absorption, excitation, intersystem crossing, vibrational relaxation, internal conversion, fluorescence, and phosphorescence are all familiar terms to photo chemists in this regard. It is somewhat underappreciated that, in the mid-20th century, a great deal of controversy surrounded the latter phenomenon of phosphorescence from organic molecules [1]. Photophysical processes may be subdivided into radiative and non-radiative process:

A*→A + hv (radiative deactivation)   **(2)**

A*→A + heat (nonradiative deactivation)   **(3)**
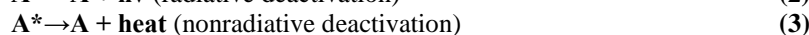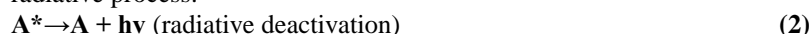
2.1.1. Non radiative processes:

(a) Internal conversion (IC): Relaxation from an upper excited electronic state such as: S_2, S_3 … to lower electronic excited state with the same multiplicity take place rapidly by radiationless process. Interconversion from the first excited to the ground state is believed to be a significant process in coordination compounds (speed ranges from 10^{-12} to 10^{-13} sec).

(b) Intersystem crossing (ISC): Radiationless transitions between electronic states of different multiplicity are forbidden, but it is a form of radiationless transitions which can lead to populate spin - forbidden states. **$S_1 \to T_1$**

This is a very important phenomenon in transition - metal complexes because it is well established that the rate constant for intersystem crossing is greatly enhanced in paramagnetic species. In many cases, their lifetime is sufficiently long to enable excited molecules to engage in chemical reaction [7].

2.1.2. Radiative processes [8]:

(a)Florescence: Involved a radiative transition (photon emission) between state of the same multiplicity (spin allowed) usually from the lowest vibrational level of lowest excited singlate state **$S_1 \to S_0$+hv**

Typical timescales for florescence emission are of the order of (10^{-12}-10^{-6}) s

(b)Phosphorescence: Is a spin forbidden radiative transition between states of different multiplicity, usually from lowest vibrational level of the lowest excited triplate state: **$T_1 \to S_0$ + hv**

Typical timescales for photon emission by Phosphorescence are of the order of (10^{-3}-10^{2}) sec.
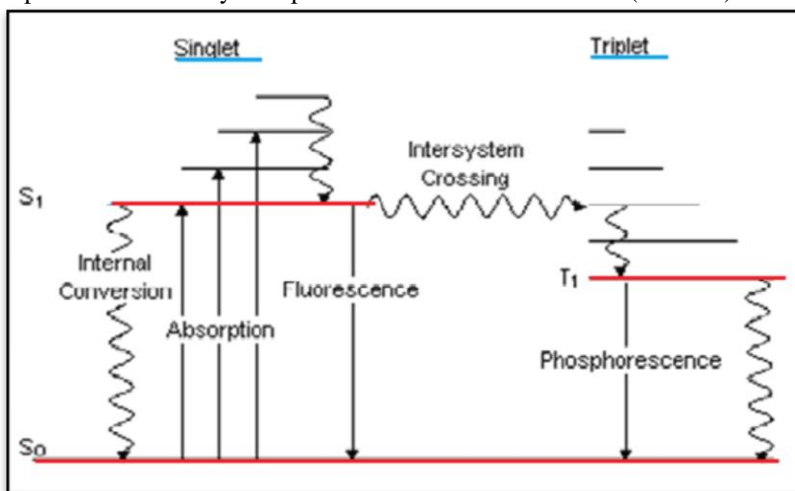

Figure 1: Jablonski diagram

3. Photochemical process steps:

Most photochemical reactions can be considered to occur in three stages:

1. Absorption of electromagnetic radiation to produce electronically excited states. 2. Primary photochemical reactions involving excited electronic states.

3. Secondary or dark reactions whereby the products of the primary photochemical reaction are converted to stable products [9].

4. Photochemical reaction:

The photon excretion of coordination compounds may cause a number of different reactions whose nature depends on the type of the metal atom and the ligands involved, the wavelength of irradiation and other experimental conditions. The photochemical reactions may be sub divided into four main types [10]:
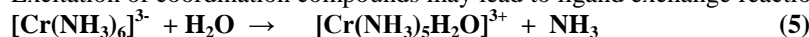
4.1. Photochemical oxidation-reduction reaction:

In a large number of photochemical processes, the overall result is the reduction of the metal and oxidation of one or more ligands. Example this reaction below:

$$[Fe(C_2O_4)_3]^{-3} \rightarrow \quad [Fe(C_2O_4)_2]^{2-} + [C_2O_4]^{2-} \qquad\qquad (4)$$
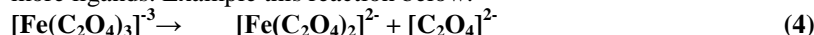
4.2. Photosubstitution reaction:

Excitation of coordination compounds may lead to ligand exchange reaction such as that shown in equation (5):

$$[Cr(NH_3)_6]^{3-} + H_2O \rightarrow \quad [Cr(NH_3)_5H_2O]^{3+} + NH_3 \qquad\qquad (5)$$

4.3. Photochemical isomerization and racemisation reactions:

A number of optically active coordination complexes exhibit a tendency to racemisephotochemically. The chromium (III) acetylonate, Cr(acac)$_3$ is an example of this type of complexes. Irradiation of dextroCr(acac)$_3$ with light of λ=546 nm has been reported to convert (with high quantum efficiency) the levo form[11-12].

$$Cr(acac)_3 \rightarrow \quad Cr(acac)_3 \qquad\qquad (6)$$
Dextrolevo

5. Laws of Photochemistry:

There are two laws of photochemistry: GrotthusDrapper Law: Although the importance of radiations involved in many chemical or biological processes (for example, photo-fading of colored materials, photosynthesis in plants, blackening of silver halides etc.) was well known but all the results used to be expressed qualitatively. It was only in 1817 that Grotthus and Drapper had formulated a law of photochemistry which stated that "only the radiation absorbed by the system can be effective in producing the chemical change" The radiation absorbed (Iabs) is given by: $Ia = I_0 - I$ **(7)**

where I_0 is the intensity of the incident light and I is the intensity of the transmitted light. These are related by the well known Beer-Lambert's law.

$$I = I_0 exp(-\varepsilon' C l) \qquad\qquad (8)$$

where 'C' is the concentration of the absorbing species in moles litre^{-1}, 'l' is the path length in cm and ε' the natural molar extinction coefficient and is a function of the frequency of radiation. The SI units for C, l and ε' are mol dm^{-3}, mm and m^2 mol^{-1}. For historical purpose, the Lambert- Beer law is the combination of two laws, i. e. Lambert law which states that the fraction of incident radiation absorbed by a transparent medium is independent of the intensity of the incident radiation and each successive layer of the medium absorbs an equal fraction of incident radiation, whereas the Beer's law states that the amount of radiation absorbed is proportional to the number of molecules absorbing the radiation, that is the concentration 'C' of the absorbing species.

the absorbance of light is directly proportional to the thickness of the media through which the light is beingtransmitted multiplied by the concentration of absorbing chromophore; that is, $A = \varepsilon bc$ where A is the absorbance, εis the molar extinction coefficient, b is the thickness of the solution, and c is the concentration [13].

Beer's law

$$A = abc = log(100/\%T) \; 2 - log \%T \qquad\qquad (9)$$

where:

A=absorbance, a=absorptivity, b= light path of the solution in cm, c = concentration of the substance of interest,

%T = per cent transmittance-the ratio of transmitted light to incident light.

Stark-Einstein' Law: The second law was first stated by Stark in 1908 and later by Einstein in 1912. The combined law states that "One quantum of light is absorbed per molecule of absorbing and reacting substance that disappears."

