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Reaction of dibutyltin oxide with amides in presence of traces of water: multinuclear NMR study and mechanism

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Abstract

The product of the reaction of primary and secondary amides with dibutyltin oxide is shown to be a dimeric 1,3-diacyloxytetrabutyldistannoxane. The reaction was studied in bulk with model amides at 180°C, avoiding perfect anhydrous conditions, in view to be transposable to transamidification with reactive extrusion process. The formation of an intermediate compound of the type 1-acyloxy-3-alkylaminotetrabutyldistannoxane is pointed out. With an excess of amide, the presence of water leads to the dimeric 1,3-diacyloxytetrabutyldistannoxane. Without an excess of amide, the hydrolysis of this intermediate leads to a more complex tetrastannoxane structure associated in a more or less perfect ladder-like structure including partially hydrolyzed and condensed forms of the distannoxane. The dimeric 1-acyloxy-3-alkoxytetrabutyldistannoxanes resulting from the reaction of esters with dibutyltin oxide are shown to give a similar stannoxane structure after hydrolysis. All the products were characterized in solution by ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectroscopy. On the basis of the spectroscopic analysis, a mechanism of the reaction is proposed and discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tin; Distannoxane; Amide and hydrolysis

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1. Introduction

Dibutyltin oxide and 1-alkoxy-3-acyloxytetrabutyldistannoxanes were shown to be at 200°C excellent catalysts for transesterification reactions and excellent crosslinking agents of ethylene-vinyl acetate copolymers (EVA) and ethylene-methyl acrylate copolymers (EMA) [1,2]. The efficiency of these catalysts allows a direct application to the crosslinking of the EVA–EMA dispersed in a polymer matrix by the reactive extrusion process [3–5]. Furthermore a rheological characterization of this crosslinking reaction was made [6,7].

Pillon and Utracki [8] have shown that block polyester–polyamide copolymers can be obtained by transamidification reactions of polyesters with polyamides using paratoluene sulfonic acid as catalyst whereas this latter was known to be a good catalyst in the ester–ester exchange reaction [9]. Inoshita et al. reported that the heating of a mixture of poly(ethylene terephthalate) and poly(amide-6,6) in the presence of zinc acetate and antimony trioxide, at 230–280°C under 0.01 Torr for 5 h results in the formation of a block copolymer by ester–amide interchange reaction [10]. A few other examples of catalyzed ester–amide interchange in a polyester/polyamide system are also reported in the literature. Korshak et al. used PbO [11] or PbO_2 [12], whereas Frunze et al. applied *iso*Bu_3Al as catalyst [13]

Some recent works in our laboratory have proved that interchange reactions between amides and polyacrylic esters can be catalyzed by dibutyltin oxide and 1-alkoxy-3-acyloxy-tetrabutyldistannoxanes at 180°C [14]. In order to elucidate the exchange reaction mecha-

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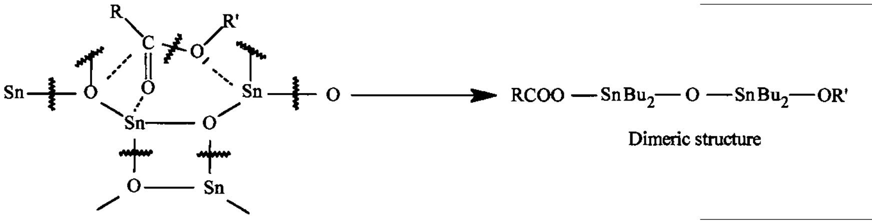
nism, this paper deals first with the reaction of dibutyltin oxide with amides in the conditions of reactive extrusion.

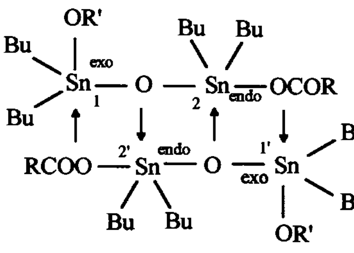
We have previously shown that dibultyltin oxide reacts with esters leading to the dimeric form of 1-alkoxy-3-acyloxytetrabutyldistannoxane (Eq. (1)).



(1)

This dimeric distannoxane has been fully characterized by ^{1}H-, ^{13}C- and ^{119}Sn-NMR [2,15]. The four tin atoms are pentacoordinated in two different ways: *endo* or *exo* (Scheme 1). Indeed two peaks of equal intensities are observed in ^{119}Sn-NMR in the resonance region of pentacoordinated tin atoms. By 2D/Sn–Sn COSY NMR spectroscopy, each tin site (*endo* or *exo*) is shown to be coupled to two tin atoms (site 1 is coupled with site 2 and site 2′) with two different coupling constants [15,16]. In ^{13}C-NMR, two butyl groups are evidenced by the presence of 2 peaks for each CH$_2$ of the butyl groups connected with the two different types of tin atoms. More generally, difunctional Bu$_4$Sn$_2$XYO (tetraorganodistannoxanes) and monofunctional Bu$_4$Sn$_2$X$_2$O are known to have a dimeric structure both in solution and in the solid state, with two types of non-equivalent pentacoordinated tin atoms [17] whereas ^{119}Sn Mössbauer spectroscopy showed only a single quadrupole split resonance. Many reports published by different authors using various techniques describe the structure of distannoxanes in solution. In particular, Otera et al. related the dimeric structure of distannoxanes, proposed by Okawara, to the general aspect of ^{119}Sn solution NMR spectra [18–20]. In certain conditions, monomer exchanges between dimer entities or ligand exchanges on tin atoms are observed [2,21,22]. Furthermore, X-ray techniques [23] and sometimes both X-ray and NMR techniques [24,25] were used in order to study the distannoxanes inclined to yield monocrystals.

Some tin compounds such as the methoxytriethyltin [Et$_3$SnOCH$_3$] and the dimethoxydimethyltin [Me$_2$Sn(OCH$_3$)$_2$)] are known to react easily with amides [26–28]. The reaction requires primary or secondary amides, cleaves the Sn–OR link and leads to a Sn–NRCO bond. In the case of the dimethoxydibutyltin, polyamides are claimed to be crosslinked. As for the bis-tributyltin oxide [(Bu$_3$Sn)$_2$O] which has a Sn–O–Sn linking, it is indicated to cleave the Sn–O link and give Bu$_3$Sn–NR′–CO–R and water [29] which seems to be contradictory. Indeed, it is worth pointing out that Sn–N bonds are very sensitive to hydrolysis [30] and in both cases, the Sn–NR′CO bond should be retained in spite of the character of Sn–N bond to be easily hydrolysed. At last, dibutyltin oxide which comprises a [Sn–O]$_n$ backbone has been shown to react with imides (–CO–NH–CO–) via a CO–N bond cleavage followed with an insertion of one O–Sn in the amide structure [31]. This reaction should lead to the following structure –CO–O–Sn(Bu)$_2$–NH–CO–. These affirmations will be discussed in the frame of the present work. Since then, to our knowledge, nothing concerning the action of organotin oxides on amides has been published. This work proposes a reaction mechanism as a conclusion of the results obtained by means of analysis by ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectroscopy.

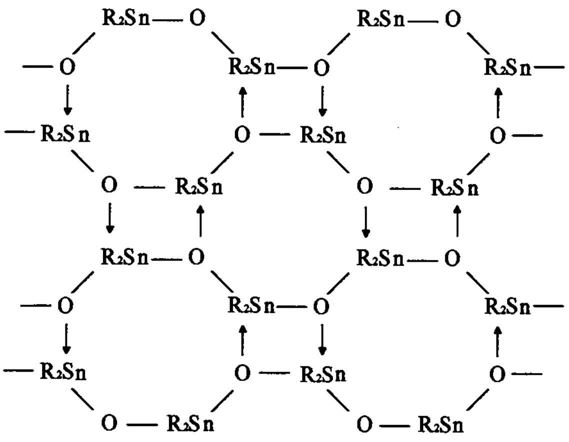


Scheme 1.

2. Experimental details

2.1. Reagents

Dibutyltin oxide, propionamide, acetanilide, *N*,*N*-di-



Scheme 2.

