

Review of organotin compounds: chemistry and applications

Duaa Ghazi, Zahraa Rasheed, Emad Yousif

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

Abstract

Organotin compounds find a bigger range of technological and industrial applications than the organic compounds of any other metal. Many of these applications involve catalysis or anticatalysis, often in polymer chemistry, and they have an importance out of all proportion to the tonnage of tin which is used. This article reviews the present standing of the non-biological applications of organostannanes, with an emphasis on the mechanisms of the reactions which are involved. The three major families of organometallic compounds which find application in technology and industry are those based on aluminium, silicon, and tin. Alkylaluminium compounds are highly reactive, and their applications depend on their chemical properties as alkylating agents, for example towards tin tetrachloride in the production of alkyltin compounds. Organotin compounds were first studied in 1852 by Löwig, who prepared diethyltin by the action of a sodium-tin alloy upon ethyl iodide. In the following year Frankland prepared tetraethyltin and in the next years a considerable number of both alkyl and aryl organotin compounds were synthesized and described. In the course of these studies more than one of the investigators became aware of the poisonous nature of some of these compounds and Frankland himself was made ill for several months, but happily recovered, and there are no reports that any of those affected actually succumbed. It was evident that certain organotin compounds, notably triethyltin hydroxide and triethyltin acetate, were highly toxic; this was confirmed in 1881 by White, who studied their effects upon dogs and other animals. A period of 70 years was to elapse before the significance of these preliminary observations was realized.

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1. Introduction

The field of organotin chemistry has a long history that started since 1849, when Frankland isolated a specimen of diethyltin diiodide [1]. In 1852, Lowich reported on the reaction of alkyl halides with a tin-sodium alloy giving alkyltin compounds [2]. This last publication is usually considered to represent the beginning of organotin chemistry. By 1935, about hundreds of publications concerning organotin chemistry had appeared in the literature. At that time, important names had played a role in the development of organotin chemistry were Krause in Germany, Kraus in the United States, and Kozeshkov in Russia. The discovery of organotin compounds industrial applications as polyvinyl chloride (PVC) stabilizers, as agrochemicals, biocides, and wood preservatives produced a revival of organotin chemistry. Particularly van der Kerk and his co-workers in Netherlands played a major role in this development [3, 4].

In early of 1960s it was found that the tin atom in organotin

compounds is capable of extending its coordination number beyond four. Based on colligative studies, the trimethyltin chloride pyridine adduct, Fig. 1, was the first documented five-coordinate triorganotin halide complex that was proven by X-ray crystal structure [5]. Though divalent tin compounds had known for a long time, bis (cyclopentadienyl) tin(II) was the first example of a divalent organotin compound that was reported in 1956 [6].

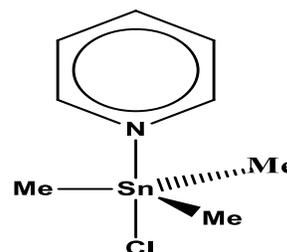


Figure 1. trimethyltin chloride pyridine adduct.

