Chapter One

Organotin Compounds

1.1 Introduction:

Organotin compounds (OTCs) are compounds that have the general formula of R_nSnX_{4-n} and have at least one Sn-C bond. R can be any alkyl or aryl groups and X can be an anionic species such as halides, oxide, and hydroxide. The first systematic studies of organotins were carried out by Sir Edward Frankland (1822-1899) in 1853 by synthesizing diethyltin diiodide and in 1859 tetraethyltin. For nearly 100 years the organotin compounds had not been utilized because no commercial application existed. Then in the 1940s when the plastics industry , particularly the production of polyvinyl chloride (PVC) began to expand and due to instability of the plastic under the influence of temperature and light, organotin compounds was synthesized and used as stabilizer (Maguire, 1987).

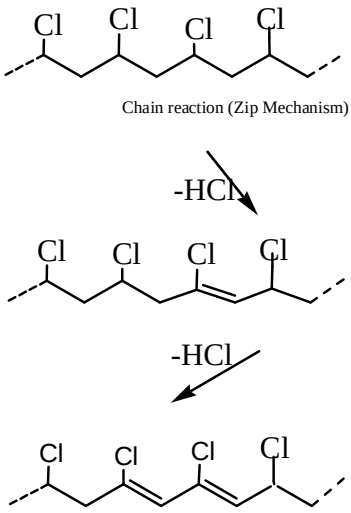
Industrial application of organotin compounds is shown in Table1.1.

Table 1.1 : Industrial applications of organotin compounds

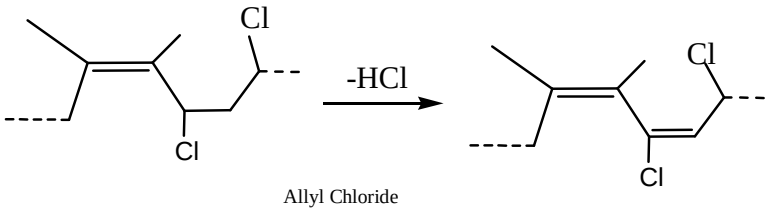
Industrial application	Function	OTC
PVC stabilizers	Stabilizer against decomposition by heat and light	R_2SnX_2 and $RSnX_3$ R=Me, Bu, Oct
Antifouling paints	Biocides	R_3SnXR=Bu, Ph
Agrochemicals	Fungicide ,insecticide, miticide, antifeedant	R_3SnXR=Bu, Ph, Cyh
Wood preservation	Insecticide ,fungicide	Bu_3SnX
Glass treatment	Precursor for tin(IV) oxide Films on glass	Me_2SnX_2 , $RSnX_3$ R = Me, Bu
Material protection (Stone, leather, paper)	Fungicide, algaecides , bactericide	Bu_3SnX
Impregnation of textile	Insecticide , antifeedant	Ph_3SnX
Poultry farming	Dewormer	Bu_2SnX_2

1.2 PVC stabilizers

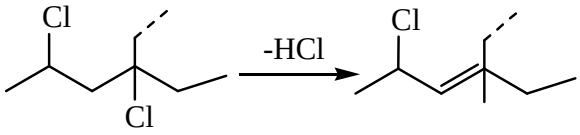
About 76% of organotin compounds produced are used as thermal stabilizers in PVC and plastics. PVC and other polymers are sensitive to light and heat. The temperature of processing causes PVC to degraded. There are some sites in polymers such as allyl chloride that are active and sensitive to temperature. Heating causes HCl release (Dietrich, 1981; Kirk Othmer, 2001), which in turn causes PVC to degrade and discolors. The brittle material lost its mechanical and rheological properties. For preventing of this action, some additives which act as thermal stabilizers should be added to PVC. Thermal degradation of PVC is the result of "zips dehydrochlorination" process that involves allyl chlorides and is accelerated in presence of hydrochloric acid.



PVC structural defects occur mainly during polymerization, increase the degradation rate and will cause changes in color.



Allyl Chloride



Tertiary Chloride

Discoloration observed during PVC degradation is due to the formation of conjugated polyene sequences (>4 double bonds). Another phenomenon known in PVC degradation is chain scission and cross linking. This step is likely to occur in presence of oxygen (auto oxidation) or during the ultimate steps of thermal degradation, leading to a dramatic change in PVC mechanical properties and rheology. PVC degradation rate is strongly influenced by structural defects concentration. HCl formation or other strong Lewis acid or bases, and oxygen, induced auto oxidation.