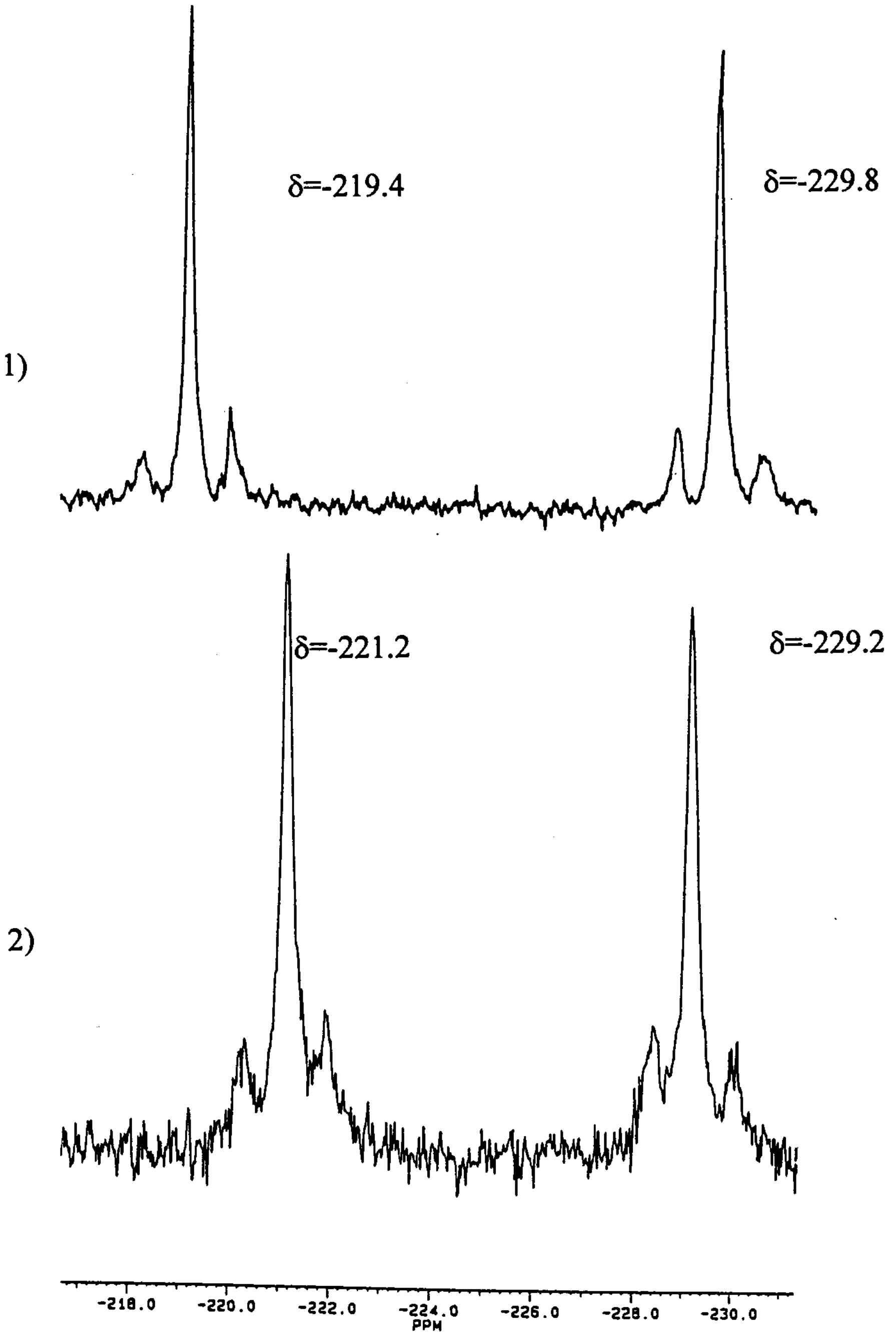


Fig. 1. NMR spectra (made at 25°C) of (1) the diacetoxytetrabutyldistannoxane and (2) the reaction product of dibutyltin oxide with propionamide.

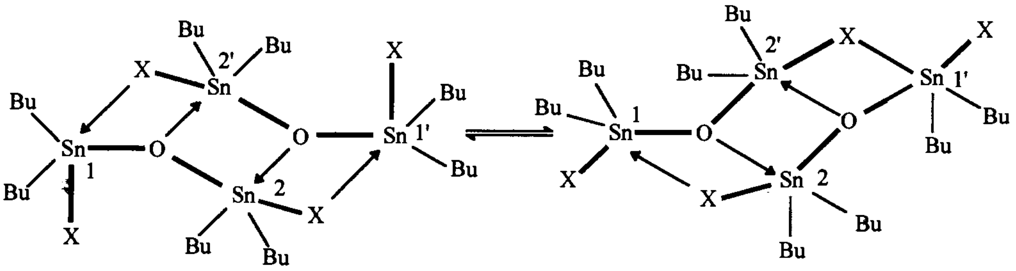
ethyldodecanamide and *iso*butylpropanoate were commercial products (Aldrich). These amides were selected for their high boiling points (213, 305 and 167°C, 2 mm).

2.2. Preparation of diacetoxytetrabutyldistannoxane (model compound)

Two methods are available [32], reaction of acetic acid with dibutyltin oxide or partial hydrolysis of dibutyltin diacetate. The latter was used here. A white crystalline distannoxane was obtained. $C_{20}H_{42}O_5Sn_2$ requires C,40.04; H, 7.01; Sn, 39.60; found: C, 40.05, H, 7.09; Sn, 40.42%. All characteristic NMR chemical shifts have yet been given [2].

2.3. Reaction of dibutyltin oxide with isobutylpropanoate (typical procedure)

Equimolar amounts of dibutyltin oxide and *iso*butyl-



Scheme 3.

propanoate were mixed in a reactor equipped with magnetic stirrer and a reflux condenser. The mixture was heated at 200°C. After cooling, an oily colorless and translucent liquid which is not crystallizable was obtained. The NMR characterization (^{1}H, ^{13}C, ^{119}Sn) of the spectral features of the 1-propyloxy-3-*iso*butoxytetrabutyldistannoxane formed was made.

2.4. Reaction of dibutyltin oxide with the model amide

The amide and 5% in mol of dibutyltin oxide were mixed in a reactor equipped with a magnetic stirrer and a reflux condenser. The mixture was heated at 160 or 180°C. After a few minutes the mixture of dibutyltin oxide in the molten amide became clear. After cooling, because of a large excess of solid amide, the mixture crystallized. In total 10% in mol of dibutyltin oxide can be used, if fractional additions are carried out, but even thus, no more than 10% in mol of dibutyltin oxide in comparison with the amide amount reacts. Because of the large excess of amide, an extraction with tetrachloroethylene is required to eliminate the excess of amide which is not soluble at ambient temperature.

2.5. Hydrolysis of the 1-propanoyloxy-3-isobutoxytetrabutyldistannoxane

To the oily colorless and translucent liquid not crystallizable obtained in the preparation of the distannoxane, a large excess of water was added at ambient temperature. A white precipitate appeared. After filtration, tetrachloroethylene was added to the precipitate which became soluble at 80°C. The NMR characterization (^{1}H, ^{13}C, ^{119}Sn) of the compound formed was made.

2.6. Hydrolysis of the intermediate compound of the reaction between dibutyltin oxide and propionamide

The product of the reaction between dibutyltin oxide and propionamide, stopped before ammoniac was evolved, was purified with an extraction with tetrachloroethylene to eliminate the excess of amide. A large excess of water was then added leading to the formation of a white precipitate which was then treated as it was previously shown below Section 2.5.

2.7. NMR spectroscopy

High resolution liquid NMR spectroscopy was carried out with a Bruker AC250 instrument working at 250 MHz for ^{1}H and 62.9 MHz for ^{13}C, and with a Bruker AC200 instrument working at 74.6 MHz for ^{119}Sn. Tetrachloroethylene/deuterated benzene (TCE/C_6D_6) mixtures (2:1 by volume) were used as solvent. Chemical shift values are in ppm with reference to internal TMS for ^{1}H and ^{13}C, and external tetramethyltin for ^{119}Sn.

3. Results and discussion

In view to conclude concerning the role of the $-N\underline{H}-$ in the reaction of amides with dibutyltin oxide, both tertiary (*N*,*N*-diethyldodecanamide) and primary or secondary amides (propionamide and acetanilide) have been used.

3.1. Preliminary observations

When the reactions were performed with propionamide and acetanilide, the opacity of the suspension of dibutyltin oxide in the molten amide disappeared completely after 10 min at 180°C. With *N*,*N*-diethyldodecanamide, the dibutyl tin oxide remained in suspension in the amide. It is well known that dibutyltin oxide [33] is amorphous, insoluble in most organic solvents even at high temperature and has a polymeric structure with about 20 tin atoms in a chain (Scheme 2). This first observation, without being a real proof of reaction, shows in the two former cases that the crosslinks in the dibutyltin oxide structure are disrupted and a reaction may have happened (that will be confi-