This law is valid for normal sources of radiation, where the average number of photon quanta emitted from such sources is between 1013 to 1015 s^{-1}. A number of exceptions to the above law have been observed using very intense laser radiation, known as multi-photon excitation.

6. Photodegradation definition

Is degradation of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared radiation, visible light, and ultraviolet light. Polymeric material, synthetic or nature or semisynthetic are photodegradable when exposed to the environment, light energy (UV part between 290-400 nm) is the most effective. A wide variety of synthetic and naturally polymers absorb solar ultraviolet radiation and undergo photolytic, photooxidative, and thermooxidative reactions that result in the degradation of the material [14].

Photodegradation includes photodissociation, the breakup of molecules into smaller pieces by photons. It also includes the change of a molecule's shape to make it irreversibly altered. Light - induced polymer degradation, or photodegradation, includes the physical and chemical changes caused by irradiation of polymers with ultraviolet or visible light[15].The degradation suffered by these materials can range from mere surface discoloration affecting the esthetic appeal of a product to extensive loss of mechanical properties, which severely limits their performance [16].Damage by UV radiation is commonly the main reason for the discoloration of dyes and pigments, weathering, yellowing of plastics, loss of gloss and mechanical properties (cracking), and other problems associated with UV light[17-19].

The existence of chromophoric groups in the macromolecules is a prerequisite for the initiation of any photochemical reaction. A common photodegradation reaction is oxidation. The oxygen absorption rate depends on the surface area and decrease with increasing film thickness. Oxidation (thermo and photo) started at the surface of polymers. Photodegradation may occur in the absence of oxygen (chain breaking or cross-linking) and the presence of oxygen (photooxidative) degradation. The photooxidative degradation process is induced by UV radiation and other catalysts (or both) and can be accelerated at elevated temperatures.Photooxidative degradation of polymers, which include processes such as chain scission, crosslinking and secondary oxidative reactions, and takes place via radical processes, similar to thermal oxidation reactions [20-21]. The term photodegradation might be distinguished from photo-oxidation of polymers, in the latter oxygen is involved in the process while in the former light energy (E=hv) is only responsible for the photodegradation [22].
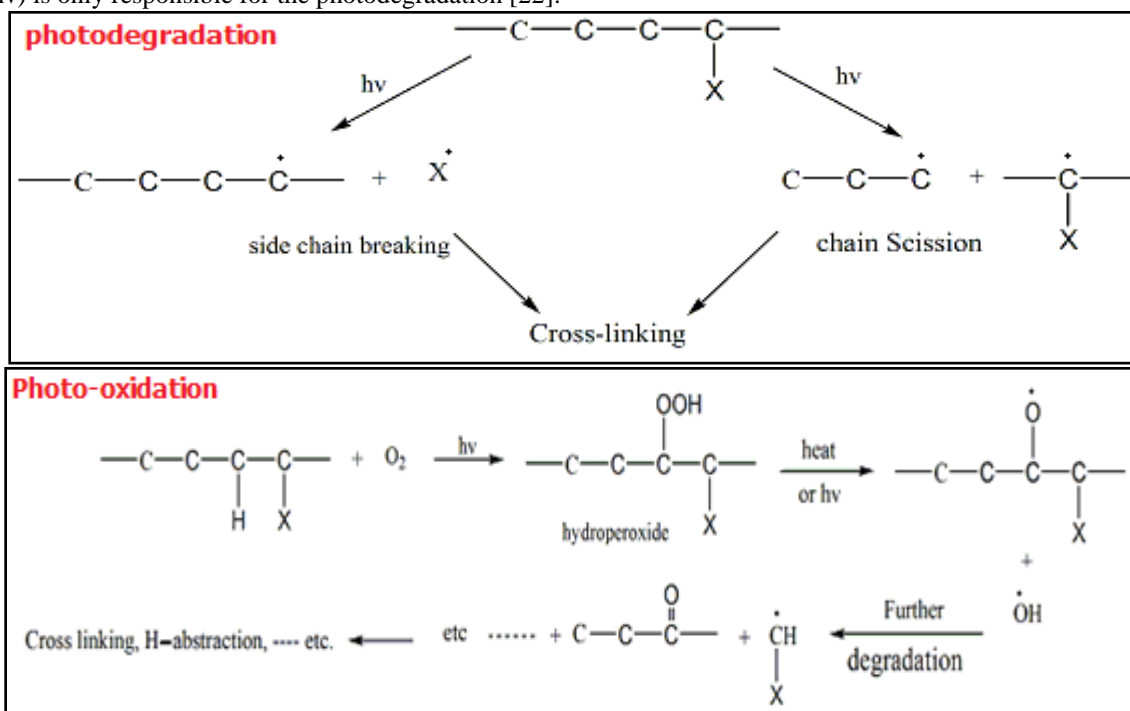
7. Steps of photodegradation:

The photo-oxidation mechanism of polymers is largely similar to the mechanism of thermo-oxidation. The photooxidation mechanism of polymer based on the mechanism proposed by (Rabek) [23]. The radicals are the main intermediate with photo-oxidation degradation of polymers. There are three main processes are involved in each degradation process [24-25]: Initiation, Propagation and Termination:

7.1. Photoinition: Internal and /or external chromophoric groups absorb light and produce low molecular weight radicals ($R^.$) and /or polymeric macro radicals ($P^.$) as follows:

$$PH \quad \rightarrow \quad P^. + H^. \qquad\qquad\qquad (10)$$

This reaction may be initiated by physical factors such as: UV radiation, heat, and ionization, ultrasonic or mechanical effects or by chemical factors (direct reaction with O_2 or atomic oxygen, catalysis or singlet O_2 $[O_2^*]^1$ excited state.

7.2. Propagation step: This step can be divided into six different steps[26-27]:A) Subsequent reaction, of low molecular radicals ($R^.$) and polymer alkyl radical ($P^.$) in a chain process similar to the abstraction of hydrogen from polymer molecule: $\quad PH \quad + \quad R^.(P^.) \quad \rightarrow \quad ^.PH + P^. \qquad\qquad (11)$

B) Reactions of polymer macro radicals with oxygen, during which polymer peroxy radicals ($POO^.$) are formed. $\quad P^. + O_2 \rightarrow \quad POO^. \ (12)$

C) Abstraction of hydrogen from another polymer molecule by polymer alkylperoxy radical, with the formation of hydroperoxide group.

$$POO + ^\backslash PH \qquad \rightarrow \qquad POOH + ^\backslash P^. \qquad\qquad (13)$$
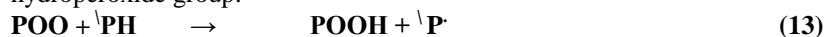
D) Photodecomposition of hydroperoxide groups with the formation of polymer alkyloxy ($PO^.$), polymer peroxy ($POO^.$), and hydroxyl radicals ($HO^.$).
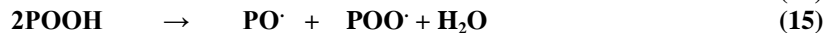
$$POOH \qquad \rightarrow \quad PO^. + {}^. OH \qquad\qquad\qquad (14)$$
$$2POOH \qquad \rightarrow \quad PO^. + POO^. + H_2O \qquad\qquad (15)$$

E) Abstraction of hydrogen from another polymer molecule by polymer alkyloxy radical with the formation of hydroxyl function groups in polymer. The formation of (OH) group during photolysis is clearly indicated by IR spectrum.

$$PO^. + PH \qquad \rightarrow \quad POH \ + \ ^.P \qquad\qquad\qquad\qquad (16)$$
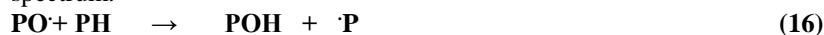
F) Dispropertionation reaction (scission process) of polymer alkyloxy radicals   with the formation of aldehyd or ketone end groups and end polymer alkyl radicals. The formation of (C=O) group during photolysis is clearly indicated by IR spectrum.

