APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 617–622 (1995)

Behaviour of $Bu(CH_2{=}CHCH_2)SnCl_2$ in Water and Water-Cosolvent Media: an Approach to Understanding the Chemical Degradation of Organotins in Aquatic Environments

Daniele Marton, Diego Stivanello and Giuseppe Tagliavini*
Dipartimento di Chimica Inorganica , Metallorganica e Analitica, Universitá di Padova, via Marzolo 1, I 35131 Padova, Italy

The behaviour of allylbutyltin dichloride in water, water–ethanol and water–hexane media, under either homogeneous or heterogeneous conditions, has been studied. 1,3-Diallyl-1,3-dibutyl-1,3-dichlorodistannoxane, butyltin di(hydroxy)chloride and butyltin trichloride arise from the solvolytic, acid–base and degradation processes. The degradation process involving the cleavage of the tin–carbon allyl bond has been interpreted to occur via an intramolecular reaction at the expense of the cation $[Bu(CH_2{=}CHCH_2)Sn(OH)(H_2O)_n]^+$. The mechanistic pathway is ascribable to an internal interaction of the electrophilic cation with a bonded water molecule. This mechanistic proposal may be of some help with understanding of the chemical degradation of diorganotin derivatives in aquatic environments.

Keywords: allylbutyltin dichloride; diorganotin derivatives; degradation; aquatic environment

INTRODUCTION

Organotins have found increasing use as fungicides, bactericides and insecticides, and as wood preservatives.[1,2] In the 1960s tributyltin compounds were used to kill snails which are intermediate hosts in the transmission of schistosomiasis.[3,4] They were also incorporated into paints used as antifouling agents on the nets of salmon-farm pens and on boat hulls, where they are more effective than the copper compounds which are the alternative active agents in antifouling paints.[5] Tributyltin compounds have also been used extensively in agriculture because of their action against algae, fungi, insects and mites.[6] As a consequence, organotin compounds are present in the environment, especially in aquatic ecosystems.

Despite the large number of studies that have been completed, understanding the role of organotins in aquatic systems is complicated by the fact that they can undergo several chemical processes, such as disproportionation, degradation (e.g. cleavage of Sn–C bonds, e.g. $R_3SnX \rightarrow R_2SnX_2$, $RSnX_3 \rightarrow SnX_4$), transmetallations (e.g. $\equiv Sn{-}R + HgX_2 \rightarrow \equiv SnX + RHgX$), etc.[7] Therefore, on the basis of our experience of the reactions of organotins in the presence of water,[8] we have untertaken studies on processes involving organotins in aqueous media with the aid of models which may help in understanding the mechanistic pathways of the processes themselves. Indeed, in our previous paper[9] we took into consideration, as a model, the behaviour of $Bu_2(CH_2{=}CHCH_2)SnCl$, looking at the disproportionation equilibrium (Eqn [1]) which takes place in the presence of water under heterogeneous conditions.

$$2Bu_2(CH_2{=}CHCH_2)SnCl \rightleftarrows Bu_2Sn(CH_2{=}CHCH_2)_2 + Bu_2SnCl_2 \qquad [1]$$

In this paper, we wish to report observations on the behaviour of $Bu(CH_2{=}CHCH_2)SnCl_2$ (**1**) in the same media: water, water–ethanol and water–hexane. This diorganotin derivative belongs to the large category of R_2SnCl_2 or $RR'SnCl_2$ derivatives, where R and R′ stand for alkyl or aryl groups. Generally, these compounds in the presence of water are solvated to aquocation complexes,[10,11] which behave as Brønsted acids. Therefore, their solutions are characterized

* Author to whom correspondence should be addressed.

CCC 0268–2605/95/070617–06

Received 11 December 1994
Accepted 9 June 1995

by pH values ranging from 1 to 25. These aquocations behave like simple aquo-inorganic ions in binding ligands. They are unusual in that they involve covalent metal–carbon bonds together with the highly polar bonds from tin to other ligands. The mixed alkyl-halogen ligand compound, $Bu(CH_2{=}CHCH_2)SnCl_2$, which has been chosen as a model bears a tin–carbon allyl bond which is kinetically more labile than a tin–carbon alkyl bond.[12] As a consequence, cleavage or redistribution processes at the tin–carbon allyl bond are expected to occur within a reasonable time.