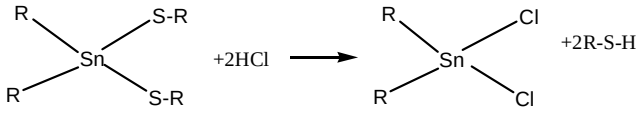
1.2.1 Mechanism of organotin compound as thermal stabilizer:

Without thermal stabilizers, the HCl released will result in the formation of conjugation bond and this in turn cause of discoloration of PVC during the processing.

Stabilizer reacts with free radicals species that is formed and able to accelerate degradation. The role of stabilizer is as the following (Tran et al., 1996):

1) Tin stabilizers acts as HCl scavenger by chemical reaction generating the corresponding tin chloride (reactions 1 and 2).
2) Thermal stabilizers also eliminate and/or replace the labile chloride which initiate dehydrochlorination (defect site destruction) (reactions 3)
3) Reaction with free radical (antioxidant) (reaction 4)

4) Prevent color development by the addition of mercaptide acids on polyenes. (reaction 5).



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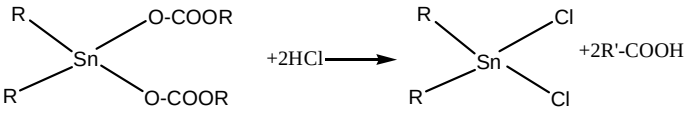

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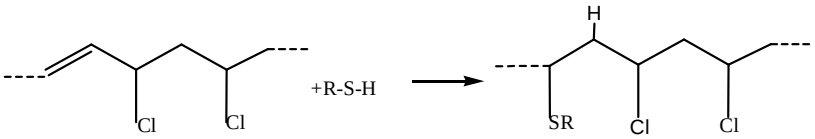

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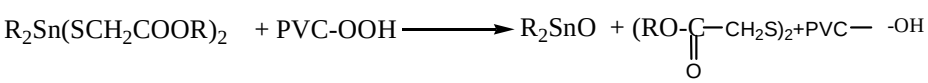

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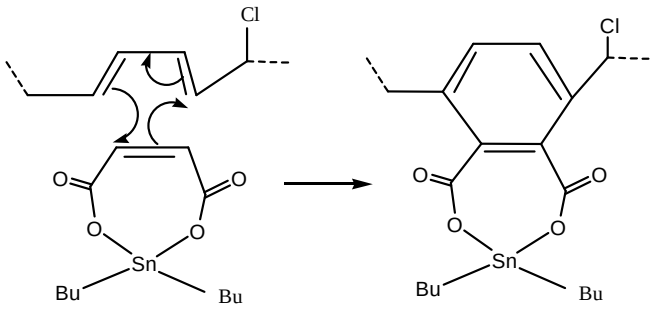

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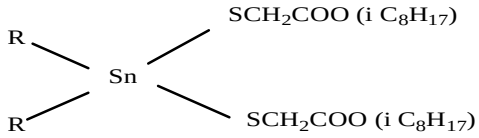
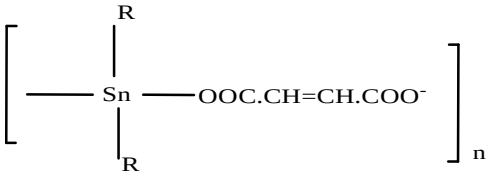
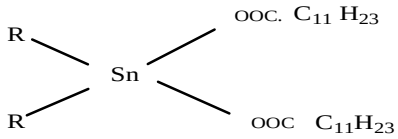
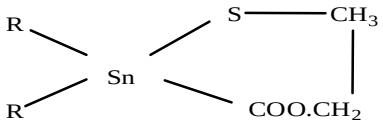
Table 1.2 Some organotin thermal stabilizer (Evans and Karpel, 1986)