where W = H   aldehyde
W = R   Ketone   (17)
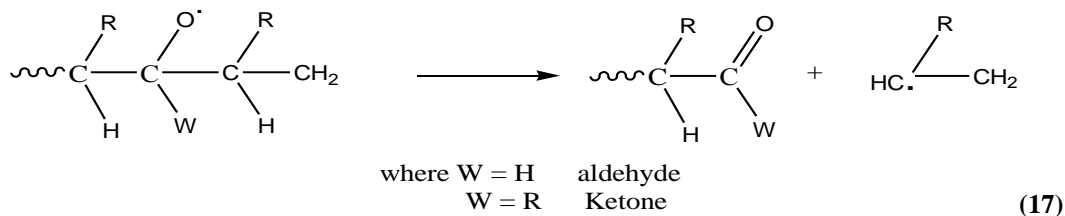
7.3. Termination step: The radicals formed in the degradation of polymers can be terminated by different combination reactions between two polymer radicals, in which inactive products are formed:

$$POO^. + POO^. \rightarrow \quad POOP + O_2 \qquad\qquad\qquad (18)$$
$$POO^. + P^. \quad \rightarrow \quad POOP \qquad\qquad\qquad\qquad (19)$$
$$P^. \quad + P^. \ \rightarrow \ P - P \qquad\qquad\qquad\qquad (20)$$

The significance of each type of the above reaction depends mainly on oxygen concentration (pressure) in the polymer matrix. When the oxygen pressure is high, the termination reaction follows reaction **(18)** almost fully. In the degradation of solid polymers when sufficient oxygen content cannot be maintained reaction **(20)** becomes significant. Polymer radicals can couple mutually as in reaction **(19)** and form crosslinkings with polymer peroxy radicals [28]. The steps of photodegradation of polymers are illustrated in figure (2) [29]:
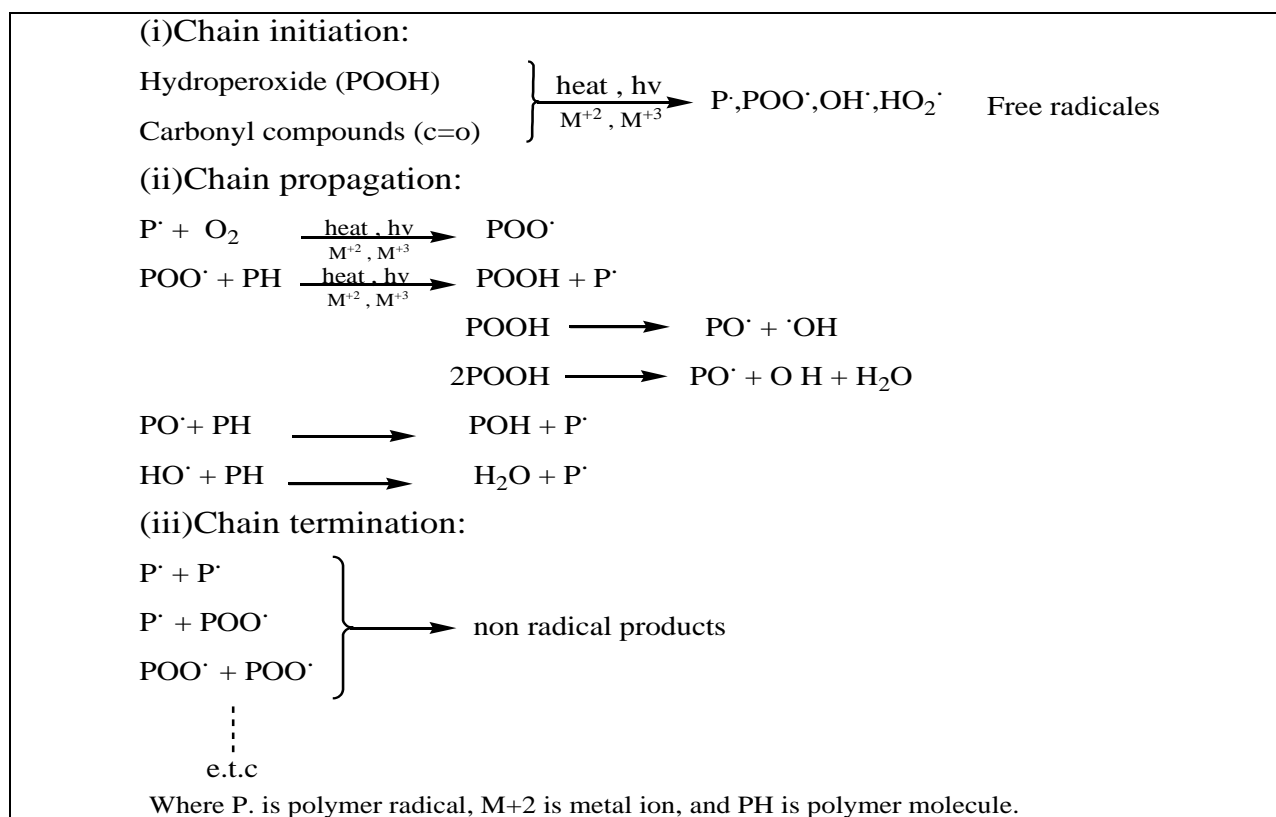
(i)Chain initiation:

Hydroperoxide (POOH)

Carbonyl compounds (c=o) $\xrightarrow[M^{+2},\ M^{+3}]{heat\ ,\ hv}$ $P^\cdot, POO^\cdot, OH^\cdot, HO_2^\cdot$ Free radicales

(ii)Chain propagation:

$P^\cdot + O_2 \xrightarrow[M^{+2},\ M^{+3}]{heat\ ,\ hv} POO^\cdot$

$POO^\cdot + PH \xrightarrow[M^{+2},\ M^{+3}]{heat\ ,\ hv} POOH + P^\cdot$

$POOH \longrightarrow PO^\cdot + {}^\cdot OH$

$2POOH \longrightarrow PO^\cdot + O H + H_2O$

$PO^\cdot + PH \longrightarrow POH + P^\cdot$

$HO^\cdot + PH \longrightarrow H_2O + P^\cdot$

(iii)Chain termination:

$P^\cdot + P^\cdot$

$P^\cdot + POO^\cdot$ $\longrightarrow$ non radical products

$POO^\cdot + POO^\cdot$

e.t.c

Where P. is polymer radical, M+2 is metal ion, and PH is polymer molecule.

Figure (2) General Oxidation and Photooxidation in Polymer

8. How to avoid UV degradation

There are several ways of avoiding UV degradation in plastics by using stabilizers, absorbers or blockers. For many outdoor applications, the simple addition of carbon black at around a 2% will provide the protection for the structure by the blocking process. Other pigments such as titanium dioxide can also be effective. Organic compounds such as benzophenones and benzo-triazoles are typical absorbers which selectively absorb the UV and re-emit at a less harmful wavelength, mainly as heat. The optimum amount of UV absorber varies with each chemical type and

application, but in most cases is in the 0.25-1.0% concentration. The benzotriazole type is good, as it has a low color and can be used at low dose rates below 0.5% [30]. Chemical materials, known as ultraviolet absorbers (UVAs) can be used to protect materials from the damaging effects of UV radiation. A UVA can be incorporated into a material to protect such a material from UV radiation, or a composition that contains UVA can be applied to a UV-sensitive substrate to protect the substrate. Ultraviolet light stabilizers are used in important materials, including films, plastics and cosmetics [31-32].

