APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 477–484 (1996)

Thio-organotin Antioxidants for Polypropylene: Reactivity towards t-Butyl Hydroperoxide

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Various thio-organotin compounds have been reacted with t-butyl hydroperoxide in order to determine whether this oxidation can be responsible for the stabilizing capacity of some thio-organotins towards polyolefin degradation. The kinetics of t-butyl hydroperoxide disappearance, in the presence of thiotin compounds, shows different reactivity according to the structure of oranometallic reagent. Product analysis indicates organotin oxide, dialkyl disulfide and t-butanol as major reaction products. The reactivity sequence towards hydroperoxide is the same as the order observed for polypropylene stabilization.

Keywords: Thio-organotins; polypropylene stabilization; tin–sulfur (Sn–S) bond; oxidation; hydroperoxides

INTRODUCTION

The processing of polypropylene generally occurs under thermal conditions which lead to the deterioration of the material properties. The addition of thio-organotin compounds to the polymer diminishes this degradation.[1]

The aging of organic compounds in air generally proceeds through free-radical chain oxidations with formation of peroxidic species which decompose and give various by-products.[2] The reaction can be visualized according to Eqn [1]

$$\mathrm{R^{\bullet}} \xrightarrow{\mathrm{O_2}} \mathrm{ROO^{\bullet}} \xrightarrow{\mathrm{RH}} \mathrm{R^{\bullet}} + \mathrm{ROOH} \longrightarrow \text{degradation products} \quad [1]$$

In this context, thio-organotin compounds can be involved at two different levels:

(1) inhibition of the propagation of the autoxidation chain by trapping of:
    (a) alkyl radicals $R^{\bullet}$,
    (b) alkylperoxyl radicals $RO_2^{\bullet}$ and
    (c) alkoxyl radicals $RO^{\bullet}$ formed by decomposition of hydroperoxides;
(2) degradation of the hydroperoxides formed during the polyolefin autoxidation.

The degradation of the material can occur at two stages: during processing or during long-term utilization (aging). Each occurs under very different experimental conditions:

(1) In the extruder the temperature stays at over 250 °C and the material can be considered as a viscous liquid. The amount of oxygen present is not negligible since polypropylene is introduced into the mixer as small spheres in an air atmosphere.
(2) During aging the processed material is a solid and the temperature lies between −30 and +60 °C.

The free radicals participating in the autoxidation process are formed differently in the two cases.

(1) During initiation, at least in part, they arise from the mechanical breaking of polymeric chains during the kneading (processing).
(2) During aging, they are formed by photochemically initiated autoxidation or photodecomposition of peroxidic compounds formed during the preceding steps.

The reactive species are the same in both cases, although the reaction rates are different in both media due to the temperature differences and (principally) to the ease of diffusion of the reagents (oxygen and radicals). Thus, analysis of the stabilizing properties of thio-organotin compounds[3] requires a study of their reactivity with alkyl and alkylperoxyl radicals as well as hydroperoxides. Models for the species arising

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CCC 0268–2605/96/070477–08

Received 27 July 1995
Accepted 14 October 1995

from the polypropylene chain have to be used, such as t-butyl or t-butylperoxyl radicals and t-butyl hydroperoxide. Indeed this type of species is expected to be formed in the autoxidation of polypropylene since it has been shown that oxyl or alkylperoxyl radicals abstract tertiary hydrogens more easily than secondary or primary ones.[4]

In order to determine whether the thio-organotin compounds, which are used industrially, owe their stabilizing properties to the degradation of hydroperoxides and/or to the trapping of radicals, we decided to study first their relative reactivities towards t-butyl hydroperoxide. This hydroperoxide is a good model for the tertiary hydroperoxides which are formed by autoxidation of polypropylene.[5,6]

First, it is important to describe the data already published. Scott and co-workers have shown that thio-organotins are able to reduce hydroperoxides.[7] Kinetic determinations and product analysis of the reaction between t-butyl and cumyl peroxides with dioctyltin bis(iso-octyl thioglycolate) led to the conclusion that a complex reaction mechanism, involving three consecutive steps, occurred:[8]

(1) oxidation of the organotin derivative in a fast reaction with a defined stoichiometry;
(2) formation of Lewis acids by alcoholysis or hydroperoxidolysis of the oxidation products of the tin compounds;
(3) Catalytic degradation of hydroperoxides by the acidic species formed in the second step.