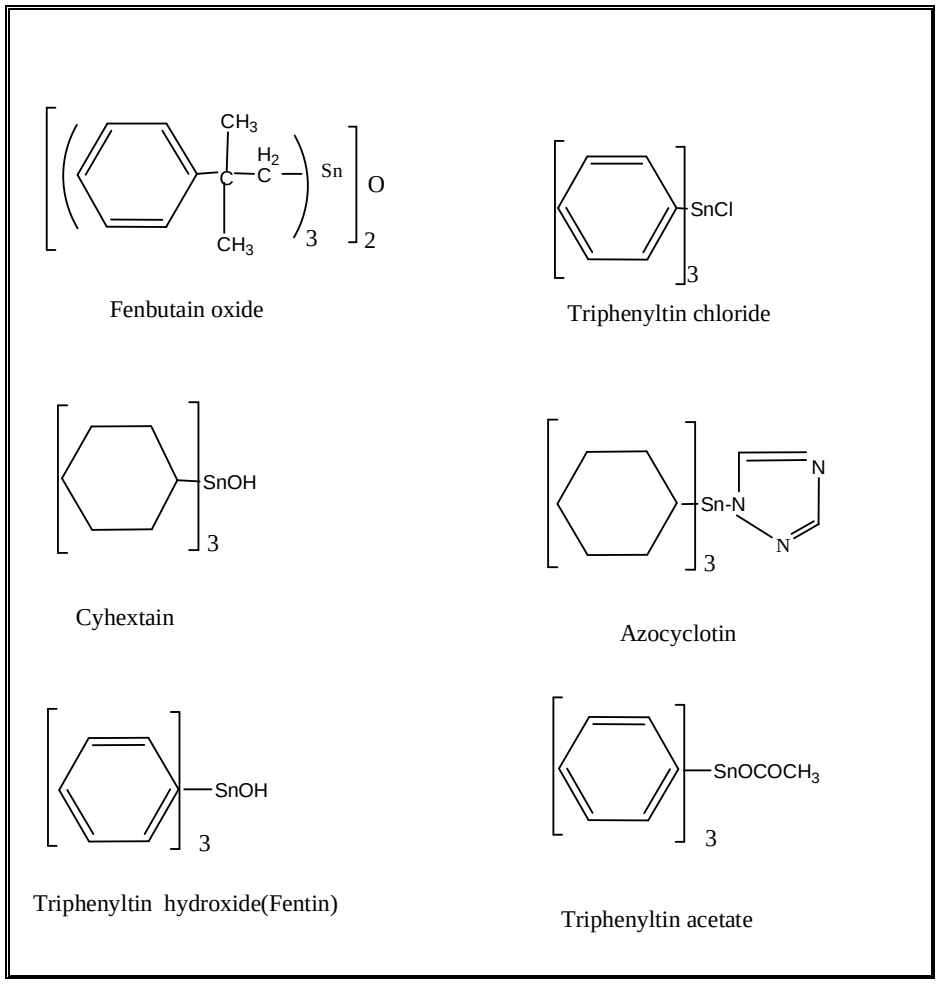
Dialkyltin diisooctylthioglycolate	 R= CH_3 , nC_4H_9 , nC_8H_{17}
Dialkyltin maleate	 R= n C_4H_9, n C_8H_{17}
Dialkyltin dilurate	 R= nC_4H_9 , nC_8H_{17}
Dibutyltin β mercaptopropionate	 R= nC_4H_9

1.3 Organotin compounds as biocides:

About 24% of OTCs used as biocides. In general, triorganotins are used as biocides and as antifouling agents in paints, for painting of ships, also in wood and stone as preservation. Since 1960s, both triphenyltin hydroxide (Fentin) and triphenyltin acetate have been used to control fungal disease which causes potato blight, leaf spots on sugar beets, celery,

onions, and rice, also used to prevent tropical plant disease in peanuts, pecans, coffee and cocoa (Champ and Seligman, 1996). Tricyclohexyltin hydroxides (TCHT) have been used in agriculture as an acaricide for the control of mite on apples, pears and citrus fruits.

Table 1.3: Application of some OTCs in agriculture (Visoottiviseth et al., 1995)



1.3.1 Organotin compounds as fungicides:

Trialkyltin compounds R_3SnX (R could be the same group or different group and X = halogen, hydroxide or oxygen) are active antifungal agent. The fungicidal is prominent in triorganotin and the X group in the series has no great influence on the antifungal activity

of the OTC (Ingham et al., 1960). The concentration of different OTCs that inhibit the growth of fungi is shown in Table 1.4.

Table 1.4: Concentration of OTCs for the inhibition growth of some fungi (Ingham et al., 1960)

OTCs	*Botrytisallii* (ppm)	*Penicilliumitalicum* (ppm)	*Aspergilusniger* (ppm)	*Rhizopusnigricnus* (ppm)
$(C_2H_5)_4Sn$	50	>1000	100	100
$(C_2H_5)_3SnCl$	0.5	2	5	2
$(C_2H_5)_2SnCl_2$	100	100	500	200
$C_2H_5SnCl_3$	>1000	>1000	>1000	>1000
$SnCl_4$	>1000	>1000	>1000	>1000
$SnCl_2.H_2O$	>1000	>1000	>1000	>1000
$(C_2H_5)_3SnOH$	0.2	>5	0.5	0.5
$(C_2H_5)_3SnCOOCH_3$	1	2	5	2
$(C_2H_5)_3SnCl$	0.5	2	5	2

1.3.2 Wood preservation:

Wood and wooden arts are attacked by fungal and insects. Few buildings dating from 16 th century exist today. Tributyl compounds of borate, carbonate, chloride, sulphide and phosphate as well as bis (tributyltin) oxide are used as wood preservative. In addition to applications of OTCs as biocides, OTCs are also used to protect stone works, paints, textiles, leather and cement. Tributyltin oxide, tributyltin naphtanate, and tributyltin phosphate are used as fungicide in wood (Evans et al., 1985).

