APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 553–559 (1995)

A Study of the Disproportionation Equilibrium for Allyldibutyltin(IV) Chloride as an Approach to Understanding the Role of Organotins in the Aquatic Environment

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

The equilibrium:

$$2\,Bu_2(CH_2{=}CHCH_2)SnCl \rightleftharpoons Bu_2Sn(CH_2{=}CHCH_2)_2 + Bu_2SnCl_2$$

takes place when the allyltin chloride is stirred in water. This has been chosen as a model to understand the extent as well as the mechanistic pathways of the disproportionation reactions $2\,R_3SnX \rightleftharpoons R_4Sn + R_2SnX_2$ which are thought to occur in the aquatic environment. The behaviour of $Bu_2(CH_2{=}CHCH_2)SnCl$ has been studied in various media: water, water–acetone, water–ethanol and water–hexane. It has also been ascertained that $Bu_2(CH_2{=}CHCH_2)SnCl$ is a product arising at room temperature from the scrambling of $Bu_2Sn(CH_2{=}CHCH_2)_2$ and Bu_2SnCl_2 either neat, in organic solvents or also in the presence of water. Equilibrium [1] has been interpreted as arising from a bimolecular interaction between the electrophilic aquo-cation $[Bu_2(CH_2{=}CHCH_2)Sn(H_2O)_n]^+$ and the nucleophilic molecule $Bu_2(CH_2{=}CHCH_2)SnCl$. Kinetic studies on R_3SnMe/Me_2SnX_2 ($X = Cl$, NO_3) systems in alcoholic solvents ($R = Me$, Et, n-Pr, i-Pr, n-Bu) support the assumption that, in dissociating media, redistribution processes can be promoted by ionic electrophilic species.

Keywords: disproportionation; triorganotin compounds; allyltins; aquatic environment

INTRODUCTION

Due to their bioactivity,[1] triorganotin compounds, R_3SnX, have had varied applications, particularly as biological agents in areas such as wood preservation and marine antifouling and as agrochemicals.[2] Therefore, these compounds, together with their organic derivatives arising from degradation processes, e.g. cleavage of Sn–C bonds, i.e.

$$R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4$$

have been introduced by man into the environment.[3] As a consequence, their occurrence and fate in the environment have received considerable attention from numerous researchers.[4] The biogenesis, the abiotic aquatic chemistry and mechanisms, and the nature of entry, transport or uptake of these organometals into environmental compartments have been the main broad categories of current research. However, many problems still need to be solved, especially towards understanding the role of triorganotin derivatives in aquatic systems,[5] where they may undergo disproportionation reactions such as

$$2R_3SnX \rightleftharpoons R_4Sn + R_2SnX_2 \qquad [1]$$

Several examples have been reported of disproportionations occurring with neat samples at high temperature,[6, 7] i.e. under conditions which are far removed from those occurring in the environment. Triorganotin halides heated at 200 °C disproportionate to some extent, according to Eqn [1]. Tributyltin chloride decomposes according to Eqn [2] on prolonged heating at 230 °C.[8] Some organotin oxides and hydroxides are particularly susceptible to disproportionation, e.g. trimethyltin hydroxide loses water and disproportionates[9] *in vacuo* at 100 °C according to Eqn [3]. A similar disproportionation occurs when triphenyltin hydroxide is heated *in vacuo* at 135–140 °C,[10, 11] while $Ph_3SnOSnPh_3$ dispro-

CCC 0268-2605/95/070553-07

Received 30 September 1994
Accepted 24 February 1995

portionates at 290 °C to Ph_4Sn and Ph_2SnO.[12]

$$2\,Bu_3SnCl \rightarrow Sn + SnCl_2 + 3\,C_4H_{10} + 3\,C_4H_8 \quad [2]$$

$$2(CH_3)_3SnOH \rightarrow (CH_3)_4Sn + (CH_3)_2SnO + H_2O \quad [3]$$

A few examples of disproportionations occurring under mild conditions have also been reported. Bis(tributyltin)oxide $[(Bu_3Sn)_2O]$, impregnated into timber, is rapidly converted to other tributyltin species (Bu_3SnOX), and these subsequently undergo disproportionation to Bu_4Sn and $Bu_2Sn(OX)_2$.[13] Dibutylvinyltin hydroxide disproportionates at room temperature with formation of dibutyldivinyltin, dibutyltin oxide and water.[14] Tetravinyl-1-RCOO-3-hydroxydistannoxanes ($R = H$, CH_3 and $ClCH_2$) disproportionate in acetone–water under heterogeneous conditions to trivinyltin carboxylates and polymeric vinyltin oxides with yields of about 90%.[15]

