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PHOTOCHEMICAL DEGRADATION OF HALOGENATED COMPOUNDS: A REVIEW

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ABSTRACT

A review of the literature with corresponding references has been given describing the pollution caused by halogenated compounds and their toxic effects. The different methods of their degradation, photochemical reactions, their types and their applications in photochemical degradation with different routes have been discussed. A literature survey of photosensitized reactions has been given. The methodology for the study of the photochemical degradation has been discussed.

Key words: Photochemical degradation, Halogenated compounds, Photosensitized reactions, Photocatalysis.

INTRODUCTION

The global environment pollution is becoming a matter of great concern. The major causes of environment pollution are industrialization and human activities. The industrial wastes, some of them are highly toxic chemicals, are discarded into the atmosphere, hydrosphere and lithosphere, become health hazard directly or indirectly to human beings and animals.

The halo-organic compounds have wide industrial and agricultural applications. The halogenated organic compound is a general term used for the organic chemicals containing a carbon directly linked with the halogen atom. The halogenated hydrocarbons and their substituted derivatives are stable compounds and show markedly low chemical reactivity. These properties make them long lasting. These compounds are also non-biodegradable. Manufacturing of halogenated compounds leave a large residue in the soil and atmosphere, which is washed by rain and finds its way into the water bodies. These compounds are passed on to the aquatic plants and animals, which are consumed as food by human beings and other animals and become a part of food chain.

The manufacture and uses of halo-organic compounds can be divided into following major categories[1]: Solvents, pesticides, dyes, drugs and explosives.

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Solvents

Halo-organic compounds form an important class of industrial solvents. Some of them are also used as starting material for the manufacture of different end products. The normal solvents, which are used in different industries are chloroform, carbon tetrachloride, dichloromethane, dichloroethane and chlorinated benzenes.

The solvents are used in the manufacture of petrochemicals, dyes, resins, pharmaceuticals, synthetic fibers, explosives and cosmetics. The solvents are normally recovered after the process and are reused. Some of them are volatile and escape to the atmosphere and others find their way into the water bodies in trace quantities even after the treatment of the effluent of the chemical processes. The solvents escaped to the atmosphere are condensed along with the rain and find their way into the water bodies. As these compounds are colorless, they are non-biodegradable and non-photodegradable.

Pesticides

Pesticides, which are the most important components of agrochemicals, are used for the management of the crop protection. Some of them are chlorinated compounds and are classified into different classes like insecticides, fungicides, herbicides etc. The compounds of these classes are:

(1) **Insecticides:** Benzene hexachloride (BHC), DDT, heptachlor, chlordane, aldrin, dieldrin, toxaphene, endrin, methoxychlor.

(2) **Fungicides:** Pentachloronitrobenzenes, chlorinated phenols, chlorinated quinones, chlorinated benzoquinones, chlorinated nephthoquinones, chloranil.

(3) **Herbicides:** Chlorophenoxyacetic acids, sodium trichloroacetate, 2-methyl-4-chlorophenoxy-acetic Acid.

Chlorinated organic compounds are also used as basic raw material for the manufacture of some of the chlorinated pesticides. N,N-dichlorourea, chlorophenols, chloroanilines, chlorobenzenes, chloral are chlorinated basic raw materials, which are used to manufacture herbicides like chlorophenoxyacetic acids, funguicides like polychlorophenol and insecticides like DDT. Pesticides are sprayed on the crops and the residual pesticide reaches to the soil and finally to the water bodies.

Dyes

Several chlorinated dyes are used for the dyeing of wool, cotton, cellulose and polymer fibers, which are toxic for living beings. The non-chlorinated dyes viz. picric acid, indigotin and some azo dyes are manufactured from starting material like chloroanilines, chlorobenzenes, chloronitrobenzenes, chloroacetic acids. The chlorinated dyes, which are used for dyeing cellulose fibers, are pendent cationic azo dye, chlorinated diazines, triazines and chlorinated anthraquinones. Chlorinated prinazines and their derivatives are used for the dyeing of cotton fibers, while chlorinated dyes like remalan, procilan, procion are used for the dyeing of wool and polyamide fibers.

Drugs

Some chlorinated compounds e.g. chloroanilines, chlorobenzenes and chloronitrobenzenes are used as basic raw materials for the manufacture of drugs like phenacetin, paracetamol, proguanil (paludrine), chloromycetin (chloramphenicol).

Explosives

The explosives are manufactured from chlorinated compounds. The final product can also be a chlorinated compound e.g. chloroacetophenones, tetryl, pentyl and hexyl are chlorinated end products, which are used as an explosives and are manufactured from chlorobenzens, chloronitrobenzenes, chloroacetyl chloride. Tear gas, which is chloropicrin, is manufactured from picric acid.

The use of halogenated raw material for the manufacture of different classes of industrial compounds like solvents, pesticides, dyes, drugs, explosives causes pollution especially of atmosphere and hydrosphere. These compounds represent major class of environmental pollutants. The food chain by which these toxic compounds reach to human beings and animals can be demonstrated by the Fig. 1 given below[2]:

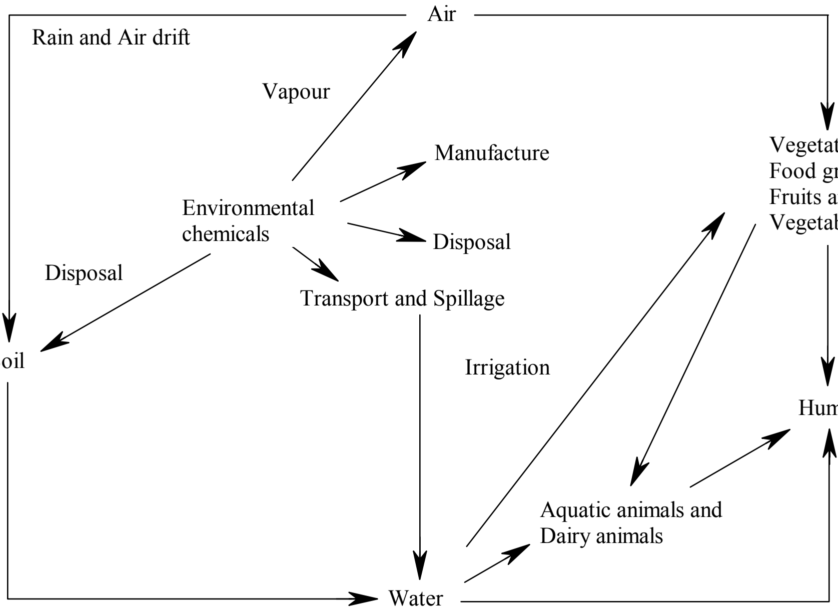

Fig. 1: Schematic diagram depicting the Food Chain

Toxic effects

The toxic effects of halogenated organic compounds have been established by various biomedical studies. The direct contact of halogenated solvent has been reported to cause irritation, pulmonary edema, and inflammation of the respiratory tract. The injury of cornea, liver damage, neurological effects, irritation of eyes, nose and throat have also been reported in the case of sever exposure[3,4]. The chlorinated pesticides induce chronic effects in the human beings and animals. The pesticides are lipophilic in nature and also contain some specific functional groups. Pesticides undergo biochemical reactions in the body, which can produce toxic effects. It has been reported that higher concentration of the chlorinated pesticides in human body can cause liver injury, pathomorphological changes in liver, urological problems, carcinogenesis, neurotoxicity and effect on the reproductive system[5-11]. The direct exposure of chlorinated dyes has been reported to cause sarcoma, cathartic effects, pathological changes in liver and urinary bladder, tubular degeneration of kidneys, high rate of mortality in human beings as well as in animals[12-14].

EXPERIMENTAL

Methods

The chlorinated compounds are stable and non-biodegradable and are regarded as pollutants. A number of methods are used for the treatment of chlorinated compounds to decrease their toxicity. The methods generally used for the treatment of contaminated sources or to convert them into other non-polluting compounds are[15]: (1) Extraction, (2) Incineration, (3) Chemical degradation, (4) Bioremediation, (5) Super-critical water oxidation, (6) Electrochemical treatment, (7) Sonochemical destruction and (8) Photochemical processes.

However until now, no completely efficient method has been developed for the detoxification of contaminated water[16]. Amongst all these methods photochemical processes have been found very useful for degradation of chlorinated compounds in low concentration especially in water effluent[17-19]. The chemical reactions induced in the presence of light are known as photochemical reactions. A number of photochemical reactions have been reported[20-22]. Photochemical degradation is one of the important techniques to convert toxic halo-organic compounds into non-toxic material[23,24]. Generally photochemical techniques are applied for the treatment of dilute solutions in the concentration range of 10^{-3} to 10^{-6} M[15]. Many chlorinated aromatic compounds have been converted into less toxic compounds[25-30]. References for a wide range of photochemical techniques have been reported for the main technologies and their applications to waste water treatment[31-34].

Photochemical reactions

Photochemical reactions are carried out in the presence of either Ultra-Violet (UV) or Visible (Vis) light. The exposed molecule absorbs the light and goes to the excited state. The product is obtained by the decomposition of the excited molecule. A number of photochemical reactions have been reported in different experimental conditions. Photochemical reactions are carried out in different solvents like water, methanol, ethanol, iso-propyl alcohol, hexane, cyclohexane, iso-octane, acetonitirle etc.[35-40] A number of methods for photochemical decomposition of hazardous chlorinated compounds such as chlorinated benzenes[41], biphenyls[42], phenols[43], naphthalenes[44], benzoquinones[45], toluenes[46], anthraquinones[47], anisoles[48] have been reported in last two decades. This reveals the importance of photochemical reactions in chemistry.

The range of UV radiations is 200-400 nm. The sources used for the UV irradiations are Hydrogen lamp, Deuterium lamp or Mercury vapour lamp, which provide radiations of wavelength 254 nm, 270 nm and 300 nm. The radiation excites $\pi \rightarrow \pi^*$ transition and is useful for colourless compounds as their absorption bands are obtained below 300 nm. The range of visible radiations is 400-750 nm. The tungsten lamp and halogen lamp are the sources for the visible radiation, which excites $n \rightarrow \pi^*$ transition and is useful for coloured compounds as their absorption bands are obtained above 300 nm. When a molecule absorbs light in UV or Visible region of spectrum, its bonding orbital electron gets excited to antibonding level. The excited state is unstable and electron returns to the ground state by losing excess of energy. The loss of energy of excited molecule can take place by two processes: Radiative process and Non-radiative or Radiationless process.

Radiative process

The radiative process of loss of energy can occur by:

(a) The bonding electrons of the molecule, which absorb energy and get excited to higher energy singlet state (S^1), having opposite spin pair electrons, return to the ground state by emitting radiations of the same wavelength, which it has absorbed and no chemical reaction will occur.

(b) When electrons of the excited molecule return from singlet-excited state to ground state, the energy loss occurs through vibrational levels. The process gives the radiation of longer wavelength called Fluorescence, and electrons remain spin paired.

(c) The molecule with relatively stable excited state may undergo transition to a meta-stable state by Inter System Crossing (ISC), which represent triplet state. The electron pair spin of singlet state is transformed to the parallel spin. The triplet state electrons return to ground state through vibrational levels and emit Phosphorescence, which has longer wavelength than absorbed radiation and for longer time. The electrons return to the ground state through stepwise vibrational levels, which takes longer time.

Non-radiative or radiationless process

The absorbed energy of molecule is converted into internal vibrational energy, which produces chemical reaction. The fluorescence or phosphorescence is either not observed or observed with very low intensity. The reaction is regarded as photochemical reaction, which gives the product by the decomposition of excited molecule. The excited molecule goes to lower energy electronic state without emitting the energy in the form of radiation, but by the process of internal conversion of energy decomposes the molecule to give product. The singlet-excited state in some cases is transformed into triplet state through ISC and vibrational energy levels of the molecule are excited and the triplet state of the molecule may decompose to give product. Both the reactions are direct photochemical reactions[49]. There are two major types of non-radiative transitions:

(a) **Internal conversion (IC):** The internal conversion involves non-radiative energy loss, occurs between the electronic manifold of the same spin type -

Singlet-Singlet, Triplet-Triplet.

(b) **Inter system crossing (ISC):** The inter system crossing involves non-radiative energy loss, occurs between the electronic manifold of the different spin type -

Singlet-Triplet, Triplet-Singlet

The excess of energy is lost to the environment in the form of thermal energy in both the non-radiative processes.