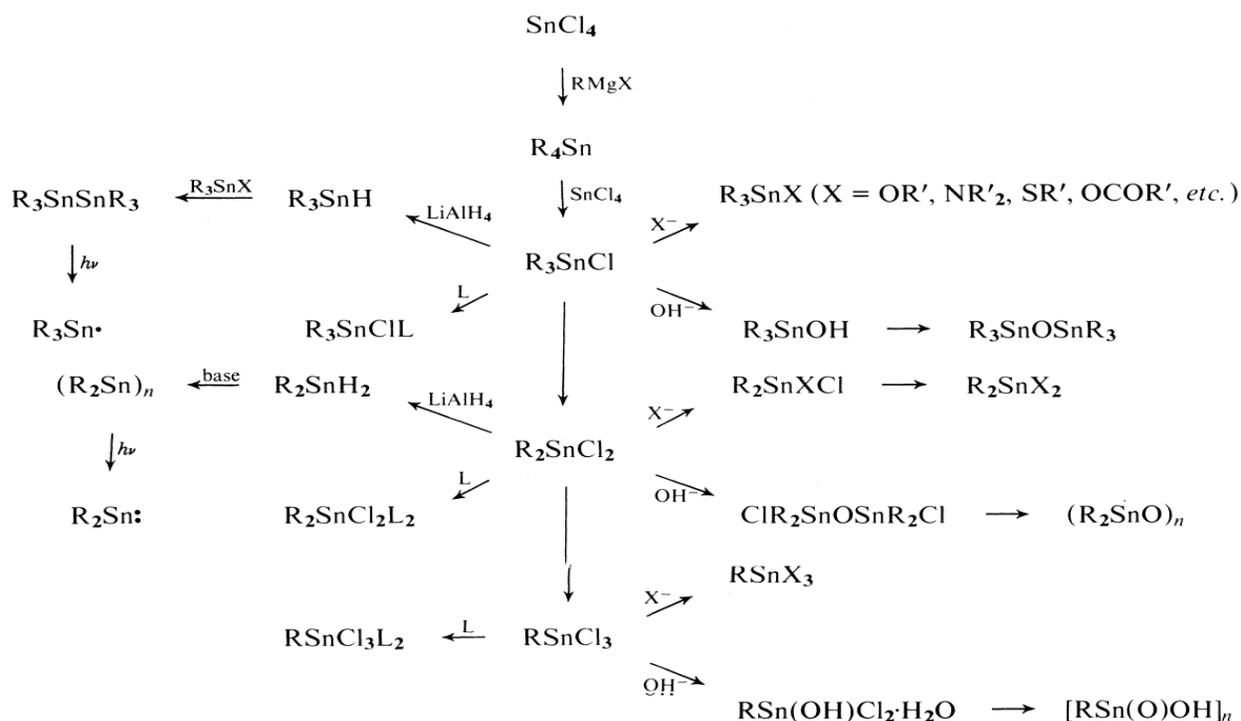
2. Industrial preparation of organotin compounds

On the industrial scale, organotin compounds are usually prepared by alkylation of SnCl₄ with organo-magnesium or -aluminium compounds.

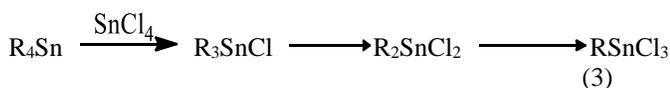
Grignard reagents, RMgX, are prepared from the metal and an alkyl or aryl halide and need large volumes of solvent and are expensive. It is difficult to stop the reaction with SnCl₄ to partial alkylation unless R is very bulky, and the reaction is usually taken to completion to give the product R₄Sn, equations (1) and (2) [7].



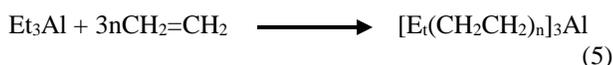
The tetraalkylstannane is then heated with the appropriate amount of SnCl₄ (the Kocheshkov reaction) when redistribution occurs to give the alkyltin chlorides R_nSnCl_{4-n} equation (3). Or scheme 1



Scheme 1



Usually in industry, the reaction is achieved with the low cost alkylaluminium compounds. Triethylaluminium can be made from aluminium metal, hydrogen and ethylene equation (4), and higher alkylaluminium compounds are then made between triethylaluminium and ethylene by the reaction of Ziegler growth, which needs no ethereal solvent equation (5). Trimethylaluminium, which is strongly dimerised, does not give this reaction, so it is the even numbered alkylaluminium compounds, e.g. n-Bu₃Al and (n-C₈H₁₇)₃Al which are readily accessible.

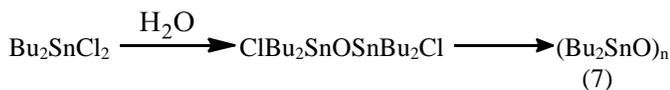


By reacting these organoaluminium compounds with SnCl₄ to give the corresponding alkyltin chlorides, the syntheses are carried out with n-butyltin compounds, such as tri-n-butyltin hydride and di-n-butyltin dichloride, due to their low cost and less toxic compared to the methyltin compounds. Unlike Grignard reagents, these reactions can be taken to the stage of partial alkylation to give the alkyltin halides directly, e.g. equation (6). dibutyl- and dioctyl-tin dichloride are made industrially by this method.