1.3.3 Antifouling Coating:

The growth of aquatic organisms on vessel hulls creates roughness which gives rise to reduced vessel speed per unit energy consumption. Ten micrometer increase of the average

vessel hull can cause an increase in fuel consumption of about 0.3-1%. Primary marine antifouling paints were based on Cu_2O, but these coating became ineffective not long often and the demand of Tributyltin (TBT) based antifouling paints began in the early 1970s (Champ and Seliggman, 1996).

Antifouling paints consist of a film forming material (matrix/binder/resin/media) and a pigment. The film forming materials and pigment can affect the following paint properties such as, strength, flexibility, water absorption and color. Antifouling paints are similar to any other paints matrix plus pigments. Biocides added to matrix by releasing a small amount of biocide at the paint surface that kill or repel the fouling organism. Different types of antifouling paints, as given below:

1.3.3.1 Free association paint:

TBT physically mixed with the paint and released or leached into the aquatic environment by diffusion through the paint matrix. Biocides leach with time exponentially from the paint. After a period, micro channels in the paint surface can be clogged up by the $CaCO_3$ and this inhibits further release of the biocide. The effective period of this paint is about 2 years.

1.3.3.2 Self polishing copolymer:

This is the most common type of antifouling paint that has been used since 1990s and more effective antifouling in comparison with the others. TBT chemically bonded polymer, this chemical bond tend to retard the release of TBT into the aquatic environment. Unlike conventional toxic antifouling paints that leach large amounts ingredients very rapidly after application, the slow release of active ingredients by copolymer paints makes them more

effective. The life time of this kind of antifouling paints is about 5-7 years (Champ and Beli, 1988).

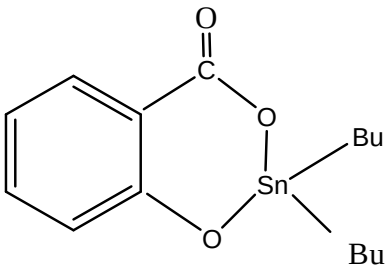
1. 4 Medical uses and biological activity of organotin compounds:

Although a great deal of research has been done in medical uses of OTCs but usage of organotin in medical application is still very small. Based on the model of *cis*platin as anti-tumor in the late 1970s. A series of diorganotin dihalide complexes $R_2SnX_2L_2$ R = methyl, ethyl, n-propyl, n-butyl, or phenyl X = chloride, bromide, iodide or thiocyanate and L = oxygen and nitrogen donor ligand were investigated for their anti-tumor activities. Two most important parameters in anticancer drugs are T/C and ID. (T/C) effectiveness is rated as the ratio of median survival time (days) of treated animals (T) and untreated animals (C), ID (Inhibitory dose) is the dose of a compound that cause a defined inhibition of a given system, the compound is considered active if T/C is $\geq$ 120. Due to the extensive toxicity of platinum compounds causing kidney damage, nausea and vomiting even at low doses, a large number of organotin compounds which mimic the platinum compounds were synthesized and have been tested in vitro for their anti - tumor activity (Evans and Karpel 1985). Many different types of organotin(IV) carboxylates compounds have also been tested in –vitro activity against a large array of tumour cell lines and have been found to be as effective as the traditional heavy metal drugs. It has been, reported that di-n-butyltin derivatives of salicylic acid and *o*-hydroxybenzyl alcohol more active in vitro than cis-platin against *P388* and *L1210 leukaemia* (Kumar et al., 1992).

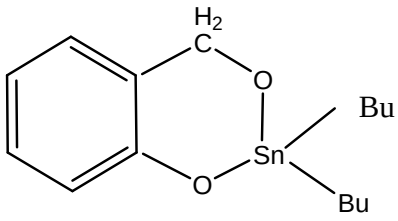
The activities of di-n-butyltin derivatives of salicylic acid (compound 1) and *o*-hydroxybenzyl alcohol (compound 2) are compared with cisplatin in Table 1.5.

Table 1.5: Estimated ID_{50} (Molar) for di-n-butyltin derivative of salicylic acid and *o*-hydroxyl benzyl alcohol (Kumar et al., 1992).

Compound	P388	L 1210
Compound 1	5.5×10^{-8}	23×10^{-8}
Compound 2	14×10^{-8}	40×10^{-8}
cis platin	45×10^{-8}	87×10^{-8}



Compound 1



Compound 2

It was found that these compounds are more active (*in vitro*) than cisplatin. The interaction of organometallic compounds with DNA is of interest for therapeutic treatment as these molecules recognize specific DNA structure, inhibit access to the activator or repressor protein and ultimately affect the gene-expression process.