Bimolecular deactivation and quenching

The bimolecular deactivation process is electronic energy transfer (ET) of an excited molecule. The energy of the excited molecule is transferred to another molecule by non-radiative mechanism, which is transparent to the particular wavelength. The second molecule gets excited and can undergo various photo-physical and photochemical processes according to its own characteristics. Bimolecular reactions inhibit emission of radiation because frequency of bimolecular collisions in solutions as well as in gas phase competes with fluorescence emission. The process is called Quenching.

$$A^* + B \rightarrow A + B^*$$

Quenching of the excited state has been widely used to investigate the photochemical reaction mechanisms[50]. Quenching process can be classified into three types: Solvent quenching, Self-quenching and Quenching by added impurity or external molecule.

Solvent quenching

Solvent molecules interact with excited molecule, which comes to the ground state by losing excess energy as heat.

$$A^* + S \rightarrow A + S + \text{Heat}$$

Polar solvents show solute-solvent interaction forming polar exciplex, which loses excess energy as heat and comes to the ground state.

$$A^* + S \rightarrow \underset{\text{Exciplex}}{(A^-S^+)^*} \rightarrow A + S + \text{Heat}$$

The excess energy loss from excited state occurs via triplet state during the complex formation between solvent and excited state of the molecule. Larger is the interaction; more will be the energy loss. In non-polar solvents, dispersion force interactions are important. Some solvents, which contain heavy atoms can produce enhancement of phosphorescence at the cost of fluorescence e.g. Ethyl iodide, nitromethane and carbon disulphide.

Self-quenching

It is also termed as direct quenching. The substrate molecule interacts with the excited state of the molecule and excess energy is lost as heat. The two molecules return to the ground state. Thus substrate molecule itself quenches the reaction and the original molecule is obtained back.

$$A^* + A \rightarrow 2A + \text{Heat}$$

The process involves transfer of energy from excited molecule to another molecule, which is in ground state. This process is called internal quenching. The excimer formation also takes place by the interaction between the ground state and excited state molecule. The excimer loses excess energy as heat and the original molecule is obtained back in the ground state.

$$A^* + A \rightarrow \underset{\text{Excimer}}{(A\,A^*)} \rightarrow 2A + \text{Heat}$$

Quenching by added impurity or external molecule

If another molecule is added to the solution, which quenches the fluorescence, the phenomenon is termed as indirect quenching and the photochemical reaction is known as an indirect photochemical reaction. The excited molecule, which shows fluorescence in the absence of added molecule, transfers its energy to the added molecule and itself comes to the ground state.

$$A^* + Q \rightarrow A + Q^*$$

Stern-Volmer equation[51,52]

The life-time of the excited state and quenching constant are determinable quantities using Stern-Volmer equation. The loss of energy of the excited state is given in term of life-time. The life-time of the excited state and quenching constant can be determined from the plot of the ratio of quantum yield in the absence of the quencher and quantum yield in the presence of the quencher (ϕ_f^0 / ϕ_f) vs. concentration of the quencher [Q]. The plot is called Stern-Volmer plot. The plot is straight line and the slope of the plot gives the quenching constant of the excited state. If reaction will occur from singlet state in competition with reaction via the triplet excimer, the Stern-Volmer plot will be linear with a positive slope, at low concentrations of the quencher but would be flattened as the concentration of the quencher increases[53,54].

This indicates that when all the triplet states are quenched at high concentration of the quencher, the singlet state continues to react. Thus the triplet excimer is the sole product determining intermediate for the photodecomposition reaction.

Now,

$$[A^*]^0 = \frac{I_a}{K_f + K_{IC} + K_{ISC}} = \frac{I_a}{K_f + \sum K_i}$$

$$[A^*] = \frac{Ia}{K_f + \sum K_i + K_q[Q]}$$

Where,

I_a = Rate of absorption or rate of formation of activated molecule

K_q = Rate constant for bimolecular quenching

K_f = Rate constant for fluorescence

K_{IC} = Rate constant for internal conversion

K_{ISC} = Rate constant for inter system crossing

$\sum K_i$ = Sum of $K_{IC} + K_{ISC}$

$[A^*]^0$ = Fluorescer concentration in the absence of the quencher

$[A^*]$ = Fluorescer concentration in the presence of the quencher

$$\phi_f^{\,0} = \frac{K_f\,[A^*]^0}{Ia} = \frac{K_f}{K_f + \sum K_i}$$

$$\phi_f = \frac{K_f\,[A^*]}{I_a} = \frac{K_f}{K_f + \sum K_i + K_q\,[Q]}$$

Where,

ϕ_f^0 = Quantum yield in the absence of quencher

ϕ_f = Quantum yield in the presence of quencher

The ratio of two quantum yields is,

$$\frac{\phi_f^{\,0}}{\phi_f} = \frac{K_f + \sum K_i + K_q\,[Q]}{K_f + \sum K_i} = 1 + \frac{K_q\,[Q]}{K_f + \sum K_i}$$

$$\frac{\phi_f^{\,0}}{\phi_f} = 1 + K_q \tau\,[Q]$$

$$\frac{\phi_f^{\,0}}{\phi_f} = 1 + K_{SV}\,[Q]$$

Where,

$K_{SV} = K_q\,.\,\tau$ = Stern-Volmer constant = the ratio of bimolecular quenching constant to unimolecular decay constant (liter/mole)

$\tau = 1/K_f + \sum K_i$ = Actual time of fluorescer molecule in the absence of bimolecular quenching.

The value of K_{SV} is obtained from the slope of the plot of ϕ_f^0/ϕ_f Vs [Q]. If τ is measured independently with the knowledge of $K_{SV,}$ the rate constant K_q for bimolecular quenching step can be determined.

Quenching by added substances occurs by two mechanisms: Charge transfer mechanism and Electronic energy transfer mechanism.