We recall our previous studies concerning the use of allyl and allyl-like tin halides, as well as $BuSnCl_3$ and other alkyltin chlorides as reactants in water either in homogeneous or heterogeneous conditions for C—C[16-19] and C—O—C[20] bond-forming reactions respectively. Particularly, the high reactivity of $Bu_2(CH_2{=}CHCH_2)SnCl$ towards carbonyl compounds in water [for example, allyldibutyltin chloride reacts rapidly (in a few minutes) with several carbonyl compounds in the presence of water to give quantitatively homoallylic alcohols and tetrabutyl-1,3-dichlorodistannoxane] has led us to study in detail the behaviour of this compound in the presence of water and other media. Indeed, we have preliminary observations[21] that $Bu_2(CH_2{=}CHCH_2)SnCl$ disproportionates in the presence of water to diallyldibutyltin and dibutyltin dichloride, as described by Eqn [1]. Therefore, we have taken into consideration the system $Bu_2Sn(CH_2{=}CHCH_2)_2$/$Bu_2(CH){=}CHCH_2)SnCl$/Bu_2SnCl_2 as a model which may contribute to a knowledge of the disproportionation of R_3SnX compounds in the presence of dissociating media; that is, under condiitons which can be found in the aquatic environment.

EXPERIMENTAL

Materials

Allyldibutyl- and dibutylcrotyl-tin chlorides were prepared as previously described.[22,23] Diallyldibutyl and dibutyldicrotyl-tin were prepared following a new procedure via coupling of allyl bromides and organotin halides.[24,25] Dibutyltin dichloride, from Aldrich, was recrystallized before use from petroleum ether (40–60 °C). The organic solvents, commercially available, were used as received. All manipulations were carried out at room temperature and under an air atmosphere.

Equipment

The ^{119}Sn and ^{13}C NMR spectra (22.49 MHz for ^{13}C and 33.35 MHz for ^{119}Sn) 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. Thin-layer chromatography (TLC) was performed on 5 cm × 10 cm plates (Polygram®, SIL G/UV_{254}, Macherey–Nagel).

Method of analysis

The progress of the disproportionation reaction for the systems listed in Table 1 was monitored by TLC in both the aqueous and organometallic

Table 1 Analytical data for System 6: the disproportionation reaction of $Bu_2(CH_2{=}CHCH_2)SnCl$ in the presence of water at room temperature

				Recovered compounds		
Run	$Bu_2(CH_2{=}CHCH_2)SnCl$ (g[mmol])	H_2O (ml)	Time of stirring (h)	$Bu_2Sn(CH_2{=}CHCH_2)_2$ (g, mmol [%])	Bu_2SnCl_2 (g, mmol [%])	$Bu_2(CH_2{=}CHCH_2)SnCl$[a] (g, mmol [%])
1	1.2 [3.88]	100	120	0.33, 1.11 [58]	0.33, 1.07 [56]	0.45, 1.45 [37]
2	1.2 [3.88]	30	170	0.40, 1.26 [66]	0.34, 1.12 [59]	0.43, 1.39 [36]
3	2.5 [8.08]	20	180	0.80, 2.54 [62]	0.72, 2.37 [59]	0.90, 2.92 [36]

[a] Amount of unreacted $Bu_2(CH_2{=}CHCH_2)SnCl$.

phases using a 10% solution of chloroform in n-hexane as irrigant. The spots were detected by spraying with a 50% solution of sulphuric acid, and their R_f values were compared with those obtained from pure standards: Bu_2SnCl_2 ($R_f = 0.13$); $Bu_2(CH{=}CHCH_2)SnCl$ ($R_f = 0.38$); $Bu_2Sn(CH_2{=}CHCH_2)_2$ ($R_f = 0.55$). Analyses showed that during the time that $Bu_2(CH_2{=}CHCH_2)SnCl$ was partitioned between the two phases, the majority was in the organometallic phase; the $Bu_2Sn(CH_2{=}CHCH_2)_2$ was almost completely in the organometallic phase; and the Bu_2SnCl_2 was partitioned between the two phases, the greater part being in the water phase.