Most of the chemotherapeutic drugs are DNA-targeted, organotin compounds are involved in cancer treatment via different mechanisms at the molecular level, and the binding ability of OTCs toward DNA depends on the coordination number of the center tin atom. The phosphate group of DNA sugar backbones usually acts as an anchoring site and nitrogen DNA base binding is extremely effective, this is often resulting in the stabilization of the tin center as an octahedral stable species. It has been well established that OTCs are very important in cancer chemotherapy because of their apoptotic inducing character (Tabassum and Pottinari, 2006; Pruchnik et al., 2003).

The di-n butyltin and tri-n-butyltin chloride are known to induce apoptosis in vitro in rat thymocytes, these OTCs inhibiting DNA synthesis and increasing RNA synthesis.

The apoptotic pathway induced by DBT and TBTCl starts with an increase of Ca^{2+} ions and is followed by the release of cytochrome C from *mitocondria*, activation of *caspases* and finally DNA fragmentation.

Some probable factors relating to the action of tin compounds of the type R_2SnX_2 against cancers are:

1. The R group determines the potential activity.
2. The X groups control the delivery of the active R_2Sn species.
3. The hydrolytic stability of the Sn-X bonds determine whether or no the potential activity of the R_2Sn species (Kumar et al., 1992).

1.5 Other applications of organotin compounds :

Some other application of organotin compounds can be summarized as following:

1.5.1 Catalyst in polymer industries

Organotin compounds used as catalysis in three main areas:

1. Polyurethane production
2. Silicone curing agent
3. Esterification reaction

80-90% of tin catalyst is used in polyurethane foam production. OTCs used in these categories are dibutyltin dilurate, dibutyltin diacetate, tin octoanate, and tin oleate.

1.5.2 Glass treatment:

An important application of monoalkyltin compounds such as n-butyltin trichloride is their use as precursor for the deposition of tin(IV) oxide layers (up to 100 nm thickness) on glass bottles. The coating formed from the cursor by chemical vapor deposition (CVD) on the hot glass surface (typically 500-600^{o}C) where the precursor pyrolyse to tin(IV) Oxide. Layers thicker than 1 micrometer are being applied as conductive films for electrode.

1.6 Pollution and toxicity of organotin compounds:

In general, the toxicity of OTC is the greatest for triorganotin compound. The nature of X group in R_3SnX derivatives has little effect or no effect on the biocide activity. An increase in the alkyl group chain length produce a sharp drop in biocide activity, long chain species like octyl tin derivative that used as thermal stabilizer in PVC food packing are not toxic. The most toxic compound of all OTC to mammals is Et_3SnOAc (Oral LD_{50} rat 4 mg/ Kg) (Smith et al., 1978). Table 1.6 shows the oral toxiticity of some OTCs TBT is one of the most toxic pollutants to aquatic life; TPT is also hazardous to aquatic life.

Table 1.6: Acute oral toxicity of several organotin compounds

(Bulten and Meinema, 1991)

OTC	LD_{50} (mg/Kg)	OTC	LD_{50} (mg/Kg)
Et_3SnOAc	4	Hex_3SnOAc	1000
Me_3SnOAc	9	$(Bu_3Sn)_2O$	150-234
Me_3SnCl	13	Bu_3SnOAc	380
Me_3SnOH	540	Bu_2SnCl_2	100
Me_2SnCl_2	74	$BuSnCl_3$	2140
$MeSnCl_3$	1370	Bu_4Sn	> 4000
Ph_3SnOH	125	Oct_4Sn	50000