Charge transfer mechanism

Two different molecules interact by some degree of charge transfer and form complex between excited fluorescent molecule and added foreign molecule, depending upon the polar nature and polarizability properties. This complex is called exciplex.

$$\mathrm{A}^* + \mathrm{B} \rightarrow \underset{\text{Exciplex}}{(\mathrm{A\,B})^*} \rightarrow \mathrm{A} + \mathrm{B} + \text{Heat}$$

The exciplex becomes an ion-pair exciplex if the charge transfer is complete. The ion pairs have normally longer lifetime. The dissociation may occur via ion-pair complex.

$$\mathrm{A}^{1*} + \mathrm{Q} \rightarrow (\mathrm{A}^1\,\mathrm{Q})^* \rightarrow (\mathrm{A}^{+/-}\text{-----}\mathrm{Q}^{-/+}) \rightarrow \mathrm{A}^1 + \mathrm{Q}$$

Molecules, which contain heavy atoms like chlorine, bromine and iodine act as quencher. The quenching occurs by the same exciplex mechanism. The change of electron spin of heavy atom facilitates the exciplex dissociation via triplet state.

$$\mathrm{A}^{1*} + \mathrm{Q} \rightarrow (\mathrm{A}^1\,\mathrm{Q})^* \rightarrow \mathrm{A}^3 + \mathrm{Q} \rightarrow \mathrm{A}^1 + \mathrm{Q}$$

Electronic energy transfer mechanism

This is one of the most useful processes in photochemistry. It has wide applications in photochemical synthesis. It allows photosensitization of physical and chemical changes in the acceptor molecule by the electronically excited donor molecule.

$$\mathrm{D} + h\upsilon \rightarrow \mathrm{D}^*$$

$$\mathrm{D}^* + \mathrm{A} \rightarrow \mathrm{D} + \mathrm{A}^*$$

The direct light absorption forms electronically excited donor (D*) molecule. It can transfer the electronic energy to suitable acceptor molecule (A), present in the solution resulting in de-excitation of D* to D and electronic excitation of A to A*. The energy transfer occurs before D* is able to radiate fluorescence and is non-radiative transfer of energy. The acceptor molecule thus excited indirectly, can undergo various photophysical and photochemical processes. The process is called photosensitization and reactions are called photosensitized reactions or indirect photochemical reactions[55]. The characteristic feature of the photosensitized reaction is that light-absorbing species remains unchanged while acceptor molecule undergoes chemical changes. One of the very well known and important photosensitized chemical reactions is the photosynthesis by plants, in which the green chlorophyll molecules of leaves are light absorbing molecules and CO_2 and H_2O are acceptor molecules.

Quenching by oxygen

Faraday discovered that oxygen is paramagnetic having two outer electrons with parallel spins[56]. The dissolved oxygen present in aqueous and non-aqueous solutions also acts as quencher for the excited molecule. The molecular oxygen deactivates the electronic excited organic molecules by collisions. The quenching efficiency of oxygen molecules is due to its paramagnetic property. They act as promoters for the ISC rates, $S_1 \rightarrow T_1$, $T_1 \rightarrow S_0$. Sometimes in the presence of high concentration and pressure of O_2, forbidden transition $S_0 \rightarrow T_1$ is also observed[57]. The substrate molecule can be oxidized and in some cases no permanent chemical change is observed. Oxygen quenching is actually diffusion-controlled process, which occurs by two types of mechanisms[57]:

(i) Charge transfer interaction

$$\mathrm{A}^{1*} + {}^3\mathrm{O}_2 \rightarrow ({}^2\mathrm{A}^+\text{-----}{}^2\mathrm{O}_2^-) \rightarrow {}^3\mathrm{A} + {}^3\mathrm{O}_2$$

(ii) Spin-orbit interaction, which mixes the singlet and triplet, states

$$A^{1*} + {}^3O_2 \rightarrow ({}^1A^{*}\text{-----}{}^3O_2) \rightarrow {}^3A + {}^3O_2$$

The absorption of ultra-violet and visible light from the sun generally leads to the electronic excitation of the molecules. Oxygen permeates most organic matter in the solutions, which quenches the electronic excited state. This results in the singlet molecular oxygen formation. Singlet molecular oxygen acts as an oxidizing agent for the organic molecule present in the solution. When the excited energy of the sensitizer molecule exceeds 94.50 KJ-mole^{-1}, singlet oxygen $^1O_2$ ($^1\Delta$ g) may be formed. For the formation of singlet oxygen $^1O_2$ ($^1\Sigma g^+$) the excited energy of the sensitizer molecule should exceed 157 KJ-mole^{-1} [58].

$$O_2\,({}^1\Delta g) + O_2\,(1\Delta g) \rightarrow O_2\,({}^1\Sigma g^+) + O_2\,({}^3\Sigma g^-) \qquad \ldots(1)$$

$$O_2\,({}^1\Sigma g^+) + Q \rightarrow O_2\,({}^1\Delta g) + SQ \qquad \ldots(2)$$

Where Q is any quenching species present in the system and O_2 ($^1\Delta g$) and O_2 ($^1\Sigma g^+$) are two excited singlet forms of molecular oxygen of high chemical reactivity and ($^3\Sigma g^-$) is excited triplet form of molecular oxygen. Reaction (2) is not 'spin-forbidden' but 'spin-allowed' process and liberates 62.4 KJ of electronic energy. Removal of the singlet delta state by quencher Q, can be written as:

$$O_2\,({}^1\Delta g) + Q \rightarrow O_2\,({}^3\Sigma g^-) + Q \qquad \ldots(3)$$

Reaction (3) is 'spin-forbidden' process and liberates 94.50 KJ of electronic energy; which can be utilized in the product formation of the reaction. The various sensitizers like anthracene, fluorescence and rose Bengal posses triplet energy more than 156.90 KJ, and the energy is transferred to O_2 molecule. They form the singlet oxygen $^1O_2$ ($^1\Sigma g^+$), which is not important as an oxidant in the reactions as it is rapidly quenched in the solution. Only $^1O_2$ (1Δ g) is responsible for the oxidation of the organic compounds[58]. Photosensitized oxidation by singlet oxygen of some pesticides has been reported[59]. Reactions involving photo-oxidation of some organo-nitrogen compounds have also been reported[60-62]. Kinetic study of the singlet molecular oxygen mediated photodegradation of some heteroaromatic compounds has been reported[63], which reveals the importance of the molecular oxygen in photochemical degradation. A kinetic and mechanistic study has been reported for the dye sensitized photo-oxidation of mononitrophenols and monochlorophenols via singlet molecular oxygen by Palumbo et al.[64] The schematic diagram of singlet and triplet state is demonstrated below in Fig. 2 [65].