EXPERIMENTAL

Materials

Triallylbutyltin

This compound was prepared via a Grignard procedure.[13] To a 2-litre three-necked flask equipped with magnetic stirrer, condenser and additional funnel, containing 93 g (3.8 mol) of magnesium turnings and 150 ml of anhydrous ethyl ether, were added over 2 h with stirring, 152.6 g (1.26 mol) of allyl bromide dissolved in 200 ml of anhydrous ethyl ether. Then the Grignard reagent was transferred to another flask, and 60 g (0.21 mol) of butyltin trichloride dissolved in 250 ml of anhydrous ethyl ether was added dropwise over 2 h. The mixture was refluxed for 6 h, then hydrolysed with ice, and the organic layer was separated and dried over sodium sulphate. After removal of the solvent by a Rotavapor, the crude liquid product was distilled under reduced pressure at 95–98 °C/0.05 mmHg, yielding 53.4 g (85%) of triallylbutyltin.

Allylbutyltin dichloride

To 6.56 g (23.6 mmol) of $BuSn(CH_2CH{=}CH_2)_3$ was slowly added (over 40 min) at 0 °C with stirring 13.32 g (47.2 mmol) of $BuSnCl_3$. The mixture was set aside for 3 h at room temperature. The pure $Bu(CH_2CH{=}CH_2)SnCl_2$ (15.0 g, 73% yield) was obtained by distillation under reduced pressure (b.p. 90 °C/0.25 mmHg).

IR (thin film): 3060 [(w, $\nu({=}CH_2)$)], 1620 [s, $\nu(C{=}C)$)], 990 [(m, δ_{oop} $(CH{=})$)], 910 [(s, δ_{oop} $({=}CH_2)$)], 350 cm^{-1} [(s, $\nu(Sn{-}Cl)$)].
$\delta(^{119}Sn$ NMR) of pure liquid referred to TMT: +80.7 ppm.
$\delta(^{13}C$ NMR) of pure liquid referred to TMS. Butyl moiety: 13.5 (CH_3), 26.2 (CH_2), 26.5 ($CH_2{-}Sn$), 26.9 ppm (CH_2). Allyl moiety: 31.7 ($CH_2{-}Sn$), 117.4 (${=}CH$), 130.3 ppm (${=}CH_2$).

The organic solvents, which were commercially available, were used as received. In all cases, pure water produced by a Millipore Milli-Q system was used.

Equipment

The ^1H, ^{119}Sn and ^{13}C NMR spectra (89.55, 33.35 and 22.49 MHz respectively) were recorded with a JEOL FX 90Q multinuclear spectrometer operating in Fourier transform mode. The IR spectra were recorded with a Perkin-Elmer model 599 B spectrophotometer using CsI optics. The pH measurements were performed with a Crison MicropH 2002, using a glass pH electrode with an AgCl internal reference electrode.

RESULTS

Allylbutyltin dichloride in H_2O–EtOH medium

Run 1

Butylallyltin dichloride (**1**) (1.25 g, 4.34 mmol) was dissolved in 20 ml : 20 ml H_2O/EtOH, and stirred at 25 °C. After 15 min the pH of the solution reached a value in the range of 1–2. After 24 h the system was still homogeneous, and 5 ml of the solution was taken off. After removal of the solvent, a crude oil residue, consisting of the sole unchanged compound **1**, was isolated.

Run 2

As in run 1, compound **1** (1.25 g, 4.34 mmol) was added to a mixture of H_2O/EtOH (20 ml : 20 ml) under stirring at 25 °C. After two days formation of turbidity was noted, then a white precipitate was formed, increasing over time. After three days the solid was filtered off, dried and weighed (0.45). It was insoluble in all common solvents. From the IR spectrum and elemental analysis it was identified as $BuSn(OH)_2Cl$ (**2**) (m.p. 112–114 °C; Lit.[14] 107–112 °C).