After an appropriate time, the two phases were separated, washed and extracted with ethyl ether. The ethereal solutions were dried with $MgSO_4$ and, after filtration, the solvent was removed by a Rotavapor. The two residues were analysed by ^{119}Sn NMR spectroscopy. As an example, the ^{119}Sn NMR spectral analysis of the reaction products of the run (1) in Table 1 gave the following result: the residue (0.88 g) recovered from the organometallic phase was a mixture of $Bu_2Sn(CH_2{=}CHCH_2)_2$ (0.33 g, 1.05 mmol), Bu_2SnCl_2 (0.1 g, 0.33 mmol), and unreacted $Bu_2(CH_2{=}CHCH)_2SnCl$ (0.45 g, 1.45 mmol); the solid residue (0.21 g) extracted from the aqueous phase was practically only Bu_2SnCl_2 (0.69 mmol) with traces of $Bu_2(CH_2{=}CHCH_2)SnCl$ and $[Bu_2SnCl]_2O$.

RESULTS

Redistribution reactions

System 1: $Bu_2Sn(CH_2{=}CHCH_2)_2Bu_2SnCl_2$ without solvent

In a round-bottomed two-necked flask (25 ml), equipped with a condenser and dropping funnel, diallyldibutyltin (3.15 g, 10 mmol) was added to an equimolar amount of solid dibutyltin dichloride (3.04 g), under magnetic stirring. After a few minutes the system became homogeneous. The resulting liquid was analysed after 20 min. The IR spectrum, as well as the ^{13}C and ^{119}Sn NMR spectra, show that the product is allyldibutyltin chloride.

IR: 3095 [w, $\nu_{(=CH)}$], 1630 [s, $\nu_{(C=C)}$], 900 [s, $\delta_{(-CH=CH_2)}$], 480 [m, $\nu_{as(Sn-C_{butyl})}$], 450 [m, $\nu_{s(Sn-C_{butyl})}$], 400 [w, $\nu_{(Sn-C_{allyl})}$], 340 [s, $\nu_{(Sn-Cl)}$] cm^{-1}.
^{119}Sn NMR referred to TMT: $\delta + 118.3$ ppm.
^{13}C NMR referred to TMS: δ (butyl moiety) 13.6 (CH_3), 17.5 (CH_2—Sn), 26.8 (CH_2), 27.8 (CH_2) ppm; δ (allylic moiety) 23.8 (CH_2—Sn), 113.3 ($=CH_2$), 134.2 ($=CH$) ppm.[26]

A further run was performed using equimolar amounts of diallyldibutyltin (41 g, 130 mmol) and dibutyltin dichloride (39 g). After 1 h the product consisted of allyldibutyltin chloride. Distillation under vacuum (93–95 °C at 1 mm Hg) furnished 75 g of pure compound (94% yield).

System 2: $Bu_2Sn(C_4H_7)_2/Bu_2SnCl_2$ ($C_4H_7 = E$- or Z-crotyl, and α-methylallyl) without solvent

The procedure was the same as that used above. $Bu_2Sn(C_4H_7)_2$ (20.1 g, 58.6 mmol)—a mixture of six isomers:[27] (*E*,*E*)-, (*E*,*Z*)-, (*Z*,*Z*)-, (*E*,*α*)-, (*Z*,*α*)- and (*α*,*α*)-$Bu_2Sn(C_4H_7)$—was added with stirring to an equimolar amount of solid Bu_2SnCl_2 (18.2 g). After 1 h the product was analysed. The IR spectrum, together with the ^{13}C and ^{119}Sn NMR spectra, revealed the complete formation of $Bu_2(C_4H_7)$ SnCl, in which the C_4H_7 group was presented as a 1:1 mixture of *E* and *Z* isomers. Distillation under vacuum (100–101 °C at 0.05 mm Hg) gave 29.6 g of pure product (80% yield).