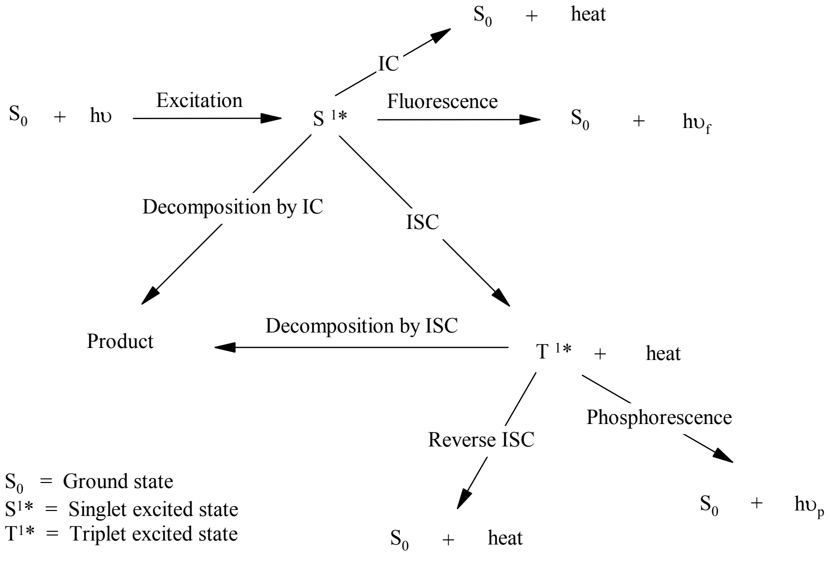

Fig. 2: The schematic diagram of singlet and triplet state

Photosensitized reactions

Photosensitized reactions are those reactions where 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.

Every year numbers of papers are published on photosensitized reactions in the area of photochemistry. A number of photosensitizers have been used for the degradation of organic compounds. A review has been published on photosensitized degradation of some important pesticides with different pathways and the reaction mechanisms of photodegradation of pesticides[24]. Photosensitizers transfer the absorbed light energy to the acceptor molecule and return back to their ground state. Thus they act as photocatalysts. A brief discussion is presented here for the different photosensitizers used.

Ketones

Choudhry et al. have studied acetone sensitized and non-sensitized photolysis of tetra-, penta- and hexachlorobenzenes in acetonitrile-water mixture and identified the photoproducts[66]. Ilenda et al.[67] have reported the determination of triplet lifetime in acetone sensitized photochemical reaction. Expressions have been derived for the treatment of quenching data for photosensitized reactions. Augustyniak[68] has carried out the photolysis of chlorobenzene in cyclohexane and n-heptane solvents using different types of ketones as photosensitizers. Hawari et al.[69] have discussed acetone induced photodechlorination of Aroclor-1254 in alkaline 2-propanol and proposed a probable mechanism by thermolysis in the presence of di-tert-butyl peroxide.

Aliphatic and aromatic amines

Several reports have been published in last few years on photochemical reactions, in which aliphatic and aromatic amines are used a photosensitizer[70-73]. Davidson and Goodin have discussed the mechanistic aspects of the triethylamine assisted photoinduced dehalogenation of some haloaromatic compounds[74]. Kuzmin et al. have quoted the reference of effects of solvent polarity on the photoelimination of halogen in 9,10-dichloroanthracene in the presence of both aliphatic and aromatic amines. The quantum yields of the photodechlorination have been determined[75]. Bunce[76] has reported the photodechlorination of chlorinated benzenes, naphthalenes and biphenyls via triplet-excited state. Ohashi et al.[70,71] have analyzed the Stern-Volmer Plot of the aliphatic and aromatic amines assisted photodechlorination of 4-clorobiphenyl and showed that the reaction from the singlet state is more efficient than that from the triplet state. Hamanoue et al.[77] have studied the photoreduction of 1,8-dichloroanthraquinone using triethylamine photosensitizer by laser spectroscopy. The authors have also reported the dechlorination of meso-substituted mono- and dichloroanthracene via their radical anions, produced by diffusion controlled reaction of the lowest excited singlet states of chloroanthracene with the ground state of aliphatic and aromatic amines in acetonitrile at room temperature[78]. Lin et al.[79] have suggested that diethylamine is very efficient photosensitizer for the photodegradation of PCB congeners using sun-simulated light. Chesta et al.[73] have studied the photosensitized dechlorination of chlorinated benzenes by using N,N-dimethylaniline. The electron transfer mechanism from both singlet and a triplet state has also been suggested. Occhiucci et al.[80] have suggested that the photolysis of PCBs was enhanced by using triethylamine as a sensitizer.

Methylene blue (MB)

Methylene blue sensitized degradation of sodium hyaluronate through photoinduced normal electron transfer and electron transfer in the upper excited state has been reported by Kojima et al.[81] Das et al.[82] have reported methylene blue sensitized decarboxylation of substituted carboxylic acids via photochemical electron transfer mechanism across liq/liq interface. Photoinduced energy and electron transfer processes between ketone triplet states and organic dyes (methylene blue, thiopyrinine, safranine and phenosafranine) have been reported by Jockusch et al.[83] Methylene blue sensitized photo-oxygenation of hydroxyl and amino derivatives of naphthalenes have been investigated by Chawla et al.[84]

Naphthalene and its derivatives

Chesta et al.[85] have reported decomposition of chlorobenzenes using naphthalene as sensitizer. The reaction has been explained via exciplex mechanism. Soumillion et al.[86] have reported the use of anionic sensitizer such as naphthoxide anion as excited donor for the photodechlorination of chloroaromatics. The reaction was compared with other sensitized systems. 1- and 2-naphthols have been widely used as photosensitizer in photochemical reactions for the study of energy transfer reactions[87-89]. Soltermann et al.[90] have reported photodechlorination of trichlorobenzenes (TCBs) sensitized by naphthalene-triethylamine. The mechanism suggested is via exciplex formation.