IR: 3490, 3380 [vs, $\nu(OH)$], 550 [m, $\nu(Sn{-}C)$], 240 cm^{-1} [m, $\nu(Sn{-}Cl)$].
Elemental analysis: Calcd for $SnC_4H_{11}O_2Cl$, mol. wt. = 245.27: C, 19.58; H, 4.52; Cl, 14.45. Found: C, 19.80; H, 4.56, Cl, 14.63%.

From the filtrate, after removal of the solvent, a heavy oil (0.72 g) was recovered, formed of unchanged starting material containing a small amount of $BuSnCl_3$ (**3**) (see below, run 3).

In conclusion, after three days, $Bu(CH_2{=}CHCH_2)SnCl_2$ is partially converted to $BuSn(OH)_2Cl$ (42%) and $BuSnCl_3$ (traces).

Run 3

The previous run 2 was repeated and observed for nine days. After this time, 0.77 g (3.14 mmol) of a white solid was recovered, showing the same chemical–physical characteristics as **2** (m.p. 113–114 °C). From the water–ethanol filtrate, a heavy liquid oil (0.29 g) was isolated.

The IR spectrum recorded as a liquid film [ν(Sn—Cl) 360 cm^{-1}] was similar to that of a pure sample of **3**. Both ^{119}Sn and ^{13}C NMR spectra of the oil in $CDCl_3$ were in agreement with those obtained from a 20% solution of pure $BuSnCl_3$ in $CDCl_3$.

δ(^{119}Sn NMR) referred to external (TMT) +3.80, vs +4.72 ppm of the reference solution.
δ(^{13}C NMR) referred to internal TMS. Butyl moiety: 13.3 (CH_3); 32.4 (CH_2—Sn); 25.6 (CH_2); 26.8 ppm (CH_2) (see ref. 15).

In this case, 72% of compound **1** was converted to compound **2**, and 24% to compound **3**, with a total recovery of tin of about 96%.

Run 4

Allylbutyltin dichloride (2.75 g, 9.6 mmol) was dissolved at 25 °C in a mixture of H_2O/EtOH (50 ml : 25 ml). Then 10.6 ml of 12.1 M HCl was added in order to achieve 1.5 M HCl solution. The system was stirred for 30 h. During this time, a white solid precipitated. It was filtered off, dried and weighed (0.5 g). It melted at 47–48 °C and was soluble in most organic solvents.

IR: 3060 [m, ν(=CH)], 1618 [s, ν(C=C)], 892 [vs, δ(C=CH_2)], 580, 530 [vs, ν(Sn—O—Sn)], 390 [w, ν(Sn—C allyl)], 280 cm^{-1} [s, ν(Sn—Cl)].
δ(^{119}Sn NMR) of a 10% solution in $CDCl_3$ referred to external TMT: −129.7 and −177.8 ppm. Both values are in agreement with a distannoxane structure. The ^{119}Sn NMR chemical shifts for tetrabutyl-1,3-dichlorodistannoxane are −94 and −145 ppm in CCl_4 solution,[16] the Δ-value being 51 ppm in comparison with the found Δ-value of 49 ppm.
δ(^1H NMR) of a 10% solution in $CDCl_3$ referred to internal tetramethylsilane (TMS): 0.6–1.1 (t, 3H), 1.1–1.6 (m, 2H), 2.4–2.6 (m, 2H), 4.5–5.5 ppm (m, 2H), 5.7–6.5 (m, 1H).

Therefore, this product was identified as a new compound: 1,3-diallyl-1,3-dibutyl-1,3-dichlorodistannoxane (**4**). Elemental analysis: Calcd. for $Sn_2C_{14}H_{28}OCl_2$, mol. wt 520.66: C, 32.29: H, 5.42; Cl, 13.63. Found: C, 32.26; H, 5.54; Cl, 13.54%. Upon exposure to moist air, compound **4** decomposes to compound **2**.