IR: 3010 [m, $\nu_{(=CH)}$], 1645 [sh, $\nu_{Z(C=C)}$], 1638 [w, $\nu_{E(C=C)}$], 955 [s, $\delta_{E(CH=CH)}$], 530 [w, $\nu_{(Sn-C_{butyl})}$], 400 [w, $\nu_{(Sn-C_{allyl})}$], 330 (s, $\nu_{(Sn-Cl)}$] cm^{-1}.
δ(^{119}Sn NMR) referred to TMT: +119.7 and +117.8 ppm for *Z*- and *E*-$Bu_2(C_4H_7)SnCl$ respectively.[28]
δ(^{13}C NMR) referred to TMS: *Z*-$Bu_2(C_4H_7)SnCl$ (butyl moiety) 13.6 (CH_3), 17.5 (CH_2—Sn), 26.8 (CH_2), 27.9 (CH_2) ppm; (crotyl moiety) 12.7 (CH_3), 18.2 (CH_2—Sn), 122.2 ($=CH$), 125.3 ($=CH$) ppm. *E*-$Bu_2(C_4H_7)SnCl$ (butyl moiety) 13.6 (CH_3), 17.5 (CH_2—Sn), 26.8 (CH_2), 27.9 (CH_2) ppm; (crotyl moiety) 17.8 (CH_3), 22.2 (CH_2—Sn), 124.2 ($=CH$), 126.2 ($=CH$) ppm.[29]

System 3: $Bu_2Sn(CH_2{=}CHCH_2)_2/Bu_2SnCl_2$ in ethyl ether

An ethereal solution of $Bu_2Sn(CH_2{=}CHCH_2)_2$ (3.15 g, 10 mmol in 10 ml of ether) was added to a solution of Bu_2SnCl_2 (3.04 g, 10 mmol in 10 ml of ether). The solution was stirred for 1 h and then the solvent was taken off. Analysis of the liquid residue confirmed the complete formation of

$Bu_2(CH_2{=}CHCH_2)SnCl$. Additional runs performed in $CHCl_3$, CH_2Cl_2, petroleum ether and other organic solvents led to the same result.

Behaviour of allyldibutyltin chloride in various media

System 4: Allyldibutyltin chloride in EtOH–H_2O (25:10, v/v)

A solution of allyldibutyltin chloride (1.25 g, 4.04 mmol) in EtOH–H_2O (25:10, v/v) was stirred at room temperature. A white precipitate was formed. After five days, the solid was separated by filtration. The dry residue (0.55 g, 50% yield) consisted of tetrabutyl-1,3-dichlorodistannoxane (m.p. 110 °C; lit.[30] 110–112 °C). Unreacted allyldibutyltin chloride (0.58 g, 46%) was recovered from the solution.

System 5: Allyldibutyltin chloride in aqueous acetone

Allyldibutyltin chloride (9.3 g, 30.05 mmol) was rapidly added with stirring to a mixture of acetone (10 ml) and water (10 ml). A white precipitate was formed very quickly. After 1 h, the solid was filtered off. It consisted of tetrabutyl-1,3-dichlorodistannoxane (7.88 g, 14.25 mmol, 95% yield). From the filtrate homoallylic alcohol, $(CH_3)_2C(OH)CH_2CH{=}CH_2$, was recovered (90% yield).

System 6: Allyldibutyltin chloride in the presence of water

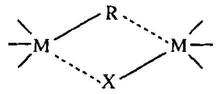
Table 1 shows the data and the results for systems involving $Bu_2(CH_2{=}CHCH_2)SnCl$ in water.

An appropriate amount of allyldibutyltin chloride (3.88–8.08 mmol) was added to distilled water (20–100 ml), and the resulting heterogeneous system was very slowly stirred for many days. An organometallic phase was always present together with an aqueous phase throughout this time, because of the low solubility of the organotin species in water. The progress and the products of the disproportionation process were analysed according to the procedure given under 'Method of analysis'. It is important to mention that at the initial stage, after dissolution of the organotin chloride, the pH of the aqueous phase decreases to a value in the range 4.5–5, typical of many aqueous solutions of R_3SnCl compounds.[31] During the reaction, the aqueous solution becomes progressively more acidic, reaching a final pH around 1–1.5, which is typical of R_2SnX_2 species.