H_2O_2, UV / H_2O_2, UV / O_3, UV / Fenton's reagent

Moza et al.[91] have studied photodecomposition of chlorophenols in aqueous medium in the presence of 55 ppm H_2O_2. The removal of chlorophenols was approximately 80-95% in around 3 hours. Photolytic mechanism of degradation of monochlorobenzenes in the presence of UV/H_2O_2 has been reported by Lain-Chuen et al.[92] 4-chlorophenol[93] and 2,4-dichlorophenol[94] have also been photochemically decomposed by using UV/H_2O_2 combination. Schulte et al.[95] have reported photo-removal of noxious matter like CCl_4, $CHCl_3$, trichlorophenol (TCP) and pentachlorophenol (PCP) using activated H_2O_2 in the presence of UV light. A comparative account of the photodegradation of some aromatic contaminants has been reported by Guittonneau et al.[96] in water by UV photolysis and UV/H_2O_2. Sedlak et al.[97] have carried out photo-oxidation of some chlorobenzenes with Fenton's reagent and photoproducts have been identified. Ruppert et al.[98] have given the comparison of advanced oxidation processes for the treatment of wastewater by using UV / TiO_2, UV / H_2O_2, UV / O_3, UV / Fenton's reagent. Koyama et al.[99] also have reported oxidative degradation of some chlorinated aromatic compounds by Fenton's reagent in the presence of UV radiation. Krutzler et al.[100] have degraded 4-chlorophenol by using Fenton's reagent with sunlight as irradiation source for wastewater treatment. Some chloro-organic compounds also have been degraded using O_3 and H_2O_2/O_3 by Ormad et al.[101]

Dienes

Smothers et al.[102] and Bunce et al.[103] have reported the photodechlorination of some chloroaromatics by using dienes as photosensitizers. The reaction mechanism of photodechlorination has been suggested via exciplex formation between diene and chlorocompound. Bunce et al. studied photoreduction of 1-chloronaphthalene in the presence of 1,3-cyclohexadiene and triethyl amine[72].

Miscellaneous

Choudhary et al.[104] have studied the photodechlorination of PCBs in the presence of hydroquinone in aqueous-alcoholic media using sunlight. Tanaka et al.[71] have discussed the effect of anthracene as photosensitizer in photochemical dechlorination by an electron transfer mechanism. Sensitized photolysis of PCBs in alkaline 2-propanol by solar radiation has been carried out by Hawari et al.[105] Nowakowska et al.[106-108] have reported that carbazole is very useful photosensitizer for the dechlorination for pentachlorophenols and polychlorinated benzenes. The process has been explained involving electron transfer mechanism from excited carbazole molecule to substrate molecule. Epling et al.[109] have studied borohydride-enhanced photodehalogenation of Aroclor-1232, 1242, 1254 and 1260. Photodechlorination of chlorobenzenes and chlorotoluenes has been reported. In recent publication, Gryglik et al.[110] have quoted the reference of rose bangal as photosensitizer for the photo-oxidation of chloropheol (CP) in alkaline aqueous solution and identified photoproducts using HPLC. Dwivedi et al.[111,112] have suggested the mechanism of photochemical degradation of chloroanisidines and chloroanilines by dye-sensitized reaction using Methylene blue.

The use of semiconductors (Photocatalytic reactions)

The metals are good conductors of electricity while non-metals are insulator and do not conduct electricity. Some elements and their compounds are metalloids, which have ability to conduct electricity to some extent. The elements like B, Bi, Ge, As, Sb, Te, Si, Ti, Zr, Mo and Cd are known as semiconductors. Some of the compounds e.g. SiO_2, TiO_2, ZnO, ZnS, CdS show properties of semiconductor.

There exits two energy bands for each semiconductor (a) Valence band (VB) and (b) Conduction band (CB). These two energy bands are separated by energy gap of particular energy. This energy gap is different for different semiconductor. The conductive mechanism of a semiconductor can be illustrated by silicon or germanium. Silicon and germanium exist in crystalline diamond structure and four other atoms surround each atom. Each pair of electrons is covalently shared between adjacent atoms. The electrons at lower temperature in ground state are not free to move. The excitation of the electron is done by exposing them to the light corresponding to energy gap of conduction band and valence band. The place within the crystal from where the electron is removed is termed as a ‘Hole’. An electron jumps from nearby atom to fill this hole and this helps in migrating the hole.

Chemical reactions in the presence of semiconductor and light are known as photocatalytic reactions. Semiconductors with suitable band gaps can act as quantum collectors. The semiconductor is irradiated by light having the energy higher than the energy of valence band and conduction band. The substrate molecule coming in contact with the surface of the semiconductor undergoes chemical reaction. The surface electrons of semiconductor are excited by the absorption of light radiation, which are promoted to the conduction band from the valence band, which results in positive holes in the valence band. Surface attracts hydroxyl group from the solution yielding absorbed $^{\bullet}OH$ radicals. The $^{\bullet}OH$ radicals attack on substrate molecule and product are formed.

Mechanism[113]

$$SC + h\upsilon \rightarrow SC^*$$

$$SC^* \rightarrow e^- (CB) + h^+ (VB)$$

$$h^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH$$

$$S + {}^{\bullet}OH \rightarrow \text{Products}$$

An electron transfer process is involved in a photocatalytic reaction from semiconductor to substrate or vice-versa. Following reactions can occur on the surface of irradiated semiconductor: The oxidation or reduction of the substrate molecule occurs via electron transfer from the conduction band electron to the substrate molecule or electron transfer from the substrate molecule to the valence band of semiconductor. The substrate molecule thus undergoes chemical reaction. However semiconductor remains unchanged. Hence it can be concluded that these reactions can be initiated so as to drive the reactions in a particular direction depending on the band gap of semiconductor. Thus many reactions can be driven under favourable conditions in the presence of semiconductor.

Environmental applications and some mechanisms of semiconductors as photo-catalysts have been reviewed in the literature for the decomposition of pollutants[114]. Ameta et al.[115] have reviewed the applications of semiconductors in photocatalytic oxidation, reduction and degradation in their review. Different semiconductors have been used in different conditions for the degradation of different compounds. Some of the work on each semiconductor is reviewed here.