Almost all synthetic polymers require stabilization against the environmental effect so it became necessary to look for ways and to prevent, or at least reduce, the damage caused by the environmental parameters such as light, air and heat. This can be achieved through the addition of special chemicals, light stabilizers or UV stabilizers, which have to be adjusted to the nature of the resin and the specific application considered. The most common stabilizers being a HALS (hindered amine light stabilizer). These absorb the excited groups and prevent the chemical reaction of the radicals [33-34]. The physical properties of additives and polymers play a very important role in determining the additives efficiency in photostabilization or photodegradation of polymers. For example, the compatibility that any type of additive (photostabilizer, antioxidant, thermal stabilizer. etc.) must be evenly distributed which requires that it be compatible with the polymer matrix [35].

9. Photochemical Electrocyclic Reactions

An electro cyclic reaction is a reversible reaction that involves ring closure of a conjugatedpolyene to a cycloalkene, or ring opening of a cycloalkene to a conjugated polyene. For example, ring closure of 1,3,5-hexatriene forms 1,3-cyclohexadiene, a product with one more bond and one fewer " bond than the reactant.
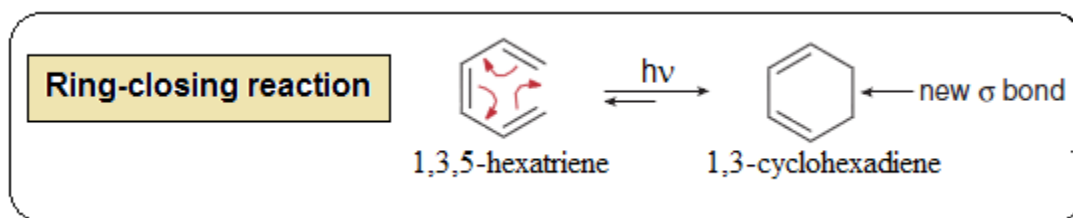
Ring opening of cyclobutene forms 1,3-butadiene,a product with one fewer bond and one more " bond than the reactant
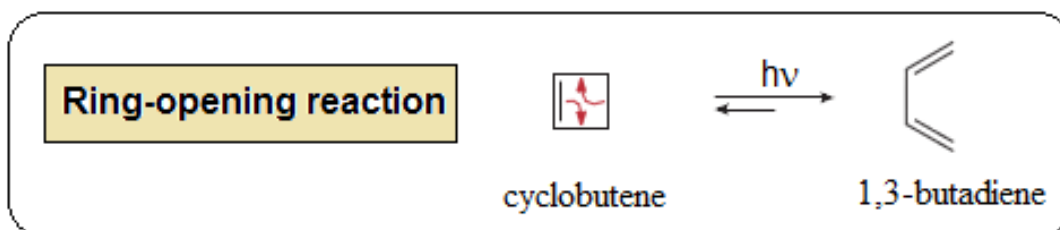
In photochemical reactions, we must consider theorbitals of the HOMO of the excited state to determine the course of the reaction. The excited state HOMO has the *opposite* orientation of the outermost *p* orbital's compared to the HOMO of the ground state. As a result, the method of ring closure of a photochemical electrocyclic reaction is *opposite* to that of a thermal electro cyclic reaction for the same number of π bonds. Photochemical electro cyclic ring closure of (2E,4Z,6E)-2,4,6-octatriene yields a cyclic product with trans methyl groups on the ring [36-37] (see Fig. 3).
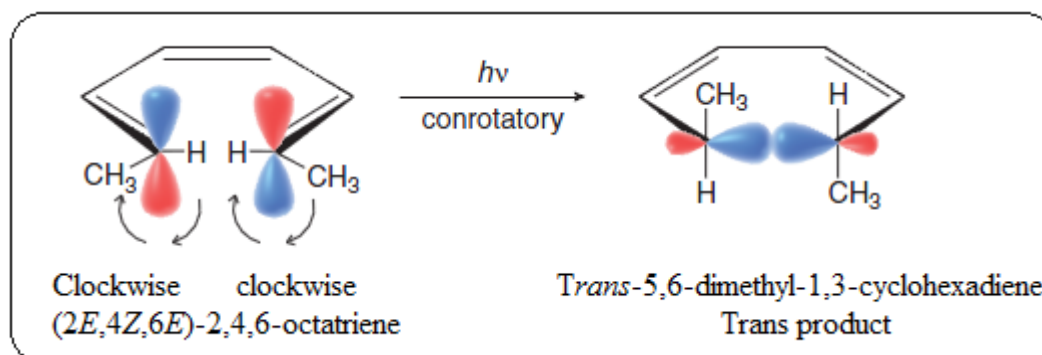

Figure (3)Photochemicalelectrocyclic ring closure.

Photochemical processes, where the reactant resides on an excited state potential energy surface and the products accumulate on the ground state, could not be easily investigated.

In photochemistry, the reaction path must have at least two branches: one located on the excited state and the other located on the ground state energy surface. The main difficulty associated with such computations lies in the correct definition and practical computation of the "funnel" region where the excited state reactant or intermediate is delivered to the ground state. In another words, photochemical reactions are recognized as being controlled by the properties of a **conical intersection** (the lowest energy point at which the ground and excited state "touch") rather than a transition state(see Fig. 4), although the selection rules derived earlier are in fact often adhered to. During the last decade, computational tools have been developed and strategies discovered to explore electronically excited state reaction paths [38-41].
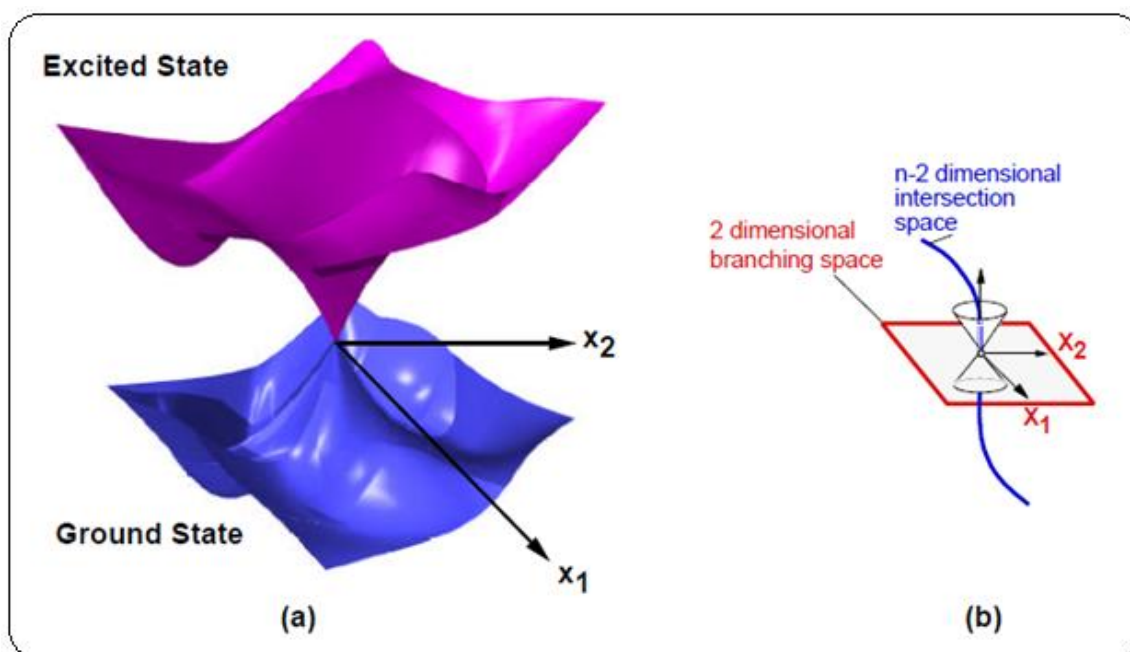
Figure (4) Typical double cone topology for a conical intersection (a), and relationbetween the "branching space" (x1, x2) and the "intersection space" (spanning theremainder of the n-2 dimensional space of internal geometric variables (b).