Allylbutyltin dichloride in a water–hexane medium

Run 5

To a solution of **1** (1.25 g, 4.34 mmol) in 10 ml of n-hexane, 20 ml of water was added under magnetic stirring, at 25 °C. The pH value of the aqueous phase was in the range 1–2. Both phases remained clear for up to seven days, then a precipitate was formed, increasing over time. After 14 days, the precipitate (0.2 g) was separated and identified as compound **2**. From the filtrate, after removal of both solvents, a heavy liquid oil (0.81 g) was recovered.

IR and ^{119}Sn NMR analyses revealed that the oil was the starting organotin dichloride containing traces of $BuSnCl_3$. Therefore, in this case, only compound **2** (0.81 mmol, 18.6% yield) was isolated.

Allylbutyltin dichloride in water

Run 6

Allylbutyltin dichloride (1.25 g, 4.34 mmol) was added to 20 ml of water at 25 °C with stirring. Under such conditions, the organotin compound was present as a solid phase, initially in equilibrium with its saturated aqueous solution. After 27 h, the system still remained heterogeneous, but with a visible change of the morphology of the solid phase. The white solid was filtered off and dried up to reach a constant weight of 0.74 g. The product was a mixture of compound **4** (0.67 g) together with compound **2** (0.07 g). From the filtrate $Bu(CH_2{=}CHCH_2)SnCl_2$ (0.28 g) and $BuSnCl_3$ (0.13 g) were identified.

The final balance of this system was as follows: unchanged **1**, 0.28 g (22.8%); **2**, 0.07 g (6.6%); **3**, 0.13 g (10.6%); and **4**, 0.67 g (59.3%); the total recovery of tin was about 99%.

Run 7

Allylbutyltin dichloride (0.5 g, 1.7 mmol) was dissolved in 20 ml of water at 40 °C under stirring.

After about 20 min, a white solid was formed, increasing over time. After 7 h, the precipitate was filtered off. The recovered solid (0.25 g, 0.48 mmol, m.p. 47–48 °C) was identified as compound **4** (56.5% yield).

Run 8

A quasi-saturated solution of **1** (0.619 g, 2.15 mmol) in 50 ml of water was stirred for 14 days at 20 °C (the solubility of $Bu(CH_2{=}CHCH_2)SnCl_2$ at 18 °C is 13 172 ppm). During this time, the solution maintained its homogeneity. From an initial value of 1.27, the pH decreased to 1.17. The volume of the solution was reduced to about 5 ml, then extraction of the organotin species was performed with three portions (each of 30 ml) of a mixture of diethyl ether–pentane (1:2, v/v). Then, after drying with magnesium sulphate ($MgSO_4$), the solvents were removed, and a crude pale yellow liquid residue (0.542 g) was recovered. It was a mixture of unchanged organotin dichloride **1** together with compound **4**. The ^{119}Sn NMR spectrum showed three well-defined signals, one at +77.7 ppm (compound **1**), the other two at −129.6 and −177.9 ppm (compound **4**). The molar ratio **1**:**4** was 85:15. In conclusion, the isolated crude liquid was a mixture of 0.408 g (1.42 mmol) of compound **1** and 0.134 g (0.26 mmol) of compound **4**. The total recovery of tin was 90%.

DISCUSSION

Water or water–ethanol solutions of allylbutyltin dichloride show a pH value in the range 1–2. This is due to solvolytic and acid–base equilibria, which takes place in such a media similarly to those of the parent compounds R_2SnCl_2 and $RR'SnCl_2$ described by Tobias.[10, 11] The equilibria may be written as shown in Eqns [2] and [3]. Both are relevant to explain the pH values encountered. Indeed, these compounds behave as monobasic acids, since the release of a second proton is negligible.

$$\begin{aligned} &Bu(CH_2{=}CHCH_2)SnCl_2 + nH_2O \\ &\rightleftarrows Bu(CH_2{=}CHCH_2)SnCl(H_2O)_n^+ + Cl^- \qquad [2] \end{aligned}$$

$$\begin{aligned} &Bu(CH_2{=}CHCH_2)SnCl(H_2O)_n^+ + H_2O \\ &\rightleftarrows Bu(CH_2{=}CHCH_2)SnCl(OH)(H_2O)_{n-1} + H_3O^+ \qquad [3] \end{aligned}$$

In our case, the species $Bu(CH_2{=}CHCH_2)Sn(OH)Cl$ (see Eqn [3]) is responsible for the formation of 1,3-diallyl-1,3-dibutyl-1,3-dichlorodistannoxane (**4**) (see Runs 4 and 6–8), according to Eqn [4].