In all cases, as one can see from Table 1, after a period of *120–180* h three main compounds are recovered: $Bu_2Sn(CH_2{=}CHCH_2)_2$ and Bu_2SnCl_2 in a ratio of approximately 1:1, and unreacted $Bu_2(CH_2{=}CHCH_2)SnCl$. Traces of tetrabutyl-1,3-dichlorodistannoxane are also obtained.

DISCUSSION

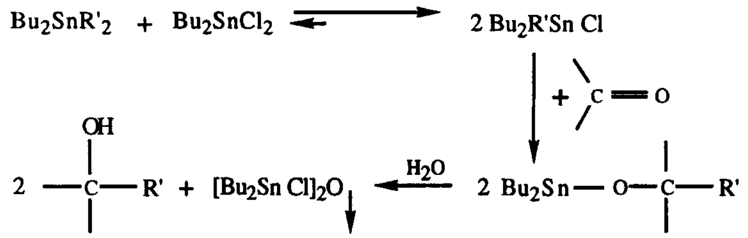
In discussing disproportionations of organometallic species, we can say that they are examples where exchanges of metal–carbon with metal–X bonds occur (X = carbon, halogen, hydrogen, etc.). The most thoroughly investigated exchange reactions in tin chemistry are the redistribution equilibria of tetraorganotins with tetrahalides and organotin halides $R_{4-n}SnX_n$ (R = organic group, X = halogen, $n = 1$–3).[32,33] These occur either under mild conditions or at high temperature, depending upon the nature of the R groups and halogens, and on the electrophilic strength of the scrambling reagent. The reaction rates decrease on passing progressively from SnX_4, $RSnX_3$, R_2SnX_2 to R_3SnX. For these reactions, second-order rate constants are observed with values and thermodynamic data (large negative activation entropies) consistent with a four-centre transition state[32,34] (**A**).



(**A**)

Kinetic results for the redistribution reaction of tetramethyltin with dimethyltin dichloride in several aprotic polar solvents, where the electrophilic agent Me_2SnCl_2 is undissociated, give evidence of a reaction which proceeds via a four-centre transition state[35] as shown. However, in alcoholic media,[36,37] where ionic electrophilic species $[Me_2Sn(solv)^{2+}]$ are present, the observed rates for redistribution reactions of trialkylmethyltins, R_3SnMe (R = Me, Et, n-Pr, i-Pr and n-Bu), with dimethyltin dichloride[36] and dimethyltin nitrate[37] are much greater than those in aprotic polar solvents. Nevertheless, in all these cases the reactions are very slow. It is a matter of fact that exchanges of tin–alkyl with tin–halogen bonds are slow in comparison with those where unsaturated organic groups, such as allyl-like groups, are involved.

From our studies on allylic systems, we wish to



Scheme 1 Allylstannation of carbonyl compounds by means of $Bu_2R'SnCl$ compounds arising from the redistribution reaction of $Bu_2SnR'_2$ with Bu_2SnCl_2 (R' = allyl or allyl-like group).

mention the following redistribution processes: (1) between tetraallyltin and tin tetrachloride at 25 °C to produce triallyltin chloride, and (2) between triallylbutyltin and butyltin trichloride at 0 °C for the preparation of allylbutyltin dichloride.[38] In addition, we recall our studies on the following systems: $Bu_3Sn(C_4H_7)/Bu_2SnCl_2$, $Bu_3Sn(C_4H_7(/BuSnCl_3$ and $Bu_3Sn(C_4H_7)/SnCl_4$, and systems where allenyl or propargyl groups are easily exchanged.[38]

In this study, we have re-examined the redistribution reaction at room temperature between diallyldibutyltin and dibutyltin dichloride either neat (cf. system 1) or in ethyl ether solution (cf. system 3): previous available data had been obtained at 80 °C.[15] All these results allow us to write the general equilibrium represented by Eqn [4],

$$Bu_2SnR'_2 + Bu_2SnCl_2 \underset{\text{disproportionation}}{\overset{\text{redistribution}}{\rightleftharpoons}} 2\,Bu_2R'SnCl \quad [4]$$

where R' = allyl or allyl-like group. The redistribution process proceeds rapidly towards the complete formation of the mixed allyltin chloride, either in neat or in aprotic polar solvents. In all cases, the electrophilic strength of the scrambling agent Bu_2SnCl_2 is the driving force moving the reaction from left to right. Also, in the presence of water, $Bu_2R'SnCl$ is formed by scrambling of $Bu_2SnR'_2$ with Bu_2SnCl_2. This is supported by the allylstannation process according to Scheme 1.