10. Electrocyclic reactions in organic synthesis

The developing mechanistic of photochemical reactions and synthetic routes encouraged the chemist to use photochemical methods in designing the synthesis of organic molecules. The Witkop cyclization constitutes an intramolecular variant of such a process, typically with an indoleheterocycle as an electron donor. The specific synthetic value of this reaction lies in a C-C bond formation without requiring any prefunctionalization of the indole system. This photoreaction has been applied to the total synthesis of natural products as complex molecular architectures.

In an indole system the C3-positon displays the highest electron density and is therefore the favored position for attack of an electrophile. The photocyclization of an indole system bearing a chloroacetamide at the 2-position gives the 2,3-annulated product except as follow. As can be seen from Scheme 1, the reaction tolerates substituents at the a-position of the chloroamide. Irradiation of **1** gave a 3:1 mixture of the diastereomers**2** and **3** in 47% yield. This tolerance enables the synthesis of azocinoindoles (related to serotobenine) using theWitkop process [42].
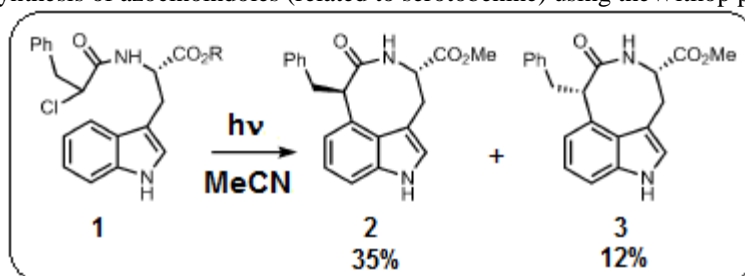
Scheme (1)Thephotocyclization of an indole system bearing a chloroacetamide.

The total synthesis of (±)-quebrachamine (**6**) by Bajtos and Pagenkopf comprises an example for a high yielding photocyclization process (Scheme 2) [43].They carried out a Witkop cyclization on **4**. The photoinducedringclosure methodology was applied and fortunately afforded the desired product **5**. The reaction proceeded smoothly in aqueous ethanol in the presence of sodium carbonate and delivered the product in 85% yield.
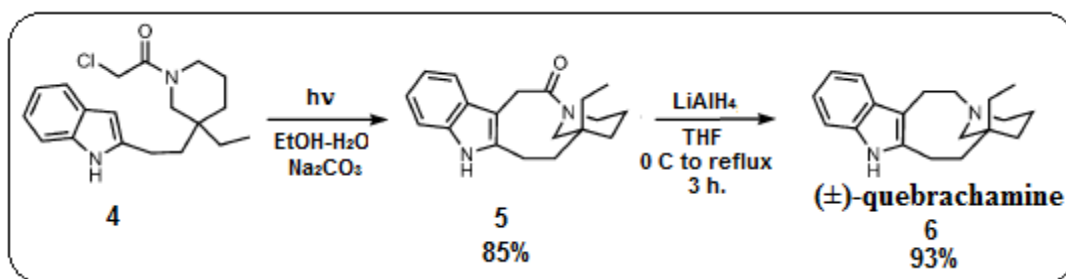
Scheme (2)Total synthesis of (±)-quebrachamine by photocyclization process.

The best known representatives are undoubtedly the [2 + 2] photocycloaddition, forming either cyclobutanes or four-membered heterocycles (as in the Paternò–Büchi reaction). In the presence of an alkene, three different modes of photocycloaddition with benzene derivatives can occur; the [2 + 2] or *ortho*, the [3 + 2] or *meta*, and the [4 + 2] or *para*photocycloaddition [44].

Fenestranes have been the targets of total synthesis by *meta* photocycloaddition reactions the starting material undergoes a selective 1,3-addition to one of the tethers. The subsequent cyclopropaneringclosure gives mainly the linear fused *meta*product in 23% yield. The *meta*compounds and two rearranged *ortho*products were isolated from the reaction mixture in a combined yield of 60%. The major *meta*product can be converted into the fenestrane by further irradiation [45] see Scheme 3:
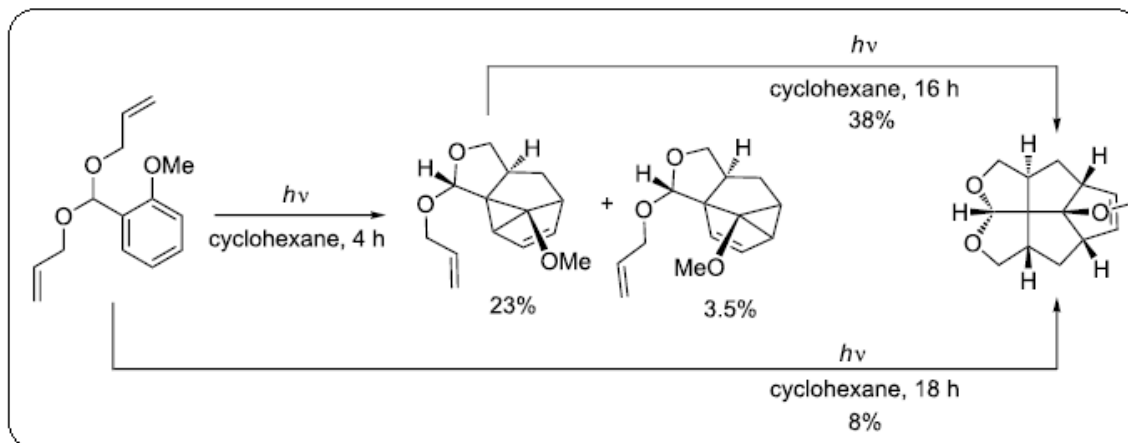
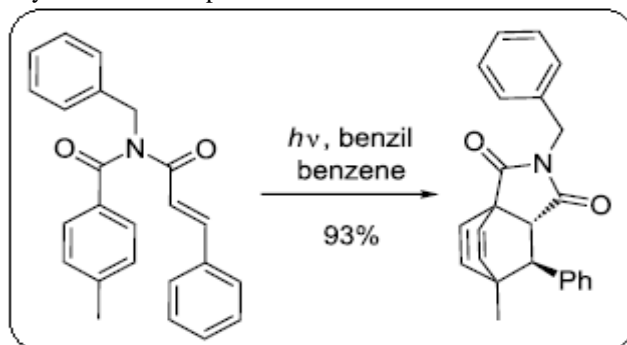**Scheme (3) Photocycloaddition reaction affording fenestrane.**

There is little data on the selectivity of the *ortho*photocycloaddition in the literature. Substituted olefins may add in an *exo*or *endo*fashion. While electron-deficient alkenes give mixtures of both possible products, electron-rich compounds show stereo selectivity towards the *exo*products (Scheme 4) [46].
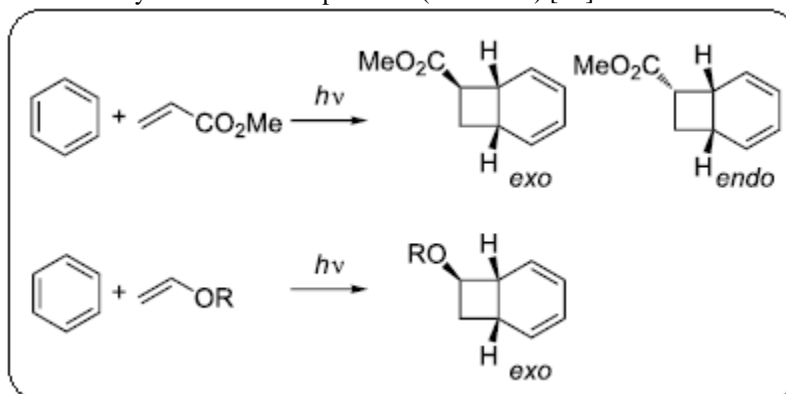
**Scheme (4) *Exo*and*endo*selectivity in *ortho*photocycloaddition.**

There are few examples leading to *para*products in high yield. However, one example is the intramolecularphotocyclo addition of a cinnamoylamide and a benzamide moiety (Scheme 5) [47]. This reaction is very efficient and leads to high yields of the bicyclo[2.2.2]octadiene derivative. In this example, the cinnamoylamide is sensitized by benzil to its triplet excited-state.