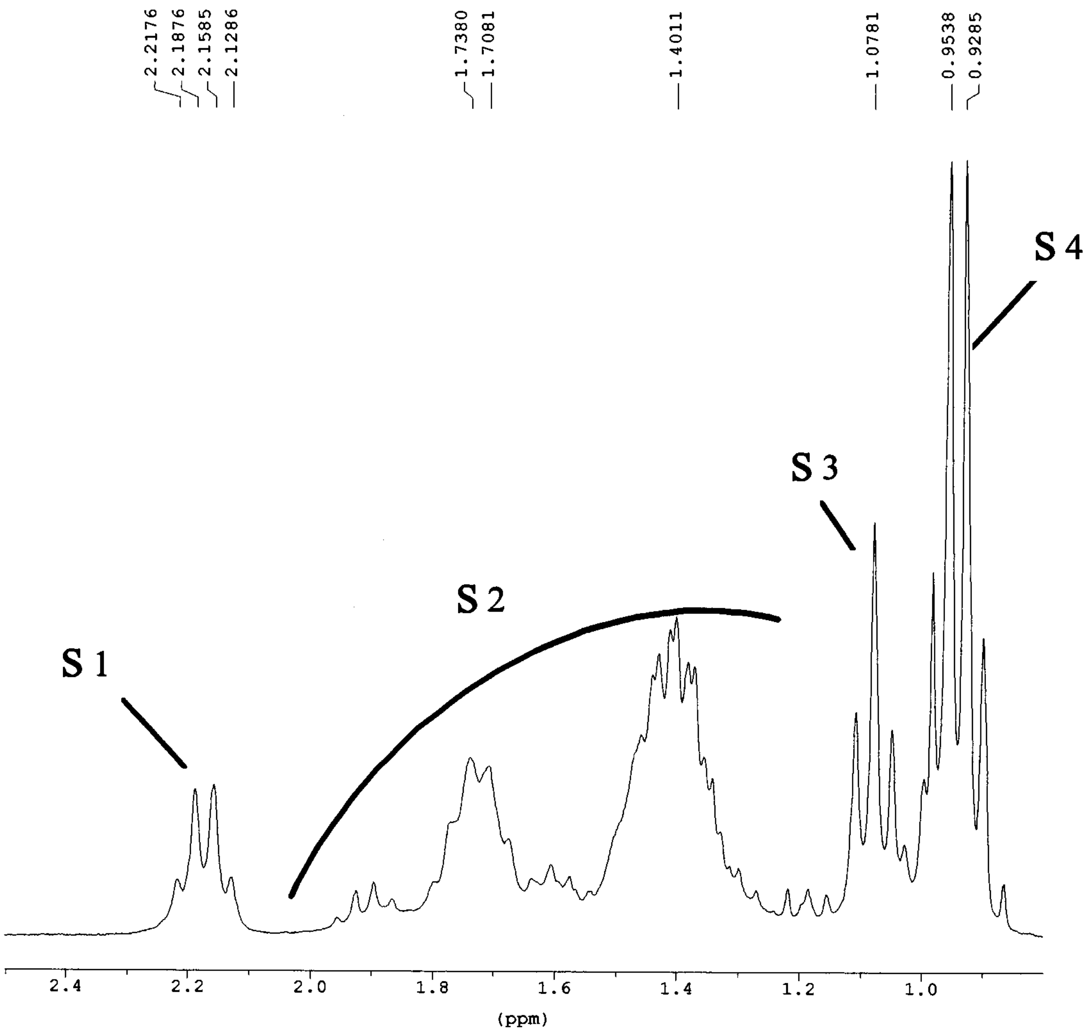


Fig. 2. ^{1}H-NMR spectrum (made at 25°C) of the reaction product of dibutyltin oxide with propionamide.

rmed by NMR spectroscopy). In addition, it is worth noticing that a great ammoniac release is observed when propionamide is used as reagent.

In the light of this observation it seems *tertiary* amides do not react with dibutyltin oxide and therefore the reaction requires the presence of a hydrogen atom only present in primary and secondary amides, as it is generally claimed with other tin compounds.

3.2. Characterization of the final reaction product

3.2.1. ^{119}Sn-NMR analysis

The ^{119}Sn-NMR spectrum of the product resulting from the reaction of propionamide with dibutyltin oxide at 170°C during 4 h presents two single resonances at δ -221.2 and -229.2 (Fig. 12). These chemical shift values are typical of pentacoordinated tin atoms. A single doublet of satellite peaks ^{119}Sn–^{119}Sn ($J = 124 \pm 3$ Hz) is observed at the basis of each tin resonance. Such a spectrum, with two equally populated tin sites and a single coupling between them could suggest a monofunctional dimeric tetraorganodistannoxane of formula $Bu_4Sn_2X_2O$. More precisely, because the two initial reagents are propionamide and dibutyltin oxide and ammoniac is evolved, this spectrum suggests it could be the dimeric dipropanoyltetrabutyldistannoxane. Although the ^{119}Sn-NMR spectrum is not sufficient to assert a result, it is worth noticing that in the same way, the^{119}Sn-NMR spectrum of a diacetoxytetrabutyldistannoxane resulting from the partial hydrolysis of the dibutyltin diacetate, shows two resonances at δ -219.4 and -229.8 (Fig. 11) with a single doublet of satellite peaks ($J = 122 \pm 3$ Hz).

The unexpected single coupling between tin sites observed by different authors on a monofunctional tetraorganodistannoxane [15,20,34], compared to the difunctional structures [Bu_2Sn_2XYO] where each tin site shows two doublets with two different coupling constant values [J_{1-2} and $J_{1-2'}$], has been recently proved to be the consequence of a rapid intradimeric rearrange-

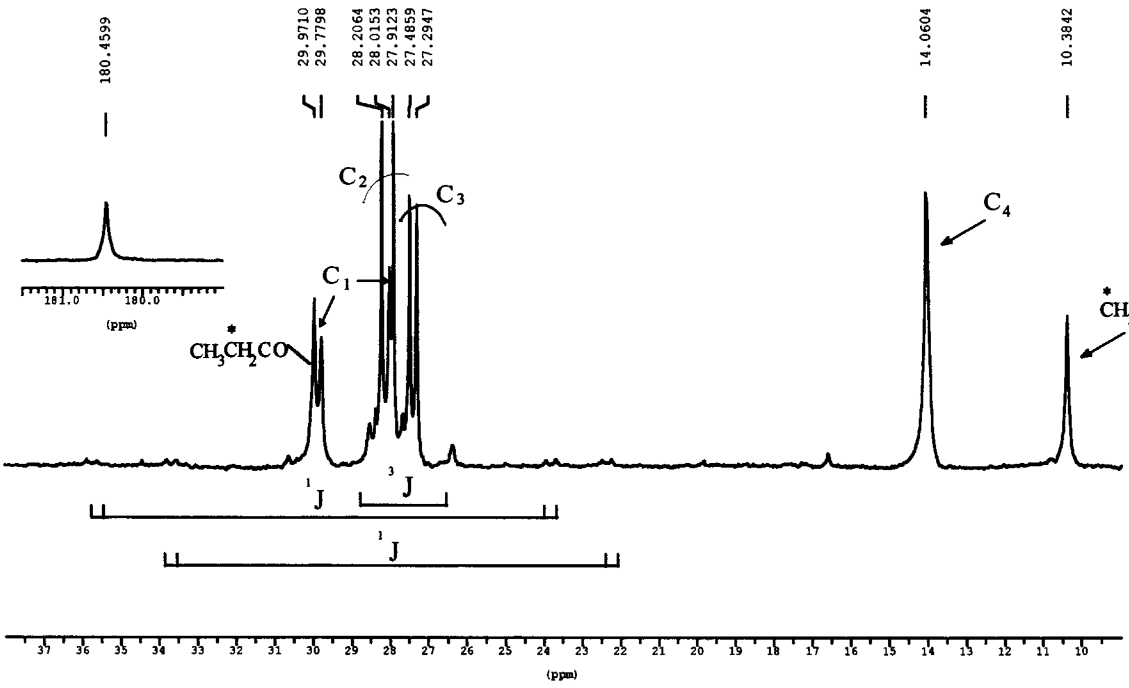
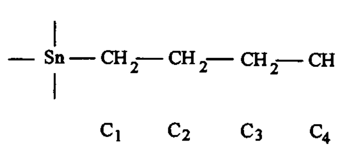


Fig. 3. ^{13}C-NMR spectra (made at 25°C) of the product of the reaction of ditbutyltin oxide with propionamide.

ment (Scheme 3, [16]). The two expected satellite doublets merge into a single one since this rearrangement exchanges the covalent bond [Sn_1–O–Sn_2] in the coordination bond [Sn_1–O→Sn_2] and reversely the coordination bond [Sn_1–O→$Sn_{2'}$] in the covalent bond [Sn_1–O→$Sn_{2'}$].

3.2.2. ^{1}H-NMR analysis

^{1}H-NMR gives complementary information, particularly concerning the stoichiometry of the compound obtained. The spectrum of the product resulting from the reaction of dibutyltin oxide with propionamide consists of four main resonance regions (Fig. 2). The quartet S_1 centered at δ 2.170 and the triplet S_3 at 1.075 correspond, respectively to the CH_2 and CH_3 protons of the propanoyl group. S_2 and S_4 should correspond to the protons of the butyl groups from a dibutyltin compound. Actually, the pseudo quartet S_4 is composed of two overlapping triplets, respectively centered at δ 0.940 and 0.920, thus indicating an equal ratio of two types of butyl tin groups. The S_2 region consists of two large multiplet resonances at about δ 1.730 and 1.400 assigned, respectively to the CH_2 protons in α position and in β plus γ position to the tin atom.



$$-\mathrm{Sn}-CH_2-CH_2-CH_2-CH_3$$

Scheme 4.

The quantitative analysis gives a relative proportion of 1.9/12.8/2.9/6.2 for the areas $S_1/S_2/S_3/S_4$. An estimate at 2/12/3/6 corresponds to the presence of one propanoyl group for two butyl groups that is to say for one tin atom if the dibutyltin structure is maintained.

Moreover the two different butyl groups indicated by the two methylic protons ($\delta = 0.940$ and 0.920) were previously observed in all monofunctional or difunctional tetrabutyldistannoxane ($Bu_4Sn_2X_2O$ and Bu_4Sn_2XYO) investigated in our laboratory. This feature is related to the dimeric structure of all these

Table 1
^{13}C Chemical shifts (δ in ppm) related to the propanoyl group in the propionamide (P) and in its reaction product (P′) with dibutyltin oxide

Sample	CH_3	CH_2	CO
P	9.70	29.05	176.00
P′	10.40	30.00	180.45

Table 2
^{13}C Chemical shifts (δ in ppm) of the two distinct butyl groups and coupling constants ^1J(Sn–C*) and ^3J(Sn–C–C–C*) (in Hz) in the dibutyltin compound obtained by reaction of dibutyltin oxide with propionamide

Carbone	C_1 (^1J(Sn–C*))[a]	C_2	C_3 (^3J(Sn–C–C–C*))	C_4
Shifts	28.00 (727–695)	27.50	27.30 (135)	14.05
	29.80 (767–734)	28.00	27.90	

[a] $^1J(^{119}$Sn–C*)–$^1J(^{117}$Sn–C*), values in parentheses.