The redistribution equilibrium in Scheme 1 is entirely confirmed by the results of system 5. When $Bu_2(CH_2{=}CHCH_2)SnCl$ is slowly stirred in a heterogeneous acetone–water medium, homoallylic alcohol $[(CH_3)_2C(OH)CH_2CH{=}CH_2]$ and tetrabutyl-1,3-dichlorodistannoxane are formed in a near-quantitative yield. It may be concluded that the redistribution process of Eqn [4] operates at room temperature in any medium.

On the contrary, different results are achieved when allyldibutyltin chloride is stirred in a homogeneous water–ethanol system (cf. system 4). After five days unreacted allyldibutyltin chloride is recovered together with tetrabutyl-1,3-dichlorodistannoxane. Similarly, we have ascertained that tetrabutyl-1,3-dichlorodistannoxane is the main product recovered when allyldibutyltin chloride, dissolved in n-hexane, is stirred in the presence of water. In both cases, the main reaction is due to the protonolysis of the tin–allyl bond: for available kinetic data about protonolysis of the tin–allyl bond see Ref. 39.

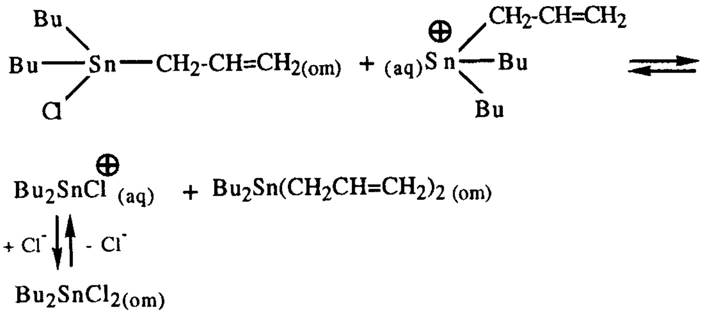
In the presence solely of water, a peculiar reaction occurs for the heterogeneous system $Bu_2(CH_2{=}CHCH_2)SnCl/H_2O$. Data in Table 1 show that a disproportionation reaction takes place in such a system. After seven days, about 60% of the starting allyldibutyltin chloride is converted to diallyldibutyltin and dibutyltin dichloride.

We now discuss some aspects of this disproportionation which, from a general point of view, is a redistribution reaction. Owing to the insolubility of allyldibutyltin chloride in water, a very dilute saturated aqueous solution of it is formed initially upon mixing the two components. The pH of the aqueous phase decreases to about 5, because the dissolved allyldibutyltin chloride attains hydrolytic equilibrium, as any organotin halide does,[31] according to Scheme 2.

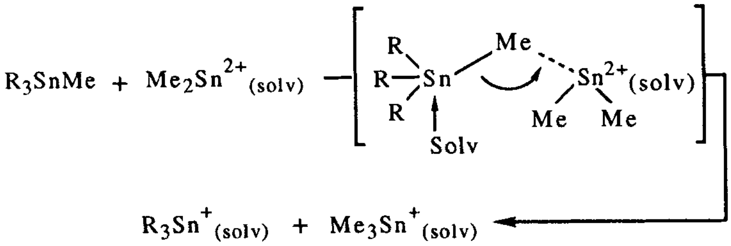
Therefore, we believe that a reaction mainly located at the boundary surface of the two phases, i.e. between the electrophilic aquo-cation $[Bu_2(CH_2{=}CHCH_2)Sn(OH_2)^+_n]$ and the nucleo-

$$Bu_2(CH_2{=}CHCH_2)SnCl_{(aq)} + nH_2O \rightleftharpoons Bu_2(CH_2{=}CHCH_2)Sn(OH_2)^+_{n(aq)} + Cl^-_{(aq)}$$
$$Bu_2(CH_2{=}CHCH_2)Sn(OH_2)^+_{n(aq)} + H_2O \rightleftharpoons Bu_2(CH_2{=}CHCH_2)SnOH_{(aq)} + H_3O^+_{(aq)}$$

Scheme 2 Hydrolytic equilibria of $Bu_2(CH_2{=}CHCH_2)SnCl$ species in the aqueous phase.