Other organotin derivatives can then be made from these chlorides. For example, treatment with sodium acetate gives the corresponding organotin acetates, and thiols under basic conditions give the tin thiolates, both of which are used as stabilizers for PVC. Progressive hydrolysis of dibutyltin

dichloride gives first the dichlorodistannoxane which is used extensively as a catalyst, and then dibutyltin oxide which is an insoluble polymer equation (7).



These dysfunctional distannoxanes, $\text{XR}_2\text{SnOSnR}_2\text{X}$, are ladder-shaped dimers which are highly soluble in non-polar solvents because they have the structure of a reversed micelle fig. (2), with a polar core surrounded by lipophilic alkyl groups, and they are excellent catalysts for a number of organic reactions apparently because of their nature as binary Lewis acids [8].

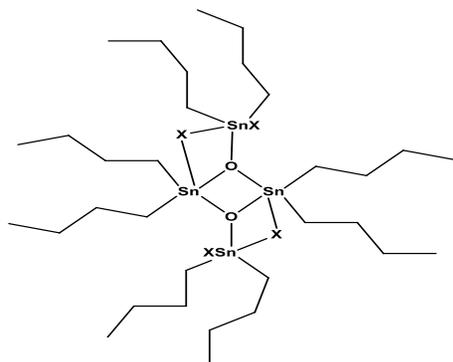
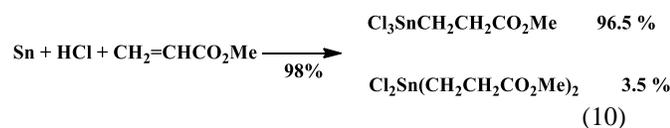


Figure 2. difunctional distannoxanes

Alternative method of forming the (Sn-C) bond was introduced in 1976 by the AKZO Company, which developed a series of PVC stabilizers (the Estertins), these are prepared by the reaction of HCl Gas with metallic tin or with SnCl_2 in an ethereal solvent to give the solvated chlorotin hydrides HSnCl_3 and H_2SnCl_2 , which add, in a heterolytic Michael fashion to acrylic esters to give β -alkoxycarbonylethyltin compounds equations (8) and (9) [9,10].

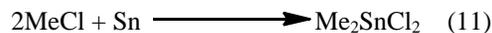


The two reactions can be combined, as shown in equation (10).



both Sn (II) and Sn (IV) the principal coordination geometries, in the case of (II) tin, it is assumed that the lone pair is also participate in the hybridization. Some general trends for organotin coordination compounds have been well established.

Extensive efforts have been made to prepare organotin compounds by the Direct reaction of metallic tin with organic halides, but the only process which as yet has been commercially successful is the preparation of dimethyltin dichloride from methyl chloride and tin in the presence of a catalyst equation (11) [11].



3. Tin Bonding and Valency

In the periodic table of the elements, tin is listed in group 14, together with the elements carbon, silicon, germanium, and lead. Tin has two stable oxidation states, the Sn (+2) and Sn (+4). For bonding The Sn (+2) utilize the 5p orbitals mainly and leaving the singlet unshared pair in the 5s orbital with a little of p character, however, the organotin (II) compounds are not very stable, due to its tendency to polymerize rapidly and it can also be easily oxidized to the organotin (IV) which is the more stable. In the valence shell of the tin atom the four electrons have the $5s^2 5p^2$ electronic arrangement that can undergo sp^3 hybridization, and therefore tetravalent tin atoms are tetrahedral. The bonding of Sn is almost entirely covalent, at least in crystalline solids, in nonpolar solvents and in the vapor phase. This is true even for tin-halogen bonds.

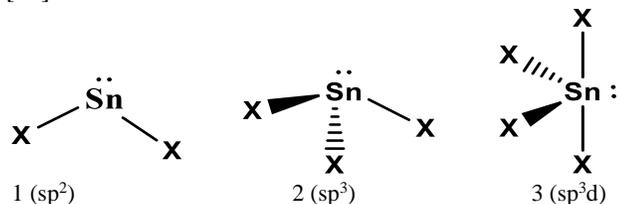
Within group 14, the bond lengths to carbon increase considerably: C-C 1.54, C-Si 1.94, C-Ge 1.99, C-Sn 2.15, and C-Pb 2.29 Å. The increased bond length for tin is the cause of the increased reactivity and the related lower thermal stability of the tin alkyls compared with their C, Si, and Ge analogs. Long bonds naturally have low strength and also lessen the screening of the central atom by the ligands. Attacking reagents thus have easier access. This is particularly evident in organo-lead compounds [5].