In contrast, Wirth and co-workers, who studied the reaction of t-butyl hydroperoxide with dimethyltin bis(iso-octyloxycarbonylmethane thiolate) at 40 °C, essentially obtained the corresponding dialkyl disulfide.[9]

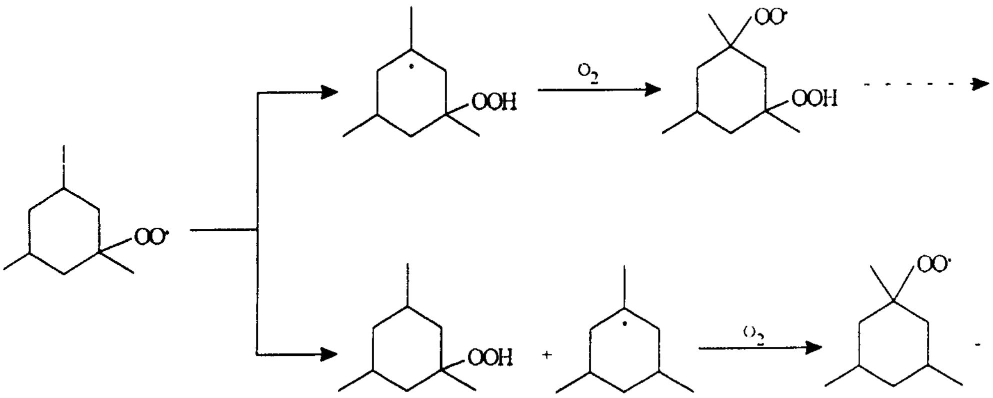
RESULTS AND DISCUSSION

Kinetics of reactions at 40 °C

First we chose a good model of polypropylene as a solvent. Without 2,4,6-trimethylheptane available (the model molecule previously used by Van Sickle[6]) we chose 1,3,5-trimethylcyclohexane, which has the same —$CH(CH_3)CH_2$— linkage. For this study, the cyclic structure should not be a drawback since we are interested in the decomposition of the hydroperoxide and not in its formation. It is important, however, to keep in mind that, due to its cyclic constitution, this model could show different behavior in the autoxidation process, inter- and intra-molecular reactions being in competition during the hydrogen transfer step, i.e. Eqns [2] and [3].

The choice of a rather low temperature (40 °C) is intended to determine a rate of hydroperoxide disappearance slow enough to allow a better differentiation of the various thio-organotin compounds. This temperature is also close to the conditions for normal use of polypropylene.

Quantitative analysis of the hydroperoxide was performed by GLC with undecane as internal standard. This method allows rapid determination of low amounts of hydroperoxide in a nondestructive way. The hydroperoxide concentrations were chosen at levels that are as close as possible to the real situation. A limit around 10^{-4} M was imposed for analytical reasons. The hydroperoxide/thiotin ratios were



[2]

[3]

defined by assuming that each Sn–S bond is responsible for part of the reducing properties. However, in some cases it was necessary to use higher quantities of hydroperoxide in order to have some hydroperoxide remaining at the end of the reaction.

Graphs representing the decomposition of t-BuOOH by the organotin compounds **1–8** are represented on Figs 1 and 2:

1 $BuSn(S)SC_{12}H_{25}$
2 $BuSn(S)SCH_2CO_2C_{18}H_{37}$
These compounds are written as the monomeric form with a tin–sulfur double bond.
3 $Bu_2Sn(SCH_2CO_2C_{18}H_{37})_2$
4 $BuSn(SCH_2CO_2C_{18}H_{37})_3$
5 $Sn(SCH_2CO_2C_{18}H_{37})_4$
6 $[Bu_2SnS]_3$
7 $Bu_2Sn(SCH_2CO_2Me)_2$
8 $Bu_3SnSCH_2CO_2C_{18}H_{37}$