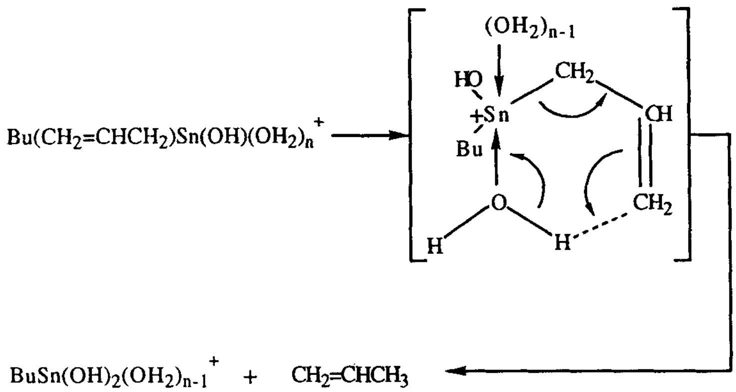
$$2\,Bu(CH_2{=}CHCH_2)Sn(OH)Cl \rightleftarrows \begin{array}{c} CH_2{=}CH{-}CH_2 \quad CH_2{-}CH{=}CH_2 \\ | \qquad\qquad | \\ Bu{-}Sn{-}O{-}Sn{-}Bu \\ | \qquad\qquad | \\ Cl \qquad\qquad Cl \\ \mathbf{4} \end{array} \downarrow + H_2O \qquad [4]$$

The new compound **4**, either in solution or in the solid state, degrades to $BuSn(OH)_2Cl$ (**2**) (see Run 4). Compound **2** is very insoluble in water and in all common organic solvents, and dissolves in HCl solution to give $BuSnCl_3$ (see Runs 3 and 6). The recovered $BuSnCl_3$ comes from the dissolution of compound **2**, according to Eqn [5]:

$$\underset{\mathbf{2}}{BuSn(OH)_2Cl}\downarrow + 2H_3O^+ + 2Cl^- \rightleftarrows \underset{\mathbf{3}}{BuSnCl_3} + 4H_2O \qquad [5]$$

The acidity required to promote this reaction (Eqn [5]) results from Eqns [3] and [4]: one can see that one equivalent of acidity is released in solution per equivalent of precipitated compound **4**.

In conclusion, distannoxane **4** is formed through solvolytic and acid–base equilibria promoted by compound **1**, in either homogeneous or heterogeneous systems. Distannoxane **4** is slightly soluble in H_2O–EtOH medium, but less soluble in water. However, it degrades to compound **2** either in solution or in the solid matrix via hydrolytic cleavage of the tin–carbon allyl bond. The free acidity remaining in solution favours the dissolution of compound **2** to form $BuSnCl_3$. Clearly, allylbutyltin dichloride is subject to a degradation process leading to monobutyltin species, i.e. $BuSn(OH)_2Cl$ and $BuSnCl_3$. The degradation process occurs owing to the cleavage of the tin–carbon allyl bond. The cleavage of this bond is interesting, since it is not due to solvated protonic species. Indeed, in the presence of free acidity (see Run 4) only distannoxane **4** is recovered, without any cleavage of this bond.



Scheme 1

We believe that a water molecule is able to promote this cleavage at the expense of an ionic electrophilic species. On the basis of proposed mechanistic pathways involving allylstannations of carbonyl compounds in the presence of water,[17,18] and the interactions between an electrophilic ion and a molecular species,[19,20] the aquo-cation $[Bu(CH_2{=}CHCH_2)Sn(OH)(H_2O)_n]^+$—which arises from the solvolysis of the species $[Bu(CH_2{=}CHCH_2)SnCl(OH)(H_2O)_{n-1}]$ — may evolve through an intramolecular reaction as shown in Scheme 1. The aquo-cation $[BuSn(OH)_2(H_2O)_{n+1}]^+$ is responsible for the formation of the insoluble $BuSn(OH)_2Cl$, which can be partially recovered as $BuSnCl_3$ depending upon the free acidity released in solution.