1.6.1 Water pollution:

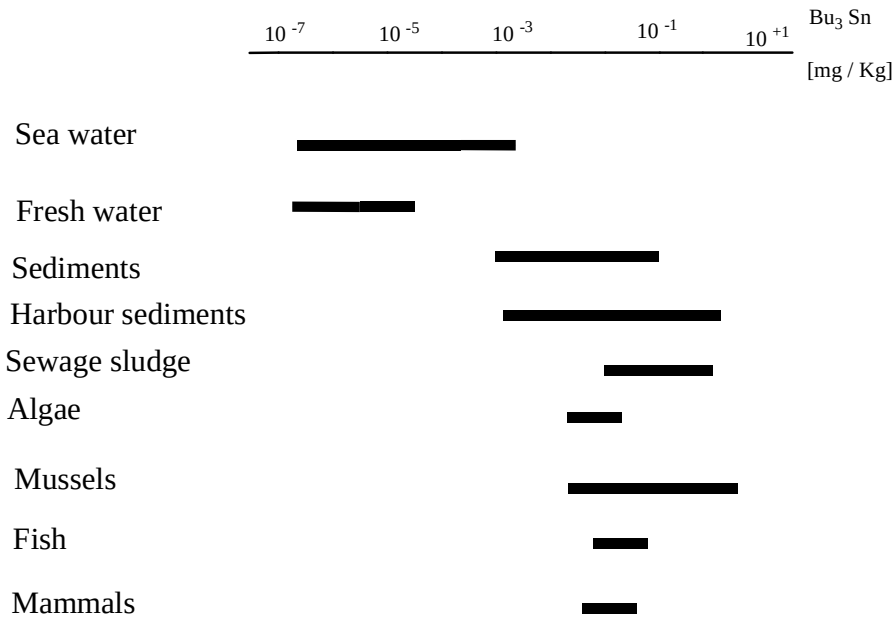
TBT and TPT pollution in aquatic systems results in various symptoms on organisms, like thickening of shell and failure of spots in oysters, imposex of neogastropods and gastropods, reduction of dog whelk population, and the retardation of growth in mussels (Bryan et al., 1988; Alzeiu et al., 1989; Gibbs et al., 1991; Salzar, 1991). Imposex was seen in some of the marine animals that are polluted by TBT. The dog whelk (*Nucella Lapillas*) was often seen at the North Sea coast in Belgium but some years after using TBT as antifouling agent, this kind of animals disappeared. This is because of imposex and extinction of females.

Tetraorganotin compounds often show a delayed toxic activity because of degradation to triorganotin. There are some reports on the presence of OTC in drinking water when water passes through the new installed PVC pipe (Vishwakiran et al., 2006). MBT and DBT were found because of leaching from PVC material (Sadighi et al., 1996a; Sadighi and Williams, 1996b). The effect of organotin compounds was reported in France, the oral application of a pharmacon was used for the treatment of skin infections causes at least one hundred deaths and over 200 intoxification (Saxena, 1987; Nicklin and Roboson, 1988).

The drug was based on diethyltin diiodide and linoleic acid and it is assumed that the highly toxic triethyltin iodide were present as impurity. The symptoms of dialkyltin and trialkyltin poisoning are vomiting, headache, visual defects and electroencephalographic abnormality. Twenty percent of TPT used in agriculture activity entered into the environment. These compounds (TBT, TPT) contaminate water, soil, sediments, and bioaccumulation in marine organism and harmful for aquatic organs and human body. Diagram 1.1, shows the range of TBT concentration in various environmental species (Tsuda et al., 1995; Jamari et al., 1999; Hoch, 2001).

Diagram 1.1: Ranges of TBT concentration in various environmental samples

(Hoch, 2001)



As shown in diagram 1.1, OTCs have a high affinity for substance containing nitrogen and oxygen hence result in higher concentration in fish, shellfish and other marine organism. Sediments are the most important organotin sink. Marine sediment plays an important role in the biogeochemical cycling of this metal. The half life of OTCs is 6 days to several months, and those in sediment which is 1-9 years, these values varied with the intensity of light, heat, types, and amounts of organotins.

In peninsular Malaysia, the concentration of TBT in sea water ranged from <3.4-20 ng/l in unexposed area (away from shipping activity) and 30-281.8 ng/l in area with high boat and ship activity. The highest reported concentration of TBT in sediment was 38000 ng/g in Fiji (Jamari et al., 1995). Cooking doesn't eliminate butyltin in food. In Australia the daily delivery intake of all butyltin from fish was estimated to be 377-416 ng/person/day based on average fish consumption of 21 g/day. In spite of banning or regulation of the usage of TBT in some countries, contamination continues in the aquatic environment and

environmental concentration remains sufficient to warrant continued concerned (Jamari et al., 1995). Triorganotin and their specific effect on species are shown in Table1.7.

Table 1.7: Triorganotin derivatives and their specific effect on species (Hoch, 2001)

Alkyl	Living specimen
CH_3(methyl)	insects
C_2H_5(ethyl)	mammals
C_4H_9(butyl)	fish, algae, mussels, mollusks, fungi
C_6H_5(phenyl)	fungi, mollusks, fish
C_6H_{11}(cyclo-hexyl)	mites, fish

1.7 Physical and chemical properties of OTCs:

In order to understand the environmental behavior of OTCs, an idea on the physical and chemical properties of OTCs is necessary. The OTCs has the general formula R_nSnX_{4-n} where R is alkyl or aryl X is halide, hydroxide, acetate etc. The number of Sn-C bond affects the physical and chemical properties of the compounds. Melting point and boiling point of some OTCs is shown in Table 1.8. The pH and salinity affect the solubility of TBT and TPT. Salting out affects on solubility and lowers the solubility of cationic species. Table 1.9 gives the solubility of TBT and TPT in various solutions at different temperature (Inba et al., 1995).