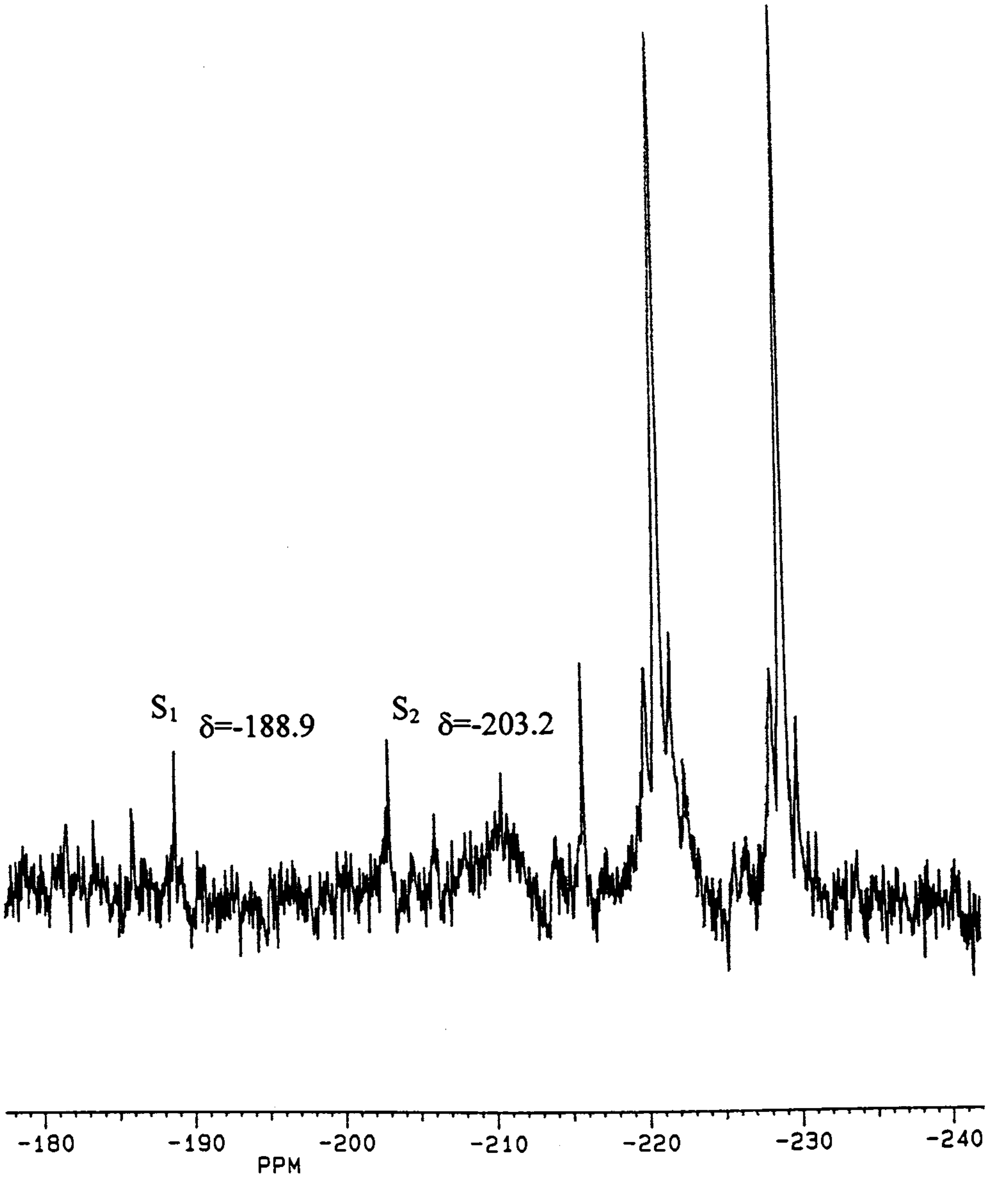


Fig. 4. ^{119}Sn-NMR spectra (made at 25°C) of the product resulting from the reaction of propionamide with dibutyltin oxide stopped before ammoniac being evolved.

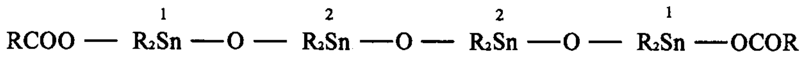
compounds and it is associated to other typical features observable in ^{13}C-NMR [2,15,20].

3.2.3. ^{13}C-NMR analysis

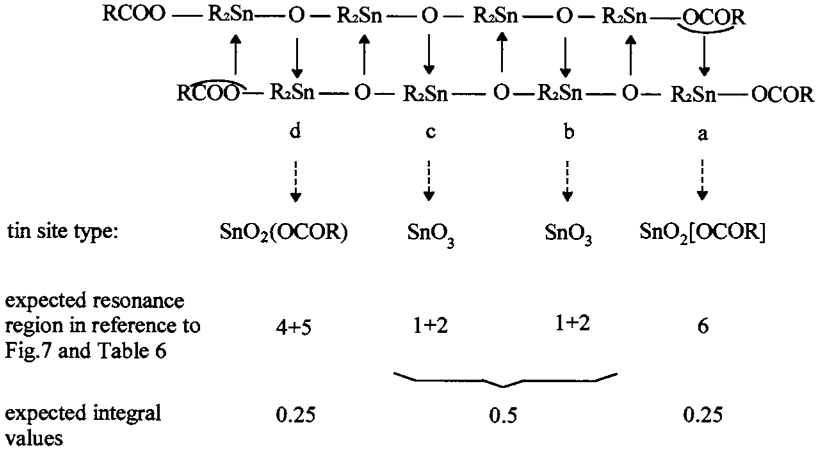
As shown on Fig. 3, the ^{13}C-NMR spectrum of the reaction product of propionamide with dibutyltin oxide shows the different resonances easily assigned to C_1–C_4 carbons of the butyltin groups (Scheme 4, Table 2). Two different butyl groups are evidenced by a couple of resonances for each methylenic carbon C_1–C_2–C_3 (Table 2). Moreover the coupling Sn–C* and Sn–C–C–C* can be observed and measured. The values of ^1J(Sn–C*) and ^3J(Sn–C–C–C*) given in Table 2 are typical of a pentacoordinated dibutyltin. All carbons of the propanoyl group compared to those of pure propionamide (Table 1) are deshielded, particularly the carbon of the carbonyl group ($\Delta\delta = 6.70$). This deshielding is consistent with the change $RCONH_2 \rightarrow RCOOSn$. Such a deshielding has been previously observed with the change $RCOOR' \rightarrow RCOOSn$ [15].

3.2.4. Interpretation and discussion

The elemental analysis provides C, 42.18; H, 7.39; O, 13.11; Sn, 36.38 and N, 0.94%. The residual N content corresponds to a 4.9% rate of amide remaining in the product of the reaction of propionamide with dibutyltin oxide after the extraction. The percentage calculated for the main product (95.1%) indicates C, 41.80; O, 12.82; H, 7.22 and Sn, 37.9%. These values are in agreement with the dipropanoyloxytetrabutyldistannoxane formu-



Scheme 5.



Scheme 6.

lae which requires C, 42.00; O, 12.70; H, 7.40 and Sn, 37.9%. The results of the ^{119}Sn-, ^{1}H- and ^{13}C-NMR spectroscopy and the elemental analysis allows to conclude that the reaction of dibutyltin oxide with a large excess of proprionamide at 160°C leads to the formation of the dipropanoyloxytetrabutyldistannoxane with ammoniac release. We notice that such a result implies the presence of water and the reaction should be globally given by Eq. (2).

$$2\ CH_3CH_2CO\text{–}NH_2 + 2\ Bu_2SnO + H_2O \rightarrow (CH_3CH_2CO\text{–}O\text{–}SnBu_2)_2O + 2\ NH_3 \quad (2)$$

In addition only primary and secondary amides react with dibutyltin oxide, thus the presence of a –NH– group is a prerequisite.

3.3. Tentative identification of the intermediate species

At this stage, without making any hypothesis on the mechanistic path involving –NH– moiety, it is clear from the final product that the CO–NH link is cleaved. Whether one or two O–Sn moieties are inserted is an outstanding question. With one [O–Sn] insertion RCOO–SnBu$_2$–NH$_2$ is expected whereas with [O–Sn]$_2$ insertion RCOO–SnBu$_2$–O–SnBu$_2$–NH$_2$ should be formed. The first should have a tetracoordinated dibutyltin site in the region (+ 200, − 60), whereas in the last case two equally populated tin sites in the pentacoordinated tin region, corresponding to a dimeric distannoxane structure, are expected.

3.3.1. Distannoxane structure of the intermediate (I)

When the reaction is stopped before the complete release of ammoniac, two weak singlets S_1 and S_2 ($\delta = -188.9$ and -203.2) are observed in the ^{119}Sn-NMR spectrum (Fig. 4). No peaks are detected in the tetracoordinated tin resonance region (+ 200, − 60). At δ − 221.2 and − 229.2 the two resonances with their coupling correspond to the dipropanoyloxy-tetrabutyldistannoxane. Therefore the formation of the dipropanoyloxytetrabutyldistannoxane by hydrolysis and condensation of a RCOO–SnBu$_2$–NH$_2$ intermediate is precluded. On the contrary, a dimeric acyloxyaminotetrabutyldistannoxane is very likely on the basis of the ^{119}Sn-NMR spectrum (Eq. (3)).