4. Principal Coordination Geometries at the Tin Center in Organotin Compounds

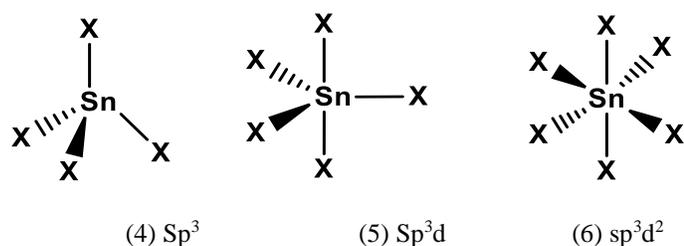
Before 1963, when Hulme used X-ray crystallography to demonstrate that the monopyridine adduct of trimethyltin chloride contains 5-coordinate tin, it had been generally assumed that most organotin (IV) compounds are simple, tetrahedral molecules containing 4-coordinate tin atoms., however, the well-established techniques of proton NMR and infrared spectroscopy have been supplemented by ^{119}Sn NMR spectroscopy [12,13], and these have stimulated X-ray investigations of a large number of organotin compounds, Many derivatives are now known that contain not only 5 and 6 but even 7 coordinate tin atoms [14].

The divalent as well as in tetravalent tin of empty 5d orbitals of suitable energy, it may be involved in the Hybridization, tin can have higher coordination numbers. In Fig. 3, shows for Based on the decreasing Lewis acidity with increasing number of organic groups present at tin, tetraorganotin compounds showed no capability to increase the coordination number due to the poor acceptor properties of the Sn in these compounds

[15].



Structures of Sn(II) compounds

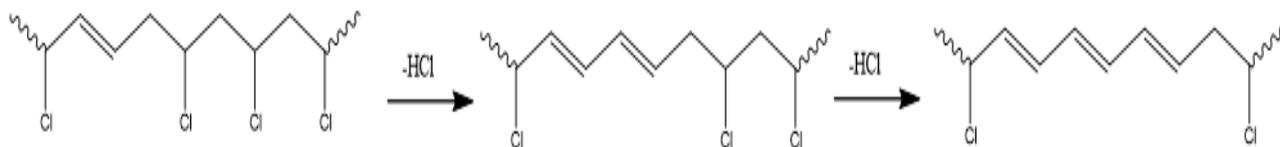
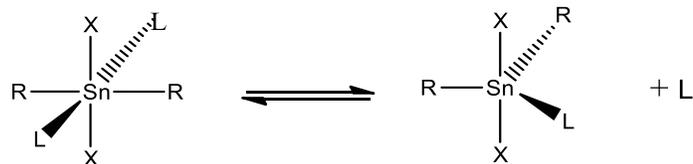


Structures of Sn (IV) compounds

Figure 3. The principal coordination geometries of divalent and tetravalent tin.

The preferred coordination geometry of the tin atom in triorganotin halides is trigonal bipyramidal, with the carbon of the ligand at the equatorial site and at the axial positions the donor atom and electronegative halide [16]. Both trigonal bipyramidal and octahedral coordination geometries have been found for the tin atom in adducts of diorganotin dihalides with Lewis bases. The solid-state structures of complexes, $R_2SnX_2 \cdot 2L$ (L = monobasic ligand), have generally two trans-oriented carbon ligands (R), whereas the two halide and the two donor molecules can adopt either mutual Trans or cis-configurations, depending upon the nature of the substituent [17].

In solution, these complexes exist in equilibrium of a hexacoordinate and a pentacoordinate species, with the latter as the predominant one [18].



(13)

Monoorganotin compounds, $RSnX$, show a remarkable tendency to undergo to a higher coordination number to 5, 6 and 7, and there are few Examples of compounds of the type $RSnX$ which contain pentacoordinate tin. The anion in tetraphenylarsonium tetrachloromonomethylstannate, $(Ph_4As)^+ (MeSnCl_2)^-$, is one such example and consists of trigonal bipyramid and methyl group take an equatorial site [19]. A similar R_2SnX_4 , type of geometry was found in the intramolecular pentacoordinate, ketiminotin trichloride.