It is noteworthy that many studies have been carried out on the equilibria of organotin cations in aqueous solutions,[10,11] but no work has been done on mechanisms dealing with the Sn—C bond breaking in such cations. The mechanistic pathways generally accepted by workers in the environmental field are those based on the wide range of chemical reactions involving Sn—C bond cleavage in non-aqueous media.[21,22] In our opinion, the chemical degradation of these cations deserves much more attention.

The present mechanism proposed for the cleavage of the tin–carbon allyl bond may be considered of some help for the understanding of the chemical degradation of compounds of the type R_2SnX_2 (R = alkyl or aryl group), which, as is well known, are present in the aquatic environment.

Acknowledgements We are indebted to the MURST (Rome) and Consiglio Nazionale delle Ricerche (Rome), Progetto Finalizzato, Chimica Fine II, for financial support.

REFERENCES

1. R. J. Maguire, *Appl. Organomet. Chem.* **1**, 475 (1987).
2. J. G. A. Luijten in: *Organotin Compounds*, Vol. 3, Sawyer, A. K. (ed.) Marcel Dekker, New York, 1973, p. 931.
3. J. G. Thayer, in: *Organometallic Compounds and Living Organisms*, Academic Press, New York, 1984.
4. N. F. Cardarelli, *Rev. Si, Ge, Sn, Pb Compounds* **8**, 169 (1985).
5. S. J. Blunden, P. A. Cusak and R. Hill, *The Industrial uses of Tin Chemicals*, Royal Society of Chemistry, London, 1985.
6. P. J. Smith, *Toxicological Data on Organotin Compounds*, Int. Tin Res., Inst. Pub. No. 538, 1978.
7. J. J. Cooney, J. H. Weber and L. R. Sherman, in *Biological Diversity: Problems and Challenges*, Majumdar, S. K., Brenner, F. J., Lovich, J. E., Schalles, J. F. and Miller, E. W. (eds.), The Pennsylvania Academy of Sciences, Easton, PA, 1994.
8. G. Tagliavini, *J. Organomet. Chem.* **437**, 15 (1992).
9. D. Marton and G. Tagliavini, *Appl. Organomet. Chem.* **9**, 553–559 (1995).
10. R. S. Tobias, *Organomet. Chem. Rev.* **1**, 93 (1966) and references therein.
11. F. E. Brinckman and J. M. Bellama (eds.), *Organometals and Organometalloids—Occurrence and Fate in the Environment*, ACS Symp. Ser. No. 82, American Chemical Society, Washington, DC, 1978.
12. V. Peruzzo and G. Tagliavini, *J. Organomet. Chem.* **66**, 437 (1974) and references therein.
13. W. T. Schwartz, Jr., and H. W. Post, *J. Organomet. Chem.* **2**, 357 (1964).
14. J. G. A. Luijten, *Rec. Trav. Chim. Pays-Bas* **85**, 873 (1966).
15. T. A. K. Al-Allaf, *J. Organomet. Chem.* **306**, 337 (1986).
16. A. G. Davies, L. Smith, P. J. Smith and W. McFarlane, *J. Organomet. Chem.* **29**, 245 (1971).
17. A. Boaretto, D. Marton, G. Tagliavini and A. Gambaro, *J. Organomet. Chem.* **286**, 9 (1985).

18. D. Furlani, D. Marton, G. Tagliavini and M. Zordan, *J. Organomet. Chem.* **341**, 345 (1988).
19. G. Plazzogna, S. Bresadola and G. Tagliavini, *Inorg. Chim. Acta* **2**, 333 (1968).
20. G. Plazzogna, V. Peruzzo, S. Bresadola and G. Tagliavini, *Gazz. Chim. Ital.* **102**, 48 (1972).
21. W. P. Neumann, *The Organic Chemistry of Tin*, Wiley, New York, 1970.
22. R. C. Poller, *The Chemistry of Organotin Compounds*, Academic Press, New York, 1970.