Table 1.8: Melting points and boiling points of some OTCs (Blunden and Chapman,1986)

OTCs	Melting point (^oC)	Boiling point (^oC)
Bu_4Sn	-97	145/1.3KPa
Bu_3SnCl	-16	172/3.3KPa
Bu_2SnCl_2	39-41	135/1.3KPa
$BuSnCl_3$	-	93/1.3KPa
Me_3SnCl	37-39	154
Me_2SnCl_2	106–108	188-190
$MeSnCl_3$	48-51	171
Ph_4Sn	227-229	
Ph_3SnCl	106-107	
Ph_2SnCl_2	42-44	
$PhSnCl_3$		132–134/15. 5
		142-143/25

Table 1.9: Aqueous solubility [Sn (mg/lit)] for some OTC (Inba et al., 1995)

Compound	Temperature ^{o}C	Solvent	[a]pH 5	Minimum Solubility[b]	pH [c]
TBTCl, TBTO	25	Distilled water	70	15	7.9
TBTCl, TBTO	25	ASTM water	2	1	7.3
TBTCl	10	Distilled water	ca 30	7.9	7.6
TBTCl	10	ASTM water	ca 1	0.5	7
TPTCl ,TPTO	25	Distilled water	4	0.8	7.2
TPTCl ,TPTO	25	ASTM water	1	0.3	7
TPTCl	10	Distilled water	2	0.4	7.5
TPTCl	10	ASTM water	ca 1	0.2	7.5

ASTM (1986) D- 1141, Section 6.
ASTM water contain (NaCl 24.53, $MgCl_2$ 5.20, $CaCl_2$ 1.16, KCl 0.7, Na_2SO_4 4.09, $NaHCO_3$ 0.2, KBr 0.1 g/l)
[a] value of solubility at pH 5 [b] Minimum value of solubility [c] value of pH that minimum Solubility was obtained.

1.8 Degradation of OTCs:

As mentioned previously, triorganotin compounds are very toxic to the environment .One of the approaches for overcoming this problem is the degradation of these compounds. There are three methods for the degradation of OTCs.

1. Photo-degradation,
2. Biological degradation,
3. Chemical cleavages.

The Sn-C dissociation energy is in the range of 190-220 KJ/mol. UV radiation with wavelength 290 nm equal to this bond energy. Hence UV radiation with wavelength less than this value can degrade the OTCs.

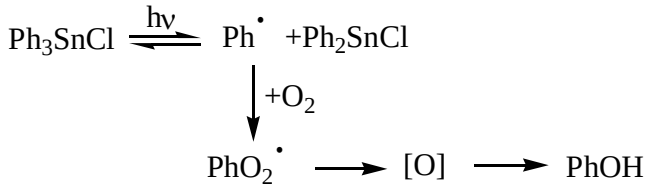
It is proposed that degradation of OTCs is based on the following steps:

$R_4Sn \rightarrow R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4$ (Inorganic tin compound)

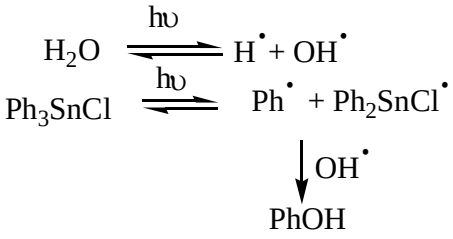
The reported half-life of OTCs in sea water is about 6 days to several months and in sediments, it is 1-9 years. UV degradation of TBT, DBT and MBT chloride in water has been studied, where the order of rates of photo-degradation is MBT >> DBT > TBT and that rate determinate step is the degradation of TBT to DBT. These results show the presence of O_2 plays negative roles on photo-degradation of TBT (Navio et al., 1980; 1997).

The investigation of degradation of triphenyltin hydroxide in water showed that TPTOH has converted to DPT oxide and then to water soluble polymeric tin. It was mentioned that acetone can be used as sensitizer and causes increase in the rate of photo-degradation. The degradation pathway of the photolysis of TPTCl in aqueous acetone is shown in Scheme 1 and Scheme 2. The UV photo assisted degraded of phenyltin chloride showed that the sequential dephenylation from TPT to MPT.

When the reaction is carried out in air, the molecular oxygen can react with the phenyl radical (Scheme 1). However, under nitrogen atmosphere the phenol derivative could be formed by the OH radicals in water (Scheme 2) (Soderquist and Crosby, 1980).