5. Preview of organotin application

In 1852 the synthesis of the first organotin compounds took place by Lowing and it was only after 80 years of the synthesis the organotins found application for transformer oils and vinyl plastics as stabilizers. Due to the development and increasing interest in the 1950s, significantly by Van der Kerk and co-workers, the organotin compounds commercial uses had expanded rapidly. There are three main areas of the utility of organotin compounds, as stabilizers of polymers, as industrial and agricultural biocides, and as catalytic agents in a many of chemical reactions.

5.1 Stabilization of PVC

Poly (vinyl chloride), PVC, is one of the most important commercial plastics, and its production is the third largest after polyethylene and polypropylene. It is used in many applications such as construction (window frames and water, sewage and drainage pipes), packaging (food and blood bags), household products (raincoats, toys, conduits and wall paper), decoration and wire coating [20]. In spite of its appropriate properties, such as low cost, non-flammability and good versatility, its stability at elevated temperature and exposure to light is considered a serious environmental and health problem. However, it is well known that PVC degrades at these conditions, giving off successive hydrogen chloride gas (autocatalytic dehydrochlorination this progresses along the chain in a zipper fashion, to give an extended conjugated polyene.

Polydimethylsiloxane is the most common siloxane polymer, that is formed when the hydrolysis of the chlorine of the monomer, dichlorodimethylsilane ($\text{Cl}_2\text{Si}[\text{CH}_3]_2$), replaced by hydroxyl (OH) groups. The product is unstable compound, silanol ($\text{Cl}_2\text{Si}[\text{OH}]_2$), that goes on condensing in fashion of step-growth to form the polymer, with association of losing water. A cyclic products that are also formed, purify by distillation and by ring-opening polymerization convert to polysiloxane.

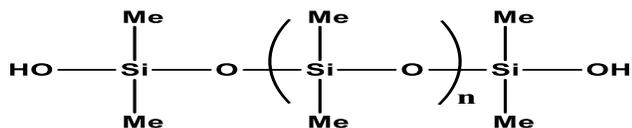
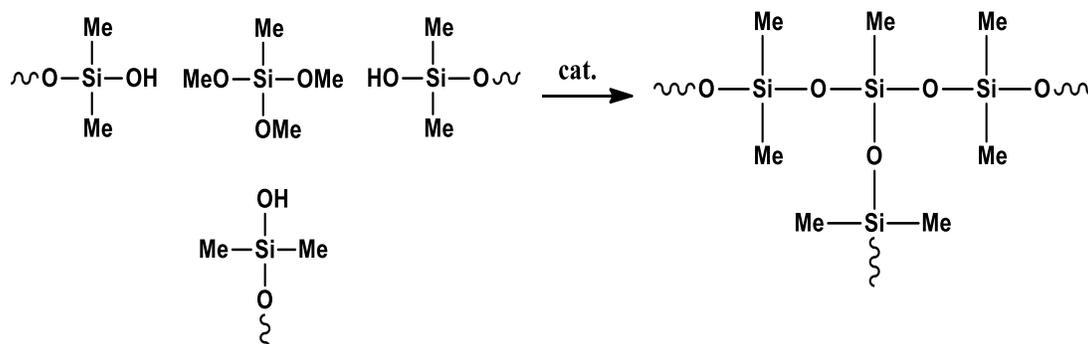


Figure 4. Polydimethylsiloxane.

The cross-linking of chains converts the silicone oils into elastomers with a wide variety of uses such as coatings, sealants, moulding compounds, release agents, encapsulants, and water repellents.