Scheme 3 Reaction at boundary of the organometallic (om) and aqueous (aq) phases.



Scheme 4 Mechanistic pathway for redistributions on alcoholic media.

philic molecular species $Bu_2(CH_2{=}CHCH_2)SnCl$, occurs according to Scheme 3. We are uncertain about the actual composition of the components in Scheme 3. The data at our disposal are those concerning the final composition of the whole system (cf. Table 1). This composition represents the overall result of the balance between the equilibria in Scheme 3 and the redistribution process in Eqn [4], which primarily occurs in the organometallic phase.

The occurrence of an ion–molecule interaction is strengthened by previous results of kinetic studies in alcoholic media of the redistributions between the R_3SnMe species (R = Me, Et, n-Pr, i-Pr, and n-Bu) and Me_2SnX_2 ($X = Cl, NO_3$).[36, 37] There, the mechanistic pathway has been interpreted assuming that an electrophilic substitution at the saturated carbon centre is operating by an ionic solvated species via an S_E2 mechanism where the assistance of the solvent is important (Scheme 4).

This mechanistic pathway may be taken into consideration to explain the disproportionation process (see Scheme 3) occurring in the aqueous phase. This may be of some utility in understanding the equilibria occurring in the aquatic environment. However, other redistribution models must be considered because of different conditions in the aquatic environment (e.g. pH, salinity, presence of metal halides which may behave as scrambling reagents such as $HgCl_2$, etc.). Indeed, the redistribution shown in Eq. [5].

$$2R_3SnOH \rightleftharpoons R_4Sn + R_2SnO + H_2O \qquad [5]$$

has also been found for mixed vinyltin derivatives.[14] In addition, many disproportionations of R_3SnX are achieved when X is a chelating group and/or a bridging group, e.g. —O—, —O_2CR or alkoxy ketone.[7] In our opinion, this field requires further investigations.

Acknowledgements We thank Dr James L Wardell (Department of Chemistry, Aberdeen University, UK), and Professor Larry R Sherman (Scranton University, PA, USA) for a critical reading of the manuscript and useful suggestions. We are also indebted to the MURST (Rome) and Consiglio Nazionale delle Ricerche (Rome), Progetto Finalizzato Chimica Fine II, for financial support.

REFERENCES

1. P. J. Smith, *Toxicological Data on Organotin Compounds*, International Tin Research Institute Publn. No. 538, 1978.
2. S. J. Blunden, P. A. Cusak and R. Hill, *The Industrial Uses of Tin Chemicals*, Royal Society of Chemistry, London, 1985.