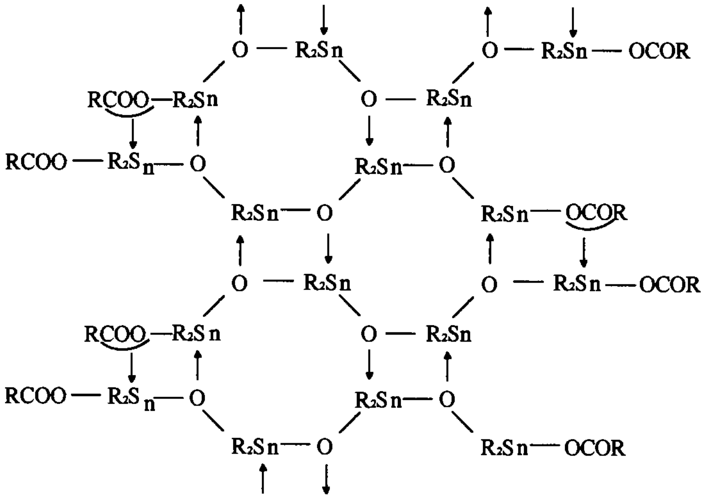
$$CH_3CH_2CO - NH_2 + 2\ Bu_2SnO \rightarrow \underset{(I)}{CH_3CH_2CO - O - SnBu_2 - O - SnBu_2 - NH_2} \quad (3)$$

Its low amount in the mixture and its disappearance after a long time reveal that it would just be an intermediate compound which should react with the excess of amide to give the dipropanoyloxytetrabutyldistannoxane and ammoniac (Eqs. (4) and (5)).

$$\underset{(I)}{C_2H_5COO - SnBu_2 - O - SnBu_2 - NH_2} + H_2O \rightarrow C_2H_5COO - SnBu_2OSnBu_2 - OH + NH_3 \quad (4)$$

$$C_2H_5COO\text{–}SnBu_2\text{–}O\text{–}SnBu_2\text{–}OH + CH_3CH_2CO\text{–}NH_2 \rightarrow (C_2H_5COO\text{–}SnBu_2)_2O + NH_3 \quad (5)$$

All attempts to separate this intermediate from the mixture failed. Only a hydrolyzed form was obtained in spite of the precautions we took. The hydrolysis done with ammoniac release, occurred with a simple contact with air (indeed Sn–N bonds are well known to be very sensitive to hydrolysis [30]).



Scheme 7.

3.3.2. Hydrolysis of the intermediate (I)

If a difunctional distannoxane, namely 1-propanoyloxy-3-aminotetrabutyldistannoxane [RCOO–SnBu$_2$–O–SnBu$_2$–NH$_2$] is the intermediate (I) formed in the reaction of dibutyltin oxide and propionamide, owing to the high sensitivity of the Sn–NH$_2$ bond to hydrolysis, then it is of interest to compare this hydrolyzed intermediate (compound I′) to the hydrolysis product of an acyloxyalcoxydistannoxane, since we have previously observed that the Sn–OR free ligand is highly sensitive to hydrolysis. To our knowledge, the hydrolysis of acyloxyalcoxydistannoxanes has not been previously investigated. The 1-propanoyloxy-3-*iso*butyloxytetrabutyldistannoxane (II) has been hydrolyzed (compound II′) and compared to the compound I′ through their ^{119}Sn-, ^{1}H- and ^{13}C-NMR spectra. In both cases three types of products can be envisaged with the same global stoichiometry [CH$_3$CH$_2$COOSn(Bu)$_2$OSn(Bu)$_2$]$_2$O (Eq. (6)): (1) a monomeric 1-7-dipropanoyloxyoctabutyltetrastannoxane (Scheme 5) (2) a perfect ladder like dimeric structure with two tetrastannoxanes (Scheme 6) (3) an associated form with more than two tetrastannoxanes and a less perfectly ladder-like structure than the previous one (Scheme 7), somewhat similar to the pentacoordinated network which is usually proposed [15] for the dibutyltin oxide structure with a central square part $[\mathrm{Bu_2\overline{Sn{-}O{-}SnBu2{-}O}{-}}]$.

$$2\ \mathrm{C_2H_5COO{-}SnBu_2OSnBu_2{-}(NH_2\ or\ OR')} + \mathrm{H_2O} \rightarrow \mathrm{(C_2H_5COO{-}SnBu_2OSnBu_2)_2O} + 2\ \mathrm{(NH_3\ or\ R'OH)} \qquad (6)$$
$$\mathrm{(I)}\quad \mathrm{(II)}\qquad\qquad \mathrm{(I')\ and\ (II')}$$

^{119}Sn-NMR is a powerful tool in a view to conclude between these three possibilities, since they will give, respectively (1) two tetracoordinated tin sites equally populated. (2) Four pentacoordinated tin sites equally populated (a, b, c and d), two of them—the central ones—(b and c) being very close to one other. (3) More than four tin sites, all of them probably pentacoordinated.

The comparison between (I′) and (II′) as previously defined is achieved by ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectroscopy. The obtained spectra show that I′ and II′ are nearly identical (Figs. 5–7 and Tables 3–5). These three analyses give complementary information concerning the structure of these compounds.

The ^{1}H spectra indicate nearly four butyl groups for one propanoyl (3.5 and 4.5 for I′ and II′, respectively). It has been proved herein that, in the presence of an excess of amide and water, the intermediate I gives [CH$_3$CH$_2$COOSnBu$_2$]$_2$O with two butyl groups for one propanoyl. On the contrary, the hydrolysis of the intermediate I after cautious extraction of the excess of amide, leads to I′ which contains four butyl groups for one propanoyl group. Moreover the two triplets corresponding to an equal molar ratio of two types of butyl groups in a distannoxane structure are no longer observed (Fig. 5). So the dipropanoyltetrabutyldistannoxane of formula [CH$_3$CH$_2$COOSnBu$_2$]O is excluded in that case.

As for ^{13}C spectra, the chemical shifts of the CO, respectively δ 180.05 for (I′) and 180.00 for (II’) compared to the CO in the dipropanoyloxytetrabutyldistannoxane (180.45), show the structure CH$_3$–CH$_2$–CO–O–Sn still remains. A set of unresolved peaks is observed for the CH$_2$ butyl carbons (Fig. 6) which supports the ^{1}H-NMR results indicating a much more complicated situation than in ladder-like 1-3-distannoxane structure where two different types of butyl groups are always found.

The nearly identical ^{119}Sn spectra (Fig. 7-1, 2) consist of more than 97.5% pentacoordinated sites in the

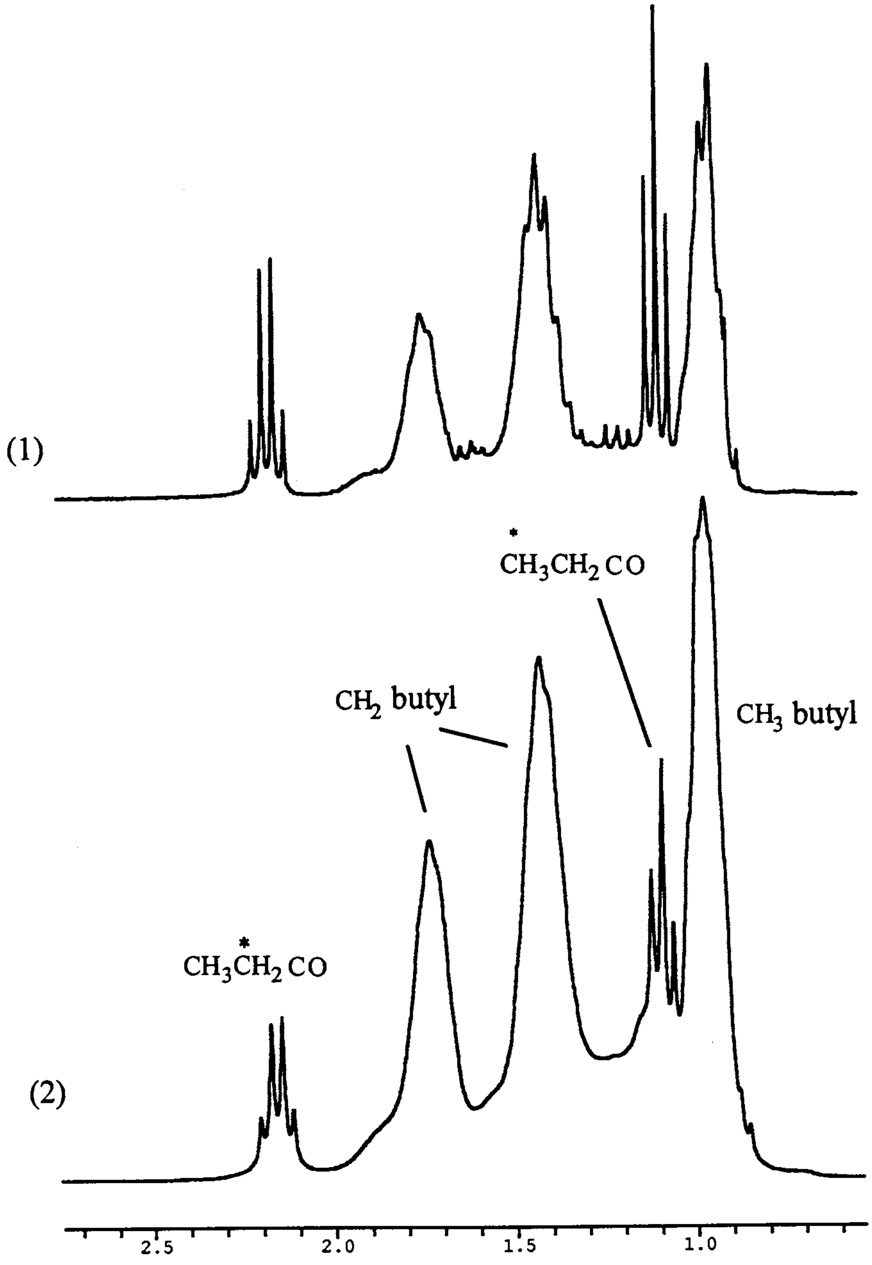


Fig. 5. ^{1}H-NMR spectra (made at 80°C) of (1) the hydrolyzed intermediate (I′) of the reaction of dibutyltin oxide with propionamide and (2) the hydrolyzed 1-propanoyl-3-*iso*butyloxytetrabutyldistannoxane (II′).