**Scheme (5) Photocycloaddition of enone with benzene.**

The Paternò-Büchi reaction is a photochemical reaction between a carbonyl compound and an alkene to give the corresponding oxetane. Recently, the reactivity of isoxazole derivatives has been revisited, showing that some derivatives, such as 3,4,5-trimethylisoxazole, gave the corresponding oxetanes in very good yield (in the case reported in the Scheme 6, almost quantitative yields were obtained) and excellent diastereoselectivity (>99:1) [48].
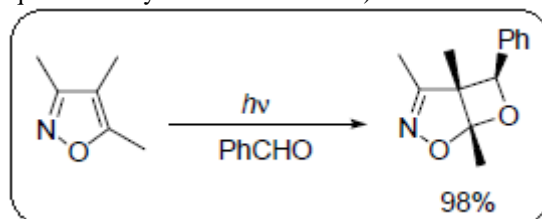
Scheme (6) Reaction of an isoxazole derivative.

On the contrary, 3-phenyl substituted derivatives did not give the Paternò-Büchi reaction, allowing one to obtain only the ring contraction products. In this case, the isoxazole was able to absorb the light giving the corresponding excited state able to give the isomerization reaction [49].

The DeMayo reaction is a photochemical reaction in which the enol of a 1,3-diketone reacts with an alkene (or another species with a C=C bond) and the resulting cyclobutane ring undergoes a retro-aldol reaction to yield a 1,5-diketone (see Scheme 7) [50].
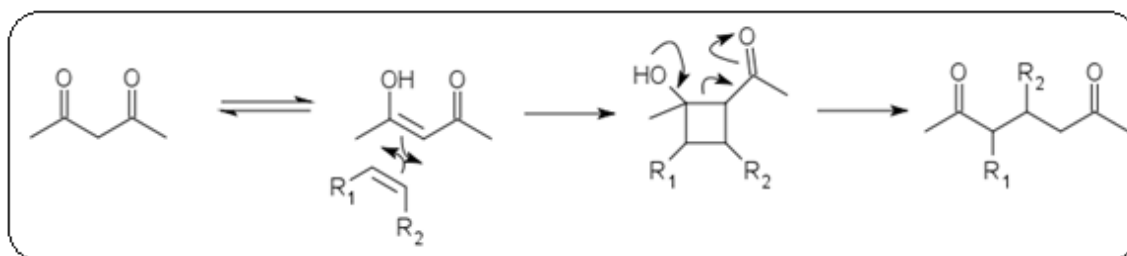
Scheme (7)GeneralDeMayo photochemical reaction.

The applications of DeMayo reaction in organic synthesis were revealed in literatures, whereas Winkler and coworkers were delighted to find that photocycloaddition of the derived allylic chloride proceeded in 60% yield to give the desired photoadduct, accompanied by the C-13chloro-isomer (5:2 ratio)(see Scheme 8) [51].
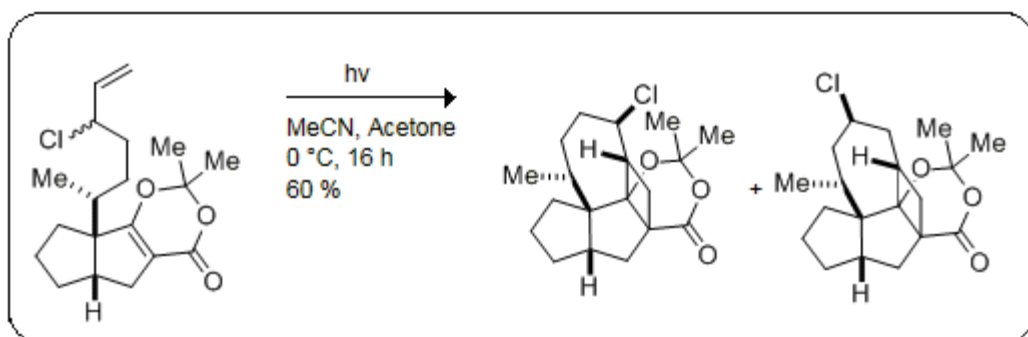
Scheme (8) DeMayo photochemical reaction ofderivedallylic chloride.

11. Photocatalytic reaction

Although the absorption of UV light by some materials can be harmful in one side, however the UV light has a lot of successive usage on other side such as the waste water treatment technology. The cumulative of contaminate wastewater streams by the continuous discharging of organic species refractory promoted the replacement of conventional methods with newer technologies able to degrade these contaminants [52].

Advanced oxidation processes (AOPs) such as ozonation, peroxone, photocatalysis, Fenton and a combination of photo-Fenton, UV/O_3, UV/H_2O_2have been widely investigated . The success of advanced oxidation process is influenced by the extent of hydroxyl radicals (HO•) production, the use of certain chemical and/or suitable forms of energy.

The free radicals have high capability in the oxidation of organic pollutants in water by completely converting them to CO_2, H_2O and harmless mineral salts [53]. Furthermore the AOPs is a green technology due to the low- or non- waste generating after the end of the process which is one of the main drawbacks of the traditional wastewater treatment processes [54]. The AOPs can be classified according to the type of the energy source applied during the reaction e.g. ozonation process [55] photochemical or photocatalytic process [56], Fenton process [57], electrichemical process [58] and ultrasonic process [59]. Among these successive processes, the photocatalytic reactions have been widely investigated during these last decades. Photocatalytic systems are mainly based on semiconductor metal oxides since these solids are extremely robust materials and do not become self-degraded. However, the performance of inorganic semiconductors may be far from optimum due to the fact that their absorption band is deep in the UV region and the absorptivity for visible light is very low. To overcome this limitation a line of research has been aimed at the preparation of doped semiconductors in which the introduction of new electronic states in the semiconductor bandgap increases their absorption in the visible. Even in cases in which a dopant is introduced, the photocatalytic activity of the resulting semiconductor may still need improvement [60].

Several studies have been reported on the degradation of organic dyes using suspensions of TiO_2 powder in the polluted solution. However, there are several limitations to use 'bare' TiO_2 due to the fact of its rapid aggregation in suspension, resulting in smaller effective surface area and lower catalytic efficiency. The small size of TiO_2 particles complicates the filtration of suspensions during the process. Moreover, owing to TiO_2 polar surface, the pollutant-adsorbing ability of TiO_2 often appears to be low especially for non-polar, organic compounds [61].

Supporting TiO_2 on different porous materials is a plausible solution to eliminate the drawbacks of using bare TiO_2. Many important considerations have to be kept in mind when choosing a good support to anchor TiO_2 such as the surface characteristics, stability of the material, hydrophilic/hydrophobic properties, etc. In addition, a good support has to increase the catalytic activity by enhancing the physical and chemical properties of the modified catalyst.

The successful results obtained from the supported TiO_2 have led to a large number of attempts to anchor TiO_2 on different types of support and investigate their catalytic activity in different reactions. García and Matos reported the effect of TiO_2 supported activated carbon on photodegradation of phenol under visible light [62]. The results showed an increase of apparent first-order rate constant (k_{app}) by a factor of 1.74 in presence of TiO_2-AC in comparison to TiO_2 alone. This difference was ascribed to a strong interaction between TiO_2 particles and activated carbon, which creates an intimate interface between both solids.