3. S. J. Blunden and A. H. Chapman, in: *Organometallic Compounds in the Environment*, Craig, P. J. (Ed.), Longman, London, 1986, and references therein.
4. F. E. Brinckman and J. M. Bellama (eds), *Organometals and Organometalloids—Occurrence and Fate in the Environment*, American Chemical Society, ACS Symp. Ser. No. 82, Washington DC, 1978.
5. J. J. Cooney, J. H. Weber and L. R. Sherman, in *Biologial 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 Science, Easton, PA, 1994.
6. J. A. J. Thompson, M. G. Sheffer, R. C. Pierce, Y. K. Chan, J. J. Cooney, W. R. Cullen and J. R. Maguire, *Organotin Compounds in the Aquatic Environment*, NRCC Assoc. Comm. Scientific Criteria Environ. Qual. Publn. No. NRCC 22494, National Research Council of Canada, Ottawa, Ontario, 1985.
7. S. J. Blunden, P. Harston, R. Hill and J. L. Wardell, *Appl. Organomet. Chem.* **4**, 383 (1990).
8. J. G. A. Luijten, and G. J. M. van der Kerk, *Investigation in the Field of Organotin Chemistry*, Tin Research Institute, Greenford, UK, 1958.
9. C. A. Kraus and R. H. Bullard, *J. Am. Chem. Soc.* **51**, 3605 (1929).
10. O. Schmitz-Dumout and H. Meyer, *Z. Anorg. Allg. Chem.* **248**, 289 (1941).
11. R. F. Chambers and P. C. Scherer, *J. Am. Chem. Soc.* **48**, 1054 (1926).
12. J. D. Donaldson, S. M. Grimes, A. F. L. Holding and M. Hornby, *Polyhedron* **4**, 1293 (1985).
13. S. J. Blunden and R. Hill, *Appl. Organomet. Chem.* **2**, 251 (1988).
14. W. J. Considine, J. J. Ventura, B. C. Kushlefsky and A. Ross, *J. Org. Chem.* **1**, 299 (1964).
15. V. Peruzzo, G. Plazzogna and D. Marton, *Inorg. Chim. Acta* **30**, 145 (1978).
16. A. Boaretto, D. Marton, G. Tagliavini and A. Gambaro, *J. Organomet. Chem.* **286**, 9 (1985).
17. A. Boaretto, D. Marton and G. Tagliavini, *J. Organomet. Chem.* **297**, 149 (1985).
18. D. Furlani, D. Marton, G. Tagliavini and M. Zordan, *J. Organomet. Chem.* **345**, 341 (1988).
19. D. Marton, G. Tagliavini and N. Vanzan, *J. Organomet. Chem.* **376**, 269 (1989).
20. G. Tagliavini, *J. Organomet. Chem.* **437**, 15 (1992).
21. G. Tagliavini, A. Boaretto, D. Marton and D. Furlani, *Fifth Int. Conf. on the Orgnometallic and Coordination Chemistry of Ge, Sn and Pb*, Padua, 1986, p. 58.
22. G. Tagliavini, V. Peruzzo, G. Plazzogna and D. Marton, *Inorg. Chim. Acta* **24**, L47 (1977).
23. A. Gambaro, D. Marton, V. Peruzzo and G. Tagliavini, *J. Organomet. Chem.* **226**, 149 (1982).
24. T. Carofiglio, D. Marton and G. Tagliavini, *Organometallics* **11**, 2961 (1992).
25. F. von Gyldenfeldt, D. Marton and G. Tagliavini, *Organometallics* **13**, 906 (1994).
26. A. Gambaro, V. Peruzzo, G. Plazzogna and G. Tagliavini, *J. Organomet. Chem.* **197**, 45 (1980).
27. T. Carofiglio, D. Marton and F. Lenzmann, *Anal. Chim. Acta* **281**, 119 (1993).
28. A. Boaretto, D. Marton and G. Tagliavini, *J. Organomet. Chem.* **321**, 199 (1987).
29. A. Gambaro, D. Marton, V. Peruzzo and G. Tagliavini, *J. Organomet. Chem.* **204**, 191 (1986).
30. R. Okawara and M. Wada, *J. Organomet. Chem.* **1**, 81 (1963).
31. R. S. Tobias, *Organomet. Chem. Rev.* **1**, 93 (1966) and references therein.
32. K. Moedritzer, *Organomet. Chem. Rev.* **1**, 179 (1966) and references therein.
33. K. Moedritzer, *Adv. Organomet. Chem.* **6**, 171 (1968) and references therein.
34. R. E. Dessy, Y. K. Lee and J. Y. Kim, *J. Am. Chem. Soc.* **83**, 1163 (1961).
35. Y. Yamashita, K. Saito, A. Yoshino and K. Takahashi, *Bull. Chem. Soc. Jpn.* **56**, 2555 (1983).
36. G. Plazzogna, S. Bresadola and G. Tagliavini, *Inorg. Chim Acta* **2**, 333 (1968).
37. G. Plazzogna, V. Peruzzo, S. Bresadola and G. Tagliavini, *Gazz. Chim. Ital.* **102**, 48 (1972).
38. G. Tagliavini, *Rev. Si Ge Sn Pb Compd.* **8**, 237 (1985) and references therein.
39. H. G. Kuivila and J. A. Verdone, *Tetrahedron Lett.* 119 (1964).