(− 150, − 240) resonance region distributed into six broad peaks. Then, both a monomeric 1,7-dipropanoyloxytetrastannoxane (Scheme 5) and a perfect ladder-like dimeric structure with two tetrastannoxanes (Scheme 6) are precluded. The integral values are nearly 2/1/2.5/0.5 for peaks (1 + 2), 3, (4 + 5) and 6, respectively (Fig. 7-1), the region (4 + 5) being more intense for the hydrolyzed acyloxy alcoxydistannoxane (Fig. 7-2). The lower field region (− 157, − 177) (peaks 1 and 2) corresponds to the region already observed when nascent dibutyltin oxide is formed by in situ hydrolysis of dimeric 1-3-dimethoxytetrabutyldistannoxane. In that case the expected sites are $Bu_2Sn[O]_3$, $Bu_2Sn[O]_2OH$ and $Bu_2Sn[O]_2OR$ corresponding to the unachieved hydrolysis and/or condensation. *Endo* tin sites of the type $Bu_2Sn[O]_2OR$ have already been observed at − 174.1 in 1,3-dimethoxytetrabutyldistannoxane (Table 6). At higher field (− 177, − 194), peak 3 is in a region where *exo* tin sites in both dialcoxy and acyloxyalcoxydistannoxanes have been previously observed (Table 6) that is to say $Bu_2SnO(OR)$ (OCOR or OR). Moreover in the 1-propanoyloxy-3-aminodistannoxane (I) and in the 1-

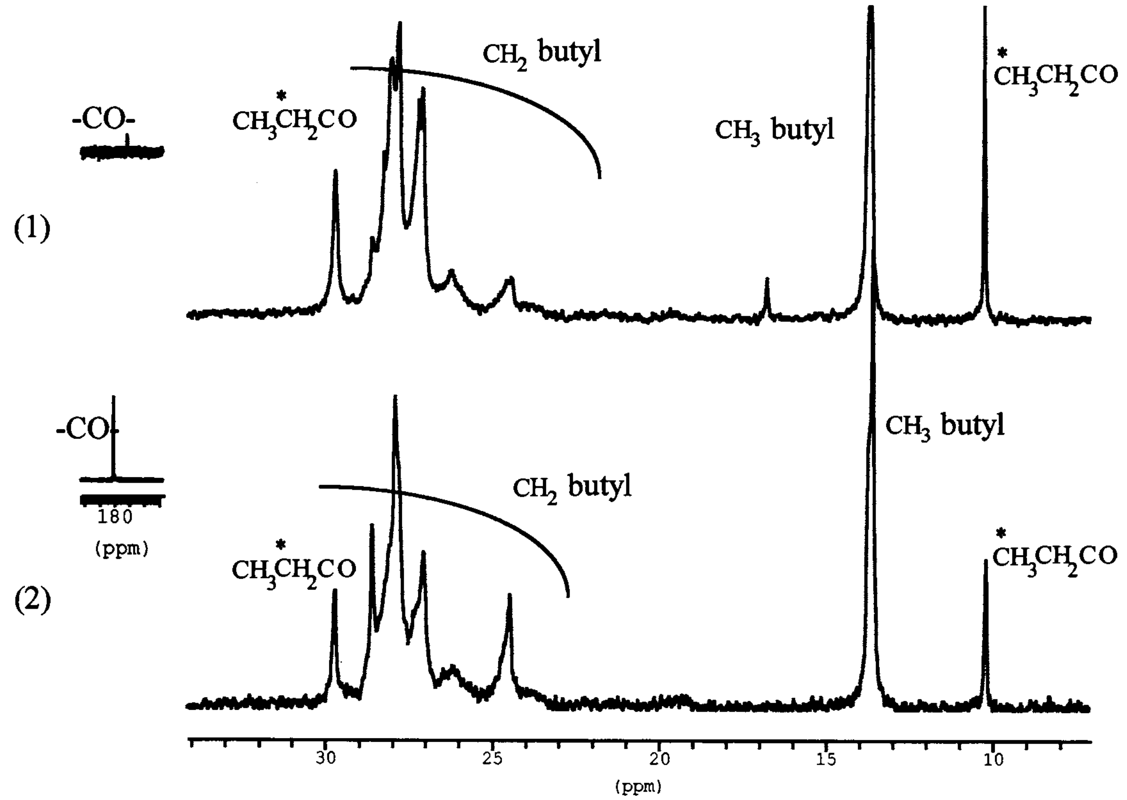


Fig. 6. ^{13}C-NMR spectra (made at 80°C) of (1) the hydrolyzed intermediate (I′) of the reaction of dibutyltin oxide with propionamide and (2) the hydrolyzed 1-propanoyl-3-*iso*butyloxytetrabutyldistannoxane (II′).

propanoyloxy-3-*iso*butoxydistannoxane (II), the *exo* tin sites are assigned, respectively to δ −188.9 for $Bu_2SnO(OCOR)(NH_2)$ and −183.4 for $Bu_2SnO(OCOR)$ (*i*-butoxy). In both cases hydrolysis will give (in I′ and II′) $Bu_2SnO(OCOR)OH$ tin sites expected in the same resonance region whereas after condensation $Bu_2SnO_2(OCOR)$ are expected at higher field. Peaks 4 + 5 (−194, −225) are assigned to internal sites of type $Bu_2Sn[O]_2(OCOR)$ both in diacyloxy and in acyloxyalkoxydistannoxane as shown in Table 6. The same chemical shift range is expected next to this internal tin site when the alkoxy group of II or the NH_2 group of I becomes an OH group by hydrolysis and unachieved condensation. Finally, peak 6 (−225, −240) is assigned to $Bu_2SnO(OCOR)_2$ sites.

This tentative assignment is in good agreement with the global stoichiometry (one $OCOCH_2CH_3$ group/ two Sn atoms) since the ratio 1.92/2.08 corresponding to the ratio (low field (1 + 2 + 3) regions/high field (4 + 5 + 6) regions) shows 1.92 tin sites without any covalent bond Sn–OCOR for 2.08 tin site with one covalent bond Sn–OCOR. Indeed the global stoichiometry (one $OCOCH_2CH_3$/ two Sn) in the tetrastannoxane structure requires two tin sites without any Sn–OCOR covalent bond (b + c) and two tin sites with one Sn–OCOR covalent bond (a + d) (Scheme 6).

As a conclusion the presence of the ladder-like dimeric tetrastannoxane is not completely ruled out since all the expected tin sites corresponding to this structure a/(b + c)/d may be present, respectively under peaks 6/(1 + 2)/(4 + 5). But the ratio 0.5/2/2.5 is far from the value 1/2/1 expected and SnO(OCOR)OH are also present (peak 3). An irregular structure represented in Scheme 8 is highly probable.

As for the resonance observed at 87.5 which represents 2.5% of tin sites, we have previously shown [15] that tributyltin acetate is a by-product sometimes observed in the formation of 1,3-acetoxyoctyloxydistannoxane by reaction of octylacetate with dibutyltin oxide. This by-product gives a single resonance at 84.4 in the region of tetracoordinated tin. Then the resonance observed in the present case could be attributed to the tributyltin propionate. The presence of such a product would be explained with a second hydrolysis mechanism of the acyloxy (alkoxy or amino) distannoxane by the way of Eq. (7).

$$\begin{aligned} & C_2H_5COO\text{–}SnBu_2OSnBu_2\text{–}(NH_2 \text{ or } OR') + H_2O \\ & \rightarrow Bu_3SnOCOC_2H_5 + BuSnOOH \\ & + (NH_3 \text{ or } R'OH) \qquad (7) \end{aligned}$$

This mechanism supposes the presence of a single tin resonance characterizing the butyltin hydroxide oxide observed at δ −230.5 for the Aldrich product, probably included in peak 6.