Van Grieken*et al.* reported the synthesis of size-controlled nanocrystalline TiO_2 supporting on two different mesoporous silica supports such as MCM-41 and SBA-15 using sol-gel method [63]. The dispersion of nanocrystalline TiO_2 with the support prevented the transformation of TiO_2 anatase to rutile phase.

The use of meso structure SBA-15 silica with proper pore diameter allows controlling the size of the obtained titania particles within the 6-7 nm range. The observed correlation between the mean pore width of this silica support and the size of the obtained titania particles was specially remarkable for materials containing up to 60 wt. % TiO_2 content. The mean titania particle size plays an important role in the photo activity as shown by the materials prepared in this work. Table 1 presents the effect of using different types of support and titanium precursor in addition to the effect of preparation method on the position of TiO_2 with respect to support structure.

It is clear that the supported TiO_2 creates differences in the surface morphology of the supports. However, the size of TiO_2 particles is obviously influenced by the TiO_2 loading, the preparation method and the type of TiO_2 precursor used. Thus, the particle size of the TiO_2 could determine its position to be either encapsulated into the pores of the support or being anchored.

Table 1: Effect of preparation method on the position of TiO_2 loaded on different supports.

Support Type	Loaded metals	Location of the loading metals	Preparation method	Refrences
NaY zeolite	$(NH_4)_2TiO(C_2O_4)_2$ $TiCl_4$	Inside the pores of zeolite Inside the pores of zeolite	Ion exchange Chemical vapor deposition	Grubert *et al.* (64)
Activated carbon	$C_{16}H_{36}O_4Ti$	On the external surface	Chemical vapour deposition	Zhang *et al*. (65)
Silica	TiO_2	Ti species enter the silica gel framework	Sol-gel method	Yao *et al*. (66)
Clay	$TiOSO_4$	On the external surface	-	Peikertova*et al*. (67)
Al-CMC-41	$C_{16}H_{36}O_4Ti$	t low loading, it enter at the pores At higher loading agglomerated on the surface	Sol-gel method	Wu and Li (68)
Natural zeolite	$C_{16}H_{36}O_4Ti$	Not mention	Sol-gel method	Zhengxian *et al.* (69)

Conclusion:

Light is illuminates our lives, and we see all aspects of life around us, without the light we don't see anything and we were unable to see the objects in our life. Without light our life remains in total darkness, light is the most important factors that help to continuous our life. Light and its applications, light has played a critical role in every aspect of human history, leading to amazing advances in science and technology. The sun is the one of light sources without it; we would not exist at all in this day. This Outlook provides a general history of light and its applications.

References:
1. Allday J., Quarks, (2002), Leptons and the Big Bang, 2nd ed., IOP Publishing, p. 98.
2. Forbes M., (2015), What We Talk About When We Talk About Light, ACS Cent. Sci., 1, 354-363
3. IUPAC, Compendium of Chemical Terminology, 2nd ed. Online corrected version: (2006) "photochemistry (the "Gold Book") (1997).
4. Townes H., (1999), How the Laser Happened: Adventures of a Scientist, Oxford University.
5. Adamson W. and Fleichauer D., (1975), Concepts of inorganic photochemistry, John Wiley, Newyork.
6. Jablonski A., (1933), Efficiency of Anti-Stokes Fluorescence in Dyes, Nature, 131, 839-840.
7. Mukherjee K., (1988), Fundamentals of photochemisty, Wiley eastern limited, New Delhi.
8. Brian Wardle John Wiley & Sons, (2009), Principles and Applications of Photochemistry**,** Science - 264 pages.
9. Kornblum, Zvi C., (2010), Photochemistry, Encyclopedia Americana.
10. Balzani V. and Caraassiti V., (1970), Photochemistry of coordination compounds, Acadmic Press, London.
11. K. Stevenson, (1972), Partial photoresolution. III. Tris (acetylacetonato) chromium(III) system, *J. Am. Chem. Soc.,* 1972, 94 (19), 6652-6654.
12. Yousif E., (2012), Photostabilization of thermoplastic polymers, Lambert Academic Publishing, Germany.
13. Hardesty J., and Attili B., (2010), Spectrophotometry and the Beer-Lambert Law: An Important Analytical Technique in Chemistry.
14. Valkoa L., Kleinb E., Kovarikb P., Simonb, HPLC stanovenie sacharidov v procese modelovaného zrýchleného starnutia papiera, (2001), P. Eur. Polym. J., 37 1123-1133.
15. Schnabel W., (1981), Polymer Degradation: Principle and Practical Applications, Chapter 14, Hanser Int, München.

16. Yousif E., Yusop R., Ahmed A., (2015), Photostabilization efficiency of PVC based on epoxidized oleic acid, Malaysian J. of Analytical Sci., 19(1): 213-221.
17. Goldshtein J., Margel S., (2011), Synthesis and characterization of polystyrene/2-(5-chloro-2Hbenzotriazole-2-yl)-6-(1,1-dimethylethyl)-4-methyl-phenol composite microspheres of narrow size distribution for UV irradiation protection, Colloid Polym. Sci., 289: 1863-1874.
18. Galdi A., Foltis P., Shah A., (2010), UV protecting composition and methods of use, US patent, Application, 2010-118415.
19. Andrady L., Hamid H., Hu X., Torikai A., (1998) Effects of increased solar ultraviolet radiation on materials J. of Photochemistry and Photobiology B: Biology, 46:96-103
20. Rnby B., Lucki J., (1980), New aspects of photodegradation and photooxidation of PS, Pure & Appl Chem., 52: 295-303.
21. Yousif E., Adel H., Haddad R., (2015), Yusop R., Effect of benzothiazole complexes on photodegrdation rate constants of polyvinyl chloride films, yanbu j. of engineering and science, 10:41-49.
22. Yousif E., Hasan A., (2015), Photostabilization of poly(vinyl chloride) - Still on the run, J. of Taibah Uni. for Sci., 9:421-448
23. Rabek J., (1974), In: Bamford CH, Tipper CF (eds) Comprehensive Chemical Kinetics, Elsevier, Amsterdam, 14: 425-431.
24. Yousif E. and Haddad R., (2013), Photodegradation and photostabilization of polymers, especially polystyrene, LAMBERT Academic Publishing, Germany.
25. Adil H., Yousif E., Salimon J., (2011), New Stabilizers for PVC Based on Benzothiazole Complexes, LAMBERT Academic Publishing, Germany.
26. Strlic M., Kolar J., (2005), Aging and stabilization of papers, distributed by the National and university Library, Turjaška 1, 1000 Slovenia.
27. Yousif E. and Haddad R., (2013), Photodegradation and photostabilization of polymers, especially polystyrene: review, Springer Plus. 2, 398-460.
28. Ruoko, (2012), Uv light induced degradation of polyethylene and polystyrene-spectroscopic and DSC study, Tampere University of Technology, M Sc thesis.
29. Yousif E., Haddad R., Noaman R., (2014), photostabilization of polystyrene films, Lambert academic publishing.
30. N. Cheremision, (1997), Hand Book of Engineering Polymeric Materi-als (Chapter 8), New York.
31. Chmela Š., Lajoie, P.; Hrdlovič, P.; Lacoste, J. Combined oligomeric light and heat stabilizers, 2001, Polym. Degrad. Stabil., 71:171-177.
32. Yousif E., El-Hiti, A., Haddad R., Balakit A., (2015), Photochemical stability and photostabilizing efficiency of poly(methyl methacrylate) based on 2-(6-methoxynaphthalen-2-yl)propanoate metal ion complexes, Polymers, 7, 1005-1019.
33. Mohammed R., Yousif E., (2015), Photochemical study of PVC films in presence of 2-[4-2)-methyl propyl) phenyl] propanoate complexes, Arab J. Phys. Chem., 2(3): 67-78.
34. Yousif E., El-Hiti G., Hussain Z. and Altaie A., (2015), Viscoelastic Spectroscopic and Microscopic Study of the Photo Irradiation Effect on the Stability of PVC in the Presence of Sulfamethoxazole Schiff's Bases Polymers, 7, 2190-2204.
35. Haddad R., Yousif E., Yusop R., (2014), Ultra Violet Spectra Studies of Polystyrene Films in presence of Some Transition Metal Complexes with 4-amino-5-pyridyl)-4h-1,2,4-triazole-3-thiol, oriental j. of chem., 30(4):1565-1569.
36. Singh J., Singh J., (2009), Photochemistry and Pericyclic Reactions, New Age Science Ltd; 3rd edition.
37. Hoffmann R. and Woodward R., (1968), The conservation of orbital symmetry, Acc. Chem. Res., 1(1):17-22.
38. Gilbert A. and Baggott J., (1991), Essentials of Molecular Photochemistry, Blackwell Scientific Publications, Oxford.
39. Michl J. and Bonacic-Koutecky V., (1990), Electronic Aspects of Organic Photochemistry, Wiley, New York.
40. Klessinger M. and Michl J., (1994), Excited States and Photochemistry of Organic Molecules, VCH Publishers, New York.
41. Roos B., (1987), The Complete Active Space Self Consistent Field Method and its Applications in Electronic Structure Calculations, in Adv. Chem. Phys. (Ab Initio Methods in Quantum Chemistry -II), K. P. Lawley, Ed., Wiley, New York, 69:399-446.