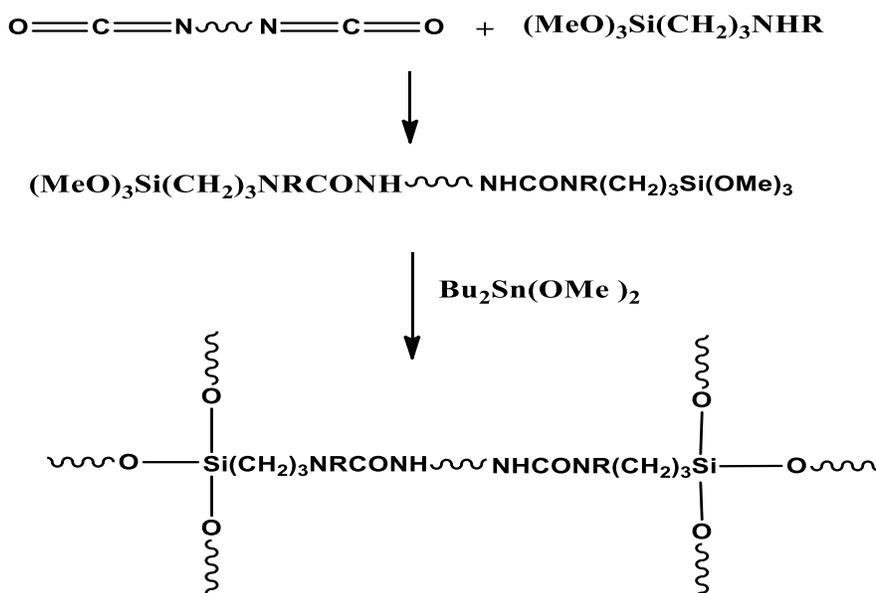
This vulcanisation can be carried out at room temperature (room temperature vulcanisation, RTV) with a tri- or tetra-functional silane as a cross-linking agent and an organotin catalyst, which is commonly dibutyltin diacetate or dilaurate [equation (16)].



(16)

The product may be supplied in two components, one consisting of the HO- terminal polysiloxane and the other containing the tri- or tetra-methoxysilane and the organotin catalyst, and reaction occurs when the components are mixed. A one-component product would contain a mixture of a MeO-terminal polysiloxane, the polyfunctional cross-linker, and the

catalyst. When the mixture is exposed to air, the terminal MeO groups are hydrolysed to OH, and vulcanisation takes place. A silanol-terminated silicone co-polymer can be crosslinked in the same way, and isocyanate-terminated polyurethanes can be end-capped with trialkoxysilyl groups and then subjected to vulcanisation, e.g. equation (17) [38].



(17)

The organotin dicarboxylate is first hydrolysed to the hydroxyl carboxylate. This reacts with the trialkoxysilane cross-linker to give a stannasiloxane, and this in turn reacts with terminal hydroxysilane groups of the polymer to cap it with a dimethoxysilane group. Repetition of this process gives a cross-linked polymer.

5.4 Transesterification and related reactions

Reactions at carboxyl groups, such as esterification, transesterification, transcarbamoylation, lactonisation, and ring opening polymerization (ROP) are important in chemical industry.



These reactions can generally be catalyzed by alkalis or protic acids, but frequently a less aggressive catalyst is needed because the reactants may be acid or base sensitive, or for avoiding corrosion of the plant, or for environmental reasons and organotin compounds are commonly used for this purpose. This is currently a very active field of study. Dibutyltin dilaurate and dibutyltin oxide are frequently used; the latter compound is an intractable polymer, but it dissolves on reaction with the carboxyl compound to give a distannoxane [39].



The outstanding advantages of the Organotin compounds as catalysts for esterification reactions, due to the catalytic with high efficiency, poor tendency to eliminate water to form olefins from secondary alcohols, the potency to produce colorless esters, and the imparting the heat of stabilization to condensation type polymers (polyesters), Also to improve the physical and electrical properties of the product

6. Marine Antifouling

Antifouling paints had been used to prevent the growth of organisms ‘fouling’ such as seaweed, barnacles, and tubeworms which produce drag and drastically reduce the propulsion of the marine structures and vessels. The paints are directed to ‘target’ organisms that settle on solid surfaces after a period time in the sea. There are two distinguished forms of Antifouling paints– with or without TBT. There is a variety of alternative TBT-free paints [40].

In the 1960s, tributyltin and triphenyltin compounds (oxide, chloride, acetate, etc.) were introduced, replacing the copper oxide which had been used previously to reduce the growth of fouling. The organotin compound was incorporated into the hull paint (“free association paints”), and slowly diffused out, providing protection for 18–24 months. During that period, the rate of release declined as antifoulant had to diffuse to the

surface from deeper in the paint [41].