Titanium dioxide (TiO_2)

Titanium dioxide is a widely used semiconductor in photocatalysis. A number of papers have been published on the photodegradation of haloaromatic pollutants[116-118]. Photocatalytic mineralization of pesticides in the wastewater has been reported[119]. Bekbolet et al.[120] have studied the photocatalytic decomposition of chlorinated benzaldehyde. Photocatalytic degradation of some chlorinated benzenes have also been reported in literature[121]. The studies of photodechlorination of polychlorobiphenyls (PCBs) in the presence of TiO_2 have been reported[122]. Several reports are published every year describing different methods and results with different experimental conditions for the photocatalytic decomposition of phenols and their chlorinated derivatives by using titania alone or the combination of it with different other catalysts[123]. The use of TiO_2 and UV light irradiation for the wastewater treatment and for the decomposition of chlorinated phenols has been reported[124]. Durand et al.[125] have reported aqueous photochemistry of chlorophenols. Ming-Chun et al.[126] have studied the effect of different metal ions such as Fe^{3+}, Cu^{2+}, Ni^{2+}, Cr^{3+} and Zn^{2+} on the photocatalytic oxidation of 2-chlorophenol in aqueous TiO_2 suspension. Complete mineralization of 4-chlorophenol in water by hydroquinone[127] and 4-chlorocatechol[128] has been achieved by photocatalytic degradation of oxygenated solutions containing suspended TiO_2. Polychlorophenols have been photocatlytically degraded by using TiO_2 suspension and UV irradiation for the purpose of wastewater treatment[129].

Zinc oxide (ZnO)

Zinc oxide (ZnO) has been found very useful photocatalyst semiconductor. Sehili et al.[130,131] have studied photocatalyzed transformation of chlorinated aromatic compounds especially chlorinated phenols using ZnO. They have also reported the photocatalyzed transformation of dichlorobenzenes in aqueous suspension of ZnO[132]. Villasenor et al.[133] have reported the photodegradation of polychlorophenols (PCPs) using ZnO.

Miscellaneous

Kawaguchi et al.[134] have studied the kinetics of Fe^{3+} promoted photodecomposition of 2-chlorophenol. Tang and Huang[135] have studied photocatalytic oxidation of 2,4-dichlorophenol using CdS in acidic and basic medium[135]. Ku and Ching-Bin[136] have reported the photodecomposition of 2,4-dichlorophenol in aqueous solution, catalyzed by CdS. The effect of pH on the photodecomposition has been studied. Wada et al.[137] have studied photoreductive dechlorination of chlorinated benzene derivative using ZnS nanocrystals. Enhancement of the rate of photocatalytic oxidation of chlorophenols in the presence of Mn^{2+} in TiO_2 suspension has been studied by Jong-Nan et al.[138] Lee et al.[139] have studied the enhancement of photocatalytic activity of TiO_2 with MoO_3 for the degradation of 1,4-dichlorobebzene. Coq et al.[140] have discussed the kinetics of hydrodechlorination of chlorobenzene over Pd/Al_2O_3 and Rh/Al_2O_3 catalysts of varying dispersion. The mechanism of photo-oxidation and reduction by irradiated semiconductor can be demonstrated by the Fig. 3 given below[116]:

(i) Excitation of an electron in conduction band of the semiconductor leaving a hole (h^+) in its valence band.

(ii) Transfer of an excited electron from conduction band of the semiconductor to the unfilled energy level of substrate (S) to produce S^-.

(iii) Transfer of an electron from lowest filled energy level of donor substrate (S) to neutralize this hole and to produce S^+.

(iv) Involves both the processes (ii) and (iii).

Quantum efficiency (ϕ)

The efficiency of a reaction initiated by absorption of photons can be expressed in terms of quantum yield or efficiency (ϕ). It is a measure of the efficiency of the use of light in photochemical reaction. This is defined as:

$$\phi = \frac{\text{Number of molecules decomposed or formed}}{\text{Number of quanta absorbed}}$$

$$\phi = \frac{\text{Number of moles decomposed or formed}}{\text{Number of einsteins absorbed}}$$

The quantum efficiency is fundamental quantity, which is useful in the study of photochemical mechanisms. The influence of the experimental variables on ϕ-value, give important information about the nature of the reaction. The quantum yields are calculated as primary quantum yield, product quantum yield, quantum yield of fluorescence, decomposition and rearrangement. Quantum yield of product has been proved very useful for the proper evaluation of a photochemical mechanism.

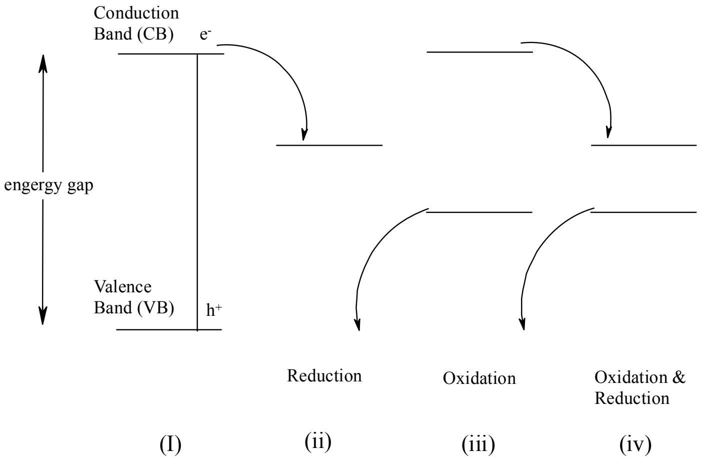

Fig. 3: Various possibilities of electron and/or hole transfer

The rate of the formation of some stable product can be measured by a chemical or instrumental method, irrespective of whether it is formed directly in primary process or in the secondary reaction involving free radicals or atoms. The quantum yield of any stable product X from the photodecomposition of reactant R may be defined as:

$$\phi_X = \frac{\text{Number of molecules or ions of X formed/cm}^3 - \text{sec}^{-1}}{\text{Number of quanta absorbed by R/cm}^3 - \text{sec}^{-1}}$$