42. Qin H., Xu Z., Cui Y., Jia Y., (2011), Total synthesis of (±)-decursivine and (±)-serotobenine: a Witkop photocyclization/elimination/O-Michael addition cascade approach, Angew. Chem., 123:4539-4541; Angew. Chem. Int. Ed., 2011, 50, 4447-4449.

43. Bajtos B., Pagenkopf B., (2009), Total Synthesis of (±)-Quebrachamine via [3+2] Cycloaddition and Efficient Chloroacetamide PhotocyclizationEur., J. Org. Chem., 1072-1077.

44. Hoffmann N., (2008), photochemical reactions as a key steps in organic synthesis, Chem. Rev., 108:1052-1103.

45. Penkett S., Woolford A., Day J., Coles J., Am, (2010), The Double [3 + 2] Photocycloaddition Reaction, Chem. Soc., 132:4-5.

46. Coxon M., Halton B., (1987), Organic Photochemistry, 5th ed., Cambridge University Press: Great Britain,162-179.

47. Kishikawa K., Akimoto S., Kohmoto S., Yamamoto M., Yamada K., (1997), Intramolecular Photo[4+2]cycloaddition of an Enone with a Benzene Ring, J. Chem. Soc., Perkin Trans. 1:77-84.

48. Griesbeck G., Franke M., Neudörfl J., Kotaka H., (2011), Photocycloaddition of aromatic and aliphatic aldehydes to isoxazoles: Cycloaddition reactivity and stability studies, Beilstein J. Org.Chem., 7:127-134.

49. D'Auria M., (2001), Photochemical and photophysical behavior of thiophene. Adv. Heterocycl. Chem., 104:127-390.

50. Jack. L., (2009), Named Reactions: A Collection of Detailed Reaction Mechanisms, Springer, 173-184.

51. Winkler D., Rouse B., Greaney F., Harrison J., Jeon T., (2002), The first total synthesis of (+/-)-ingenol, J. Am. Chem. Soc., 124, 9726-9728.

52. Augugliaro V., Litter M., Palmisano L., Soria J., (2006), The combination of heterogeneous photocatalysis with chemical and physical operations: A tool for improving the photoprocess performance, J. of Photochemistry and Photobiology C: Photochemistry Reviews 7:127-144.

53. Alwash A., Abdullah A., Ismail N, Zeolite Y., (2012), encapsulated with Fe-TiO$_2$for ultrasound-assisted degradation of amaranth dye in water, J. of Hazardous Materials, 233-234 184-193.

54. Aleksić M., Kušić H., Koprivanac N., Leszczynska D. and Božić A., (2010), Heterogeneous Fenton type processes for the degradation of organic dye pollutant in water-The application of zeolite assisted AOPs. Desalination, 257:22-29.

55. Tehrani-Bagha R., Mahmoodi M. and Menger M., (2010), Degradation of a persistent organic dye from colored textile wastewater by ozonation Desalination, 260:34-38.

56. Zhou W., Yin Z., Du Y., Huang X., Zeng Z., Fan Z., Liu H., Wang J. and Zhang H., (2013), Synthesis of Few-Layer MoS$_2$ Nanosheet-Coated TiO$_2$ Nano belt Hetero structures for Enhanced Photocatalytic Activities, 9:140-147.

57. Bouasla C., Samar M., E.-H. and Ismail F., (2010), Degradation of methyl violet 6B dye by the Fenton process, Desalination, 254:35-41.

58. Kalathil S., Lee J., and Cho H., (2013), Catalytic role of Au/ TiO$_2$ nanocomposite on enhanced degradation of an azo-dye by electrochemically active biofilms: a quantized charging effect, J. of Nano particle Research, 15:1-6.

59. Kobayashi D., Honma C., Suzuki A., Takahashi T., Matsumoto H., Kuroda C., Otake K. and Shono A., (2012) Comparison of ultrasonic degradation rates constants of methylene blue at 22 kHz, 127 kHz, and 490 kHz., Ultrasonics Sonochemistry, 19:745-749.

60. Alvaro M., Carbonell E., Espla M., Garcia H., (2005), Iron phthalocyanine supported on silica or encapsulated inside zeolite Y as solid photocatalysts for the degradation of phenols and sulfur heterocycles, Applied Catalysis B: Environmental, 57:37-42.

61. Wang C., Lee C., C.-K., Lyu, M.-D. and Juang, L.-C., (2008) Photocatalyticdegradation of C.I. Basic Violet 10 using TiO$_2$catalysts supported by Y zeolite: An investigation of the effects of operational parameters., Dyes and Pigments, 76:817-824.

62. García A. and Matos J., (2010), Photocatalytic Activity of TiO$_2$ on Activated Carbon Under Visible Light in the Photodegradation of Phenol, The Open Materials Sci. J., 4:2-4.

63. Grieken V., Aguado R., López-Muñoz J., M. J. and Marugán J., (2002), Synthesis of size-controlled silica-supported TiO$_2$ photocatalysts, J. of Photochemistry and Photobiology A: Chemistry, 148:315-322.

64. Grubert G., Stockenhuber M., Tkachenko O. and Wark M., (2002), Titanium oxide species in molecular sieves: Materials for the optical sensing of reductive gas atmospheres, Chemistry of Materials, 14:2458-2466.

65. Zhang X., Zhou M. and Lei L., (2005), Preparation of photocatalytic TiO2 coating of nanosized particles on activated carbon by AP-MOCVD. Carbon, 43:1700-1708.

66. Yao P., Hu W., Bao Y., Zhang C., Zhu B., Liu W. and Bai Y., (2011), Synthesis and characterization of novel Ti-containing mesoporoussilicas support, J. of Ceramic Processing Reasearch, 12:289-293.

67. Peikertova P., Rebilasova S., Groplova K., Euwirthova L., Kukutschova J. and Matejka V., (2011), Raman study of clay/TiO$_2$ composites. In: 3rd International Conference (Nanocon), Brno, Czech Republic, EU.

68. Wu Q., and Li S., (2011), Synthesis of TiO$_2$ /Al-MCM-41 Composites with Coal Measure Kaolin and Performance in Its Photocatalysis, Materials Sci. and Applications, 2:14-19.

69. Zhengxian M., Ning Z. and Jiang L., (2012), Preparation and Characterization of Ions Doped TiO$_2$ /Natural Zeolite Photocatalyst, Advanced Sci. Letters, 5:525-529.