Scheme 1



Scheme 2

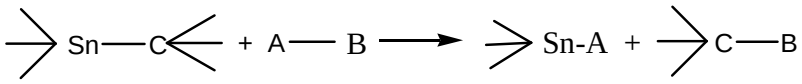
1.8.1 Biodegradation of OTCs:

There are a few reports on the biodegradation of TBT by microorganism such as bacteria, fungi, cyanobacteria, and green algae in the aquatic environment. It was reported that gram negative bacteria viz *P.areuginosa*, *A.facalis*, fungi viz *tratmis versicolor* and *chaetomium globosum* could degradate TBTO via dealkylation process. Because of the high lipid solubility of these compounds, gram negative bacteria have the capability to accumulate TBTO without its breakdown .The elimination of such hydrophobic compounds is facilitated by their bio-transification to water soluble polar compounds, thus the metabolism of a compound generally reduces persistence, increases removal or elimination and results in a reduction of toxicity (Dubey and Roy, 2003).

1.8.2 Chemical cleavage:

The Sn-C bond can be attacked by both nucleophilic and electrophilic reagent, such as (mineral acid, carboxylic acid, thiol, phenol , alcohol, metallic or non metallic halides,

alkali and alkali metals and so on.



By using electrophilic or nucleophilic reagents, heterolytic cleavage of the Sn-C bond is possible (Poller, 1970).

1.9 Analysis of organotin compounds:

Most of the analytical techniques that have been developed for the speciation of OTCs are based on GC owing to its high resolution and availability of sensitive detectors (Takeuchi et al 2000; Masahiro et al., 2000). The method should have a low detection limit, low quantitation limits, should be able to discriminate among different tin compounds, good precision and accuracy.

For GC analysis, the polar ionic species need to be extracted from the sample matrix and be converted to their fully alkylated more volatile forms which can be analysed by this analytical technique (Leery et al., 1998). For the analysis of OTCs in environmental samples (water, sediments, organs), some pretreatments procedures included digestion, extraction, derivatization and purification are needed. Some samples such as tissues, organs, and sediments should be digested or leached in acidic media. Hydrolysis of the tissue samples can be carried out using acetic acid, tetramethyl ammonium hydroxide, or alcoholic potassium hydroxide (Nagase et al., 1995; Ikonomou et al., 2002). The main procedure for organotin pretreatment for biological sample and sediments are based on use of acid reagent in aqueous or methanolic media by sonication, stirring, shaking or soxhlet extraction (Stab et al., 1993).

1.9.1 Extraction:

The organic solvent, the type and concentration of acids, and the complexing agent used will affect on the extraction of butyl and phenyl tin compounds from mussel tissue. An acidic medium and the use of tropolone in non polar organic solvent enhance the extraction efficiency of these compounds. A number of methods of extractions for butyl and phenyltin compounds had been investigated and was found tropolone, and diethyldithiocarbamate to be effluent complexing agents (Pellergino et al., 2000).

1.9.2 Derivatization:

For GC analysis, polar compounds should be converted into fully alkylated more volatile forms. There are three methods for derivatization of OTCs.

1. Alkylation by Grignard reagent
2. Hydride formations by sodium borohydride
3. Ethylation by sodium tetraethylborate.

Non polar solvents such as hexane, benzene, toluene, chloroform, pentane or dichloromethane extract non polar TBT but high polar mono and dibuyltin (MBT, DBT) need complexation or acidification of the sample. In addition to classical extraction methods there are more recent approaches for extraction , such as microwave assisted extraction (MAE), supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), solid phase extraction (SPE), and solid phase micro extraction (SPME) (Gomez–Ariza et al., 2001).

1.9.2.1 Alkylation by Grignard reagents:

This derivatization method has to be performed in aprotic solvent, and in dry condition. Grignard reagents react with the triorganotin to form volatile tetra alkylated derivatives.

Some authors avoid using methylation and butylation because these species have been claimed to occur in the environment. The low boiling point of methyl derivatives may also leads to losses of organotin derivative. Hexa alkylated tins are more thermally stable; ethylation and pentylation have been applied successfully for environmental samples (Maguire et al., 1998). Grignard methods for the derivatization of OTCs are known to be very time consuming.

1.9.2.2 Hydride generation by $NaBH_4$:

The reaction of tin, alkyl and phenyl tin with $NaBH_4$ can produce tin hydride species. This method of derivatization has been successfully carried out for preparation of methyl and butyltin compounds. The reaction requires a slight acidification of the water using acetic acid or nitric acid. This technique requires the use of inert atmosphere. Hydrides may be generated in the presence of organic solvent (Mathias et al., 1986).

1.9.2.3 Ethylation by $NaB(Et)_4$:

This method made the sample preparation faster and easier because it enables an *in situ* derivatization and extraction of the ethylated organotin compounds into an organic phase (hexane, isooctane) which is subsequently analysed by gas chromatography (Morbito et al., 2000).