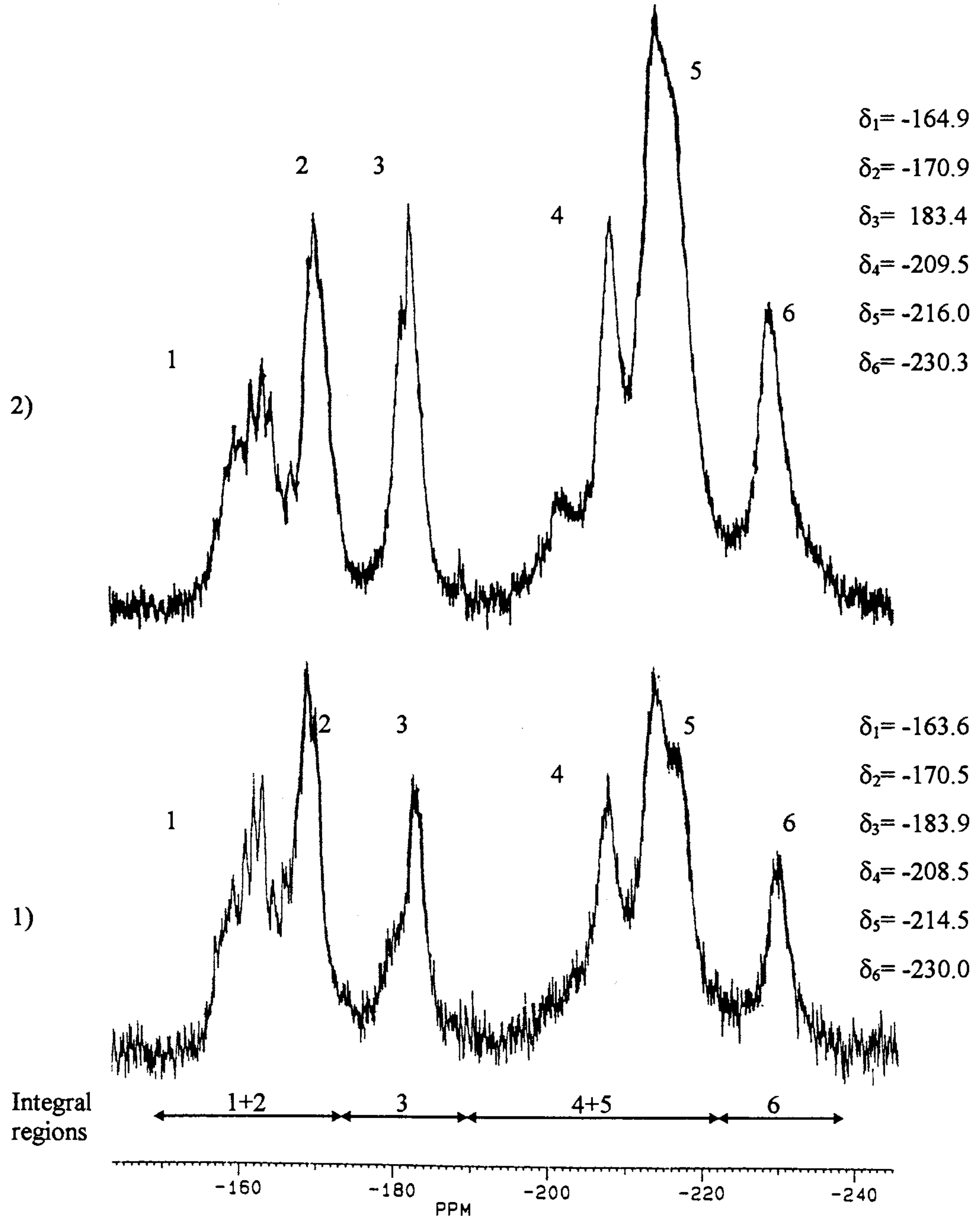


Fig. 7. ^{119}Sn-NMR spectra (made at 80°C) of (1) the hydrolyzed intermediate (I′) of the reaction of dibutyltin oxide with propionamide and (2) the hydrolyzed 1-propanoyl-3-*iso*butyloxytetrabutyldistannoxane (II′).

3.3.3. Nature of the intermediate species (I)

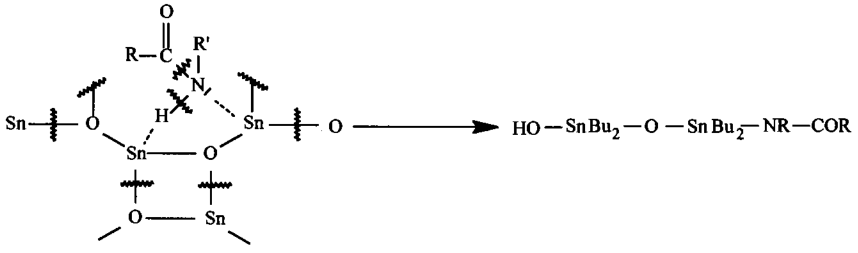
In view of the distannoxane structure observed by ^{119}Sn-NMR (Fig. 4) and the tetrastannoxane structure obtained after hydrolysis, the intermediate species (I) in the reaction of propionamide with dibutyltin oxide can reasonably be assigned to the 1-propanoyloxy-3-aminotetrabutyldistannoxane. The real nature of the amino ligand has not been certainly identified. But the ammoniac release observed during the formation of the dipropanoyloxytetrabutyldistannoxane and the easy hydrolysis leading to the tetrastannoxane structure support the 1-propanoyloxy-3-aminotetrabutyldistannoxane structure.

3.4. Reaction of acetanilide with dibutyltin oxide

An identical study was made with acetanilide. The presence of two resonance peaks of equal intensities was observed in ^{119}Sn-NMR at δ -187.8 and -200.6 before the appearance of the resonance of the diacetoxytetrabutyldistannoxane. In the case of propi-

Table 3
^{13}C Chemical shifts (δ in ppm) of (I′) and (II′) at 80°C

Sample	Propanoyl			Butyl	
	CH_3	CH_2	CO	CH_3	CH_2
Product (I′)	10.25	29.70	180.05	13.70	24.45/27.10/28.00/28.60
Product (II′)	10.20	29.75	180	13.60	24.50/27.10/27.90/28.60

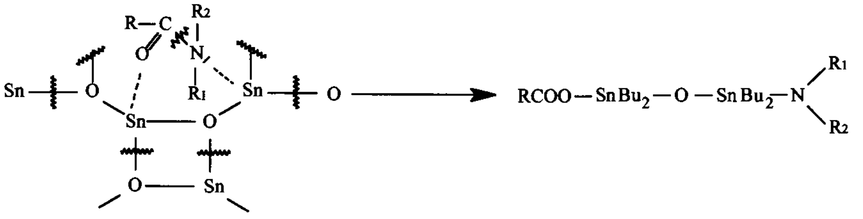


(9)

onamide two similar peaks were found at δ −188.9 and −203.2 ppm. So, like propionamide, acetanilide gives a 1-acyloxy-3-alkylaminotetrabutyldistannoxane in presence of dibutyltin oxide.

3.5. Proposition of mechanisms for the reaction of amides with dibutyltin oxide

Considering the highly probable formation of 1-acyloxy-3-alkylaminotetrabutyldistannoxane as an intermediate in the reaction of amides with dibutyltin oxide, one could reasonably propose a nitrogen–acyl bond cleavage mechanism (Eq. (8)) similar to the O–CO bond cleavage in the reaction with esters (Eq. (1)).



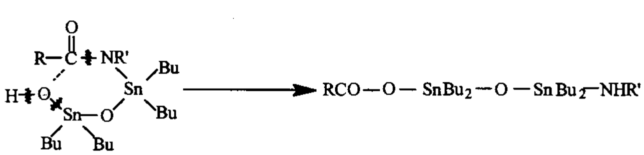
(8)

But such a mechanism should not take into account the fact that *tertiary* amides do not react. So we propose a mechanism in two steps involving the free hydrogen only present in primary and secondary amides. The first step consists of the hydrogen–nitrogen bond cleavage instead of the nitrogen–acyl one (Eq. (9)).

Table 4
^{1}H Chemical shifts (δ in ppm) of (I′) and (II′) at 80°C

Sample	Propanoyl		Butyl		
	CH_3	CH_2	CH_3	α CH_2	β and γ CH_2
Product (I′)	1.090	2.170	0.940	1.740	1.420
Product (II′)	1.050	2.160	0.950	1.750	1.420

The second step is an intramolecular rearrangement obtained through a nucleophilic attack of the carbonyl group by the oxygen of the hydroxyl end group SnOH (Eq. (10)).



(10)

When formed, the 1-acyloxy-3-alkylaminotetrabutyldistannoxane reacts with the amide excess to give the diacyloxytetrabutyldistannoxane (Eqs. (11) and (12)).

$$RCO\text{–}O\text{–}SnBu_2\text{–}O\text{–}SnBu_2\text{–}NHR' + H_2O \rightarrow RCO\text{–}O\text{–}SnBu_2\text{–}O\text{–}SnBu_2\text{–}OH + R'NH_2 \qquad (11)$$

$$RCO\text{–}O\text{–}SnBu_2\text{–}O\text{–}SnBu_2\text{–}OH + RCO\text{–}NHR' \rightarrow \{RCO\text{–}O\text{–}SnBu_2\}_2O + R'NH_2 \qquad (12)$$

This reaction requires the presence of water possibly supplied by the great hygroscopical character of amides. When the amide excess is eliminated the hydrolysis of the acyloxyalkylaminodistannoxane with additional water leads first of all to tetrastannoxanes (Eq. (13)) associated in a more or less perfect ladder-like structure including partial hydrolysed forms of the distannoxane (Scheme 8). A secondary hydrolysis mechanism (2.5% of tetracoordinared tin sites) involving a butyl group transfer can be proposed releasing tri-

Table 5
^{119}Sn Chemical shifts (δ in ppm) of (I′) and (II′) at 80°C

Sample	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
Product (I′)	−163.6	−170.5	−183.9	−208.5	−214.5	−230.0
Product (II′)	−164.9	−170.9	−183.4	−209.5	−216.0	−230.3

Table 6
^{119}Sn Chemical shifts in some distannoxane compounds compared with Fig. 7 resonances