There is a consequence of using the organotin as antifoulants that is their exceptional toxicity to marine organisms ‘non target’. In a diverse range of species the organotin interfere with the biological processes. In the 1980s scientific evidence of worldwide demonstrated the extreme negative impacts on the marine environment by organotin compounds, TBT found in marinas with high concentrations and related to the growth with abnormalities in mussels and oysters and a decrease in their abundance

The use of these paints was progressively restricted in the 1980s due to its high toxicity on the marine environment, a ban on their use came into effect in January 2008 [42], but the technology that was developed is now being adapted to the design of self-polishing copper polyacrylates which work on the same principle

7. Wood protection

Successful trials have been made in the preservation of various woods against insects, fungi, bacteria and wood-boring marine animals. Tributyltin(IV) complexes show effective biological activities against microorganism and are used for preservations of wood. An important properties of the organotin compounds is that they impart neither color nor odor to the treated wood. The treatment of wood with organotin(IV) compounds occur in a vacuum, into the wood the results released in a flow of the organotin(IV), which is attached with terminal OH groups of the cellulose to prevent the damage by microorganisms [43].

8. Glass coating

By using Atmospheric Pressure Chemical Vapor Deposition (AP-CVD) techniques to form electrically conductive thin films on the surface of glass by using Organotin(IV) [44]. Due to its wide range commercial applications and economical reason, as a precursor Tin chloride is used for the formation of transparent conductive oxide (TCO) films. Strength, thermal stability and resistance to oxidation are provided by the coating. TCO film also control the heat lossing through glass which is because of the deposition on glass surface by metal oxide film.



Using Tin Oxide for Coating glass have a different of important applications, Coated glass used in deicing wind shield screens, security glass, or display systems [45], due to their low electrical resistance and high resistance to chemicals. A layer 1-μm thick can be used to fills in the imperfections in the of the glass surface so that thinner bottles can be used (e.g. milk bottles) which uses less glass and are bear to fewer breakages [46]. Coating can act as a p-type or n-type semiconductor or conductor. If doping the SnO₂ with about 3% of fluoride makes it an n-type semiconductor; the filled and empty orbitals band gap is reduced into the infrared region, so that the glass becomes transparent to solar radiation, also

reflective toward heat radiation. Doping with antimony and with indium is also common, though the latter (ITO, indium tin oxide) has a largely indium content. These semiconductors are used in a variety of electronic devices such as diodes, transistors, solar cells, heated windows, antistatic coatings, and sensors [47].

9. Biological Applications

organotin(IV) carboxylates uses for any specific biological activity is related to the nature and number of organic groups R directly which are attached to the tin atom and the carboxylate groups attached to the tin atom by Sn-O bonds. The effectiveness of organotin(IV) compounds are decided by these factors for required purposes. The nature of the R group determines its site of attack for organotin(IV), binding to the different sites in the body, such as carbohydrates, nucleic acid derivatives, amino acids [48] and to proteins [49]. Hetero atoms presence such as N, O or S in the ligand play a major role in the geometry and therefore effect the biological activity of these complexes [50]. The effective biological activity of organotin(IV) compounds motivate their applications in pharmaceutical.

10. Pharmaceutical Applications

Metal ions have outstanding role in different physicochemical processes that take place in vivo and they are distinguished for their metallopharmaceutical applications such as organotin(IV) compounds are used as effective biological agent against various diseases [51]. Study of organotin(IV) effectiveness and their mode of act by interaction with various parts like ATPase and hemoglobin's are studying model for interactions of drugs with the human body [52,53]. Attempts to develop new drugs for different purposes, synthesis of organotin(IV) complexes with new ligands and different coordination geometries are taken place. Applications in the fields of muoluscicides, veterinary science, antibacterial, antifungal, antitumour, schizonticidal, antimalarial and amoebicidal agents are due to the potential biological activity of organotin(IV) complexes [54-68].

11. Conclusion

Organotin compounds find a bigger range of technological and industrial applications than the organic compounds of any other metal. Many of these applications involve catalysis or anticatalysis, often in polymer chemistry, and they have an importance out of all proportion to the tonnage of tin which is used. This article reviews the present standing of the biological applications of organostannanes, with an emphasis on the mechanisms of the reactions which are involved.

Acknowledgments

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