Normally maximum quantum efficiency of a primary photochemical reaction is less than 1. The decomposition of excited molecule giving the product can have maximum value of ϕ as 1. In some cases the product formation may be much higher than excitation. The formation of free radical is normal in such reactions and they are chain reactions. Small quantum yields of all decomposition products ($\phi << 1$) indicate deactivation, fluorescence or other processes that lead to a small chemical change. Large quantum yields ($\phi >> 1$) indicate the photochemical change forming the products. The sensitized quantum yield of the product formation can be defined as the number of molecules formed from energy acceptors divided by the number of quanta absorbed by energy donors. The shape of the plot of inverse of quantum yield ($1/\phi$) against the inverse of the concentration of the substrate (1/[C]) gives an important clue to the reaction mechanism. The relationship between ϕ and concentration of substrate suggests that whether the reaction will occur via singlet state or triplet state 1[109]. If the plot of inverse of quantum yield (1/ϕ) against the inverse of the concentration of the substrate (1/[C]) is linear with zero slope, the product formation will take place via singlet-excited state and the quantum yield of the photochemical reaction will be independent of the substrate concentration. The reaction is independent of the substrate concentration as the substrate molecule directly decomposes from singlet-excited state to give product 2). If the plot of inverse of quantum yield (1/ϕ) against the inverse of the concentration of the substrate (1/[C]) is linear with a positive slope, the product formation will take place via singlet-excited state and the quantum yield of the photochemical reaction will be dependent on the substrate concentration. The substrate molecule decomposes from singlet-excited state via exciplex or excimer mechanism to give product, which increases with the increase in the concentration of the substrate 3). If the plot of inverse of quantum yield (1/ϕ) against the inverse of the concentration of the substrate (1/[C]) is curved, the singlet excited state forms product in competition with the triplet excited state via excimer formation and the quantum yield of the photochemical reaction will be dependent on the substrate concentration. The substrate molecule goes to triplet state via ISC and then it decomposes via exciplex or excimer mechanism to give product.

Bunce[141] has developed expressions to calculate the quantum efficiency of the reaction in solution, where the reaction products compete with starting material for absorption of the incident light. He determined the quantum yield of the reaction and tested whether the excimers participate or not in selected photoreactions. These expressions are less useful (i) if the products are themselves photo-labile or (ii) if the products interact photochemically with the starting materials by energy transfer or electron transfer processes. In the photodissociation of aniline derivatives, the ϕ-value of the process increased with the increase of the excitation energy and decreased with increase in substrate concentration. ϕ-Value of some chloroaromatics in different solvents has been reported in the literature[142-144].

Methodology

Progress of the reaction

The progress of the photochemical reaction and the rate of the reaction can be followed by different techniques such as Fluorimetry[145], UV-Vis Spectrophotometry[146], Gas chromatography (GC)[127], Gas chromatography-Mass Spectroscopy (GC-MS)[147], Thin Layer Chromatography (TLC)[148], High Performance Liquid Chromatography (HPLC)[149], Liquid Chromatography-Mass Spectroscopy (LC-MS)[150] and Nuclear Magnetic Resonance (NMR)[151]. The progress of the photochemical reaction and information about the formation of the intermediates can be revealed by using TLC[152].

Study of different parameters

The effects of different variables like pH, concentration of the sensitizer, concentration of the substrate, the intensity of light and the temperature on the rate of the reaction can be studied. The removal of chlorine from the substrate can be tested with silver nitrate solution.

Rate of the reaction

Rate of reaction can be calculated by percentage area normalization by using techniques like GC[212] and HPLC[149]. UV-Visible spectrophotometry can be also used to determine the rate of photochemical reaction. The plot of 2 + log OD vs. time can be used for the calculation of rate constant, which is a straight line. The rate constant of the reaction can be determined using the following expression[153]:

Rate constant (k) = 2.303 x Slope

Quantum yield

The quantum yield can be determined by measuring the intensity of the incident light i.e. number of quanta falling per unit time. A number of methods are available for the standardization of light sources. The procedure is known as actinometry. Ferrioxalate, uranyl oxalate, malachite green leucocyanide (MGL) and Reinecke's salt are used as actinometer for the measurement of light intensity. Here the quantum efficiency (ϕ) has been calculated by using potassium ferrioxalate actinometer[154].

Parker and Hatchard developed photodecomposition of Potassium ferrioxalate as an actinometer. It is accurate and widely used actinometer, which covers the range of wavelength between 250 nm to 577 nm. Fe^{3+} can be reduced to Fe^{2+} by the irradiation of ferrioxalate solution, which could be estimated colorimetrically using 1,10-phenanthroline as complexing agent.

$$2Fe^{3+} + C_2O_4^{\;2-} \xrightarrow{h\upsilon\,/\,0.1\,N\,H+} 2Fe^{2+} + 2CO_2$$

The optical density of the complex of Fe (II) can be compared with a standard at 510 nm of the deep red color produced. The quantum yield for the formation of Fe^{+2} is nearly constant within the wavelength range and shows negligible variation with temperature, solution, composition and light intensity. The intensity of light can be expressed in number of quanta m^{-2} s^{-1} or Einstein s^{-1} m^{-2} [155]. If a light source of power (p watt) emits monochromatic radiation of wavelength λ (nm), the intensity (I) is given by the following expression:

$I = 8.36 \times 10^{-9} \times \lambda$ (nm) x p Einstein s^{-1} m^{-2}. The quantum efficiency (ϕ) for the photochemical degradation of halo-organic compounds can be calculated by the following expression:

$$\phi = \frac{\text{Number of moles of product formed/cm}^3 - \text{sec}^{-1}}{\text{Number of moles of Fe}^{2+}\text{formed /cm}^3 - \text{sec}^{-1}}$$

Product identification

The product formed in the photochemical degradation of the chloro-organic compounds can be identified by using techniques like (TLC)[152], (GC)[127], or (HPLC)[149] by comparison of retention time with authentic sample. With the help of GC-MS[147] and LC-MS[150], the structure of the photodecomposition product can be identified by following the fragmentation pattern of the mass spectrum. Proton NMR and ^{13}C NMR have been used for the identification of the structure of photodecomposition product[151] technique. The formation of the product in photochemical degradation can be confirmed by UV-Visible spectrophotometry and fluorimetry. It can be followed by the comparison of UV-Visible[146] or fluorescence[145] spectra with standard spectra.

CONCLUSION

Photochemical degradation is a very useful and efficient technique to solve many environmental problems, especially for water treatment, since it's a low cost tool, easy to implement and it's able to decompose or convert the toxic compounds into compounds with low toxicity for wide range of halogenated contaminants. It can be utilized for the decomposition of organic and inorganic compounds, and removal of trace metals as well as destruction of viruses and bacteria. It can also be used to decompose natural organic matter (humic substances), which has many environmental and industrial impact. However the technique does not solve the problem entirely but it can definitely help to reduce the water, air and soil pollution in the world.

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