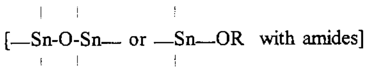
Tin site and integral regions	Tin site type	Chemical shift value	Region[a]	Reference
Internal site in dimeric				
1,3 Dimethoxy-TDS[b]	$Bu_2SnO_2(\underline{OR})$[c]	−174.1	1+2	[2]
External site in dimeric				
1,3-Dimethoxy-TDS	$Bu_2SnO(OR)(\underline{OR})$[c]	−180.1	3	[2]
1,3-Nonanoyloxy,methoxy-TDS	$Bu_2SnO(OCOR)(\underline{OR})$[c]	−181.4	3	[2]
1,3-Acetoxy, octyloxy-TDS	$Bu_2SnO(OCOR)(\underline{OR})$[c]	−182.5	3	[2,15]
1,3-Propanoyloxy, *iso*butoxy-TDS	$Bu_2SnO(OCOR)(\underline{OR})$[c]	−183.4	3	This work
1,3-Propanoyloxy, amino-TDS	$Bu_2SnO(OCOR)(\underline{NH_2})$[c]	−188.9	3	This work
Internal site in dimeric				
1,3-Propanoyloxy, amino-TDS	$Bu_2SnO_2(\underline{OCOR})$[c]	−203.2	4	This work
1,3-Propanoyloxy,*iso*butyl-TDS	$Bu_2SnO_2(\underline{OCOR})$[c]	−209.5	5	This work
1,3-Acetoxy, octyloxy-TDS	$Bu_2SnO_2(\underline{OCOR})$[c]	−214.5	5	[2,15]
1,3-Nonanoyloxy, methoxy-TDS	$Bu_2SnO_2(\underline{OCOR})$[c]	−218.2	5	[2]
1,3-Diacetoxy-TDS	$Bu_2SnO_2(\underline{OCOR})$[c]	−219.4	5	[15]
1,3-Propanoyloxy-TDS	$Bu_2SnO_2(\underline{OCOR})$[c]	−221.2	5	This work
External site in dimeric				
1,3-Propanoyloxy-TDS	$Bu_2SnO_2(OCOR)(\underline{OCOR})$[c]	−229.2	6	This work
1,3-Diacetoxy-TDS	$Bu_2SnO_2(OCOR)(\underline{OCOR})$[c]	−229.8	6	[15]

[a] Corresponding region observed in Fig. 7.
[b] TDS, tetrabutyldistannoxane.
[c] Underlined group, group linked to the tin atom by covalent bond.

butyltin acyloxy and butyltin hydroxide oxide (Eq. (14)). Identical mechanisms are proposed for hydrolysis of 1-acyloxy-3-alkoxytetrabutyldistannoxane (Eqs. (13) and (14)).

$$2\ RCOOSnBu_2OSnBu_2(OR'\ \text{or}\ NHR') + H_2O \rightarrow \{RCOOSnBu_2OSnBu_2\}_2O + 2\ (R'OH\ \text{or}\ R'NH_2) \quad (13)$$

$$RCOO{-}SnBu_2{-}O{-}SnBu_2{-}(NHR'\ \text{or}\ OR') + H_2O \rightarrow Bu_3Sn{-}OCOR + BuSnOOH + (R'NH_2\ \text{or}\ R'OH) \quad (14)$$



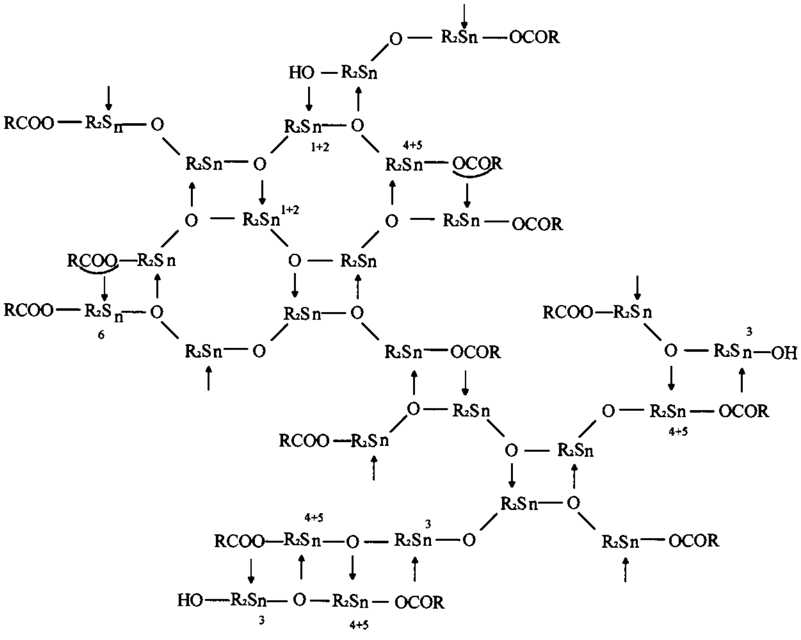
$$[{-}Sn{-}O{-}Sn{-}\ \text{or}\ {-}Sn{-}OR\ \text{with amides}]$$

4. Conclusion

This paper deals with the reaction of dibutyltin oxide with amides and consequently it sheds light on the contribution of dibutyltin oxide in the catalyst of exchange reaction between polyamides and polyesters in extrusion reactive process.

In comparison with the reactivity with esters, the reactivity of dibutyltin oxide with primary and secondary amides is found to be very low. In excess of amide, a perfect ladder-like diacyloxytetrabutyldistannoxane is obtained if only a trace amount of water is present in the mixture whereas in presence of water and without excess of amide a less perfectly organized tetrastannoxane structure is obtained. In the presence of both amides and esters, dibutyl tin oxide reacts preferentially with esters giving the 1-acyloxy-3-alcoxytetrabutyldistannoxane. As shown by some recent works in our laboratory [14] on model amide–ester and amide–polyacrylic ester, this distannoxane is the predominant catalytic entity of the exchange reaction between esters and amides.

As for the very few examples of reaction of amides or imides with organotin compounds presented in the



Scheme 8.

literature [26–29] many years ago, we can make the following comments in light of our results. In some cases the Sn–O link is claimed to be cleaved and the CONH link retained leading to the formation of Sn–NHCO in presence of water (or ROH) which is a quite questionable assertion owing to the highly hydrolyzable character of Sn–N link. In other cases (dibutyltin oxide with imides) the cleavage of CO–NHR′ is claimed with insertion of one [Sn–O] and the formation of COO–$SnBu_2$–NHR′. From our results the cleavage of CO–NHR′ proceeds only in a second step, the first being the insertion of two [Sn–O] giving a first distannoxane $HOSn(Bu)_2OSn(Bu)_2N(R')COR$. This latter quickly rearranges to give another one $R'N(H)Sn(Bu)_2$-$OSn(Bu)_2OCOR$ which reacts again in presence of water with the excess of amide leading to a quite stable diacyloxydistannoxane. The same mechanism but supposing only one [Sn–O] insertion should give $RCOOSn(Bu)_2NHR'$ which—in presence of water—should give the diacyloxytetrabutyldistannoxane by hydrolysis and condensation. But it is completely ruled out by our NMR characterization of the distannoxane intermediate.

References

[1] C. Gondard, A. Michel, Sotra Industries and CNRS, US patent, 5 244 982, 1993.

[2] I. Espinasse, R. Pétiaud, M.F. Llauro, A. Michel, Int. J. Polym. Anal. Charact. 1 (1995) 137.

[3] A. De Loor, P. Cassagnau, A. Michel, L. Delamare, B. Vergnes, Int. Polym. Process. XI 2 (1996) 139.

[4] A. De Loor, P. Cassagnau, A. Michel, B. Vergnes, J. Appl. Polym. Sci. 53 (1994) 1675.

[5] A. De Loor, P. Cassagnau, A. Michel, B. Vergnes, J. Appl. Polym. Sci. 63 (1997) 1385.

[6] I. Espinasse, P. Cassagnau, M. Bert, A. Michel, J. Appl. Polym. Sci. 54 (1994) 2083.

[7] P. Cassagnau, M. Bert, V. Verney, A. Michel, Polymer 34 (1) (1993) 124.

[8] L.Z Pillon, L.A. Utracki, Polym. Eng. Sci. 24 (17) (1984) 1300.

[9] M. Fieser, L. Fieser, Reagents for Organic Synthesis, vol. 1, Wiley, New York, 1966.

[10] K. Inoshita, M. Terakowa, T. Yasuda, Japan patent, 7228.916 (1972), CA, 76:114155d (1972).

[11] V.V. Korshak, S.V. Vinogradova, M.M. Teplyakov, F.D. Fedorova, G.Sh. Papava, Vysokomol. Soedin. 8 (1966) 2155.

[12] V.V. Korshak, S.V. Vinogradova, M.M. Teplyakov, A.D. Maksimov, Izv. Vyssh. Uchebn. Zaved. Khim. i Khim. Technol. 10 (1967) 688.

[13] T.M. Frunze, V.V. Kurashev, L.B. Danilevskayo, B.A. Rozenberg, V.V. Korshak, Vysokomol. Soedin. Ser. A 16 (1974) 1250.

[14] E. Colomb, M. Grégoire, J. Gimenez, R. Pétiaud, M.F. Llauro, A. Michel, 12th European Symposium on Polymer Spectroscopy, Lyon, July 8–10, 1996.

[15] J. Bonetti, C. Gondard, R. Pétiaud, M-F. Llauro, A. Michel, J. Organomet. Chem. 481 (1994) 7.

[16] O. Primel, M.F. Llauro, R. Pétiaud, A. Michel, J. Organomet. Chem. 558 (1998) 19.

[17] R. Okawara, M. Wada, J. Organomet. Chem. 1 (1963) 81.

[18] R. Okawara, M. Wada, J. Organomet. Chem. 8 (1967) 261.

[19] J. Otera, T. Yano, K. Nakashima, R. Okawara, Chem. Lett. (1984) 2109.

[20] T. Yano, K. Nakashima, J. Otera, R. Okawara, Organometallics 4 (1985) 1501.

[21] D.C. Gross, Inorg. Chem. 28 (1989) 2355.

[22] V.K. Jain, V.B. Mokal, P. Sandor, Magn. Reson. Chem. 30 (1992) 1158.