In the case of the more reactive compounds **1** and **3**, the kinetic study was performed while bubbling oxygen or argon through in order to search for possible hydroperoxide degradation through alkyl free radicals. Indeed, the high reactivity of alkyl radicals with oxygen,[10] leading to new hydroperoxides, would correspond to very different rates of decomposition of t-butyl hydroperoxide. A much less rapid decomposition of t-butyl hydroperoxide should be observed in the presence of oxygen, because of the formation of hydroperoxides arising from autoxidation of trimethylcyclohexane. The organotin compound, in a substoichiometric amount with respect to t-butyl hydroperoxide, would also degrade trimethylcyclohexyl hydroperoxide with, as a result, a higher amount of residual t-butyl hydroperoxide at the end of the reaction. Figures 1 and 2 indicate only a very weak effect when argon is replaced by oxygen.

It is interesting to note that in all cases where the amount of degradation is significant, the reactions are quite fast in the initial stages. Later, it is difficult to establish whether the small changes in the concentration of hydroperoxide are due to a decomposition catalyzed by the degradation products of the organotin species (comparison with a blank experiment). Thus it seems possible to estimate the stoichiometry of the initial step, from the ratio of moles of the hydroperoxide consumed per mole of thio-organotin compound, in the reaction of t-butyl hydroperoxide and the organotin compound,

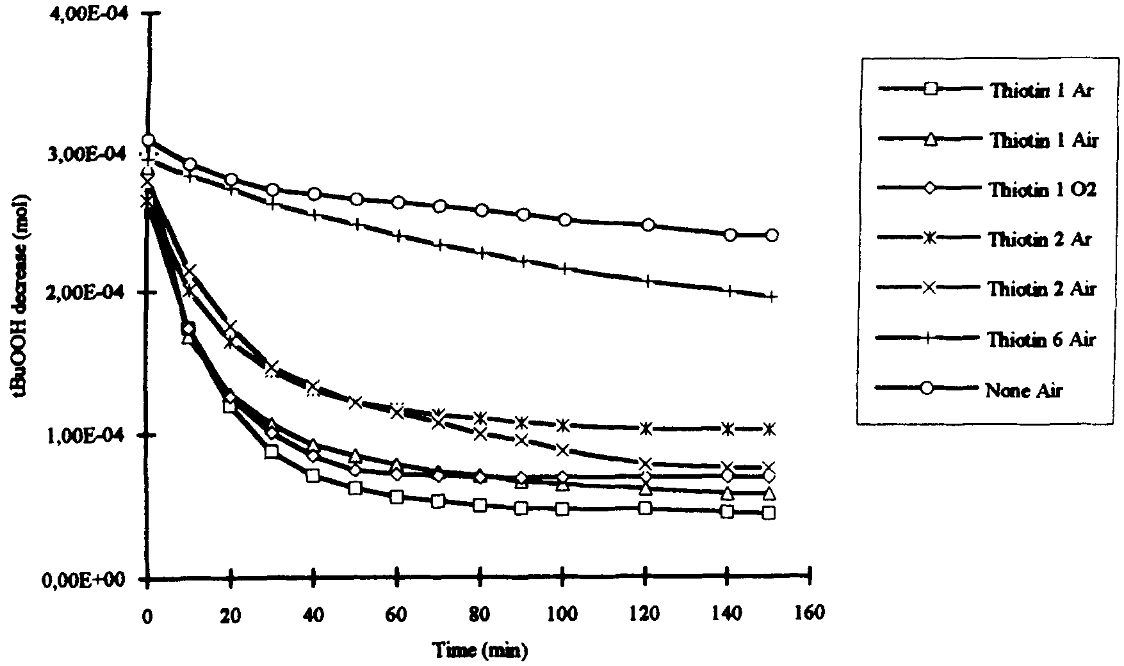


Figure 1 Disappearance of t-BuOOH, in presence of thio-organotin compounds, in trimethylcyclohexane, under a controlled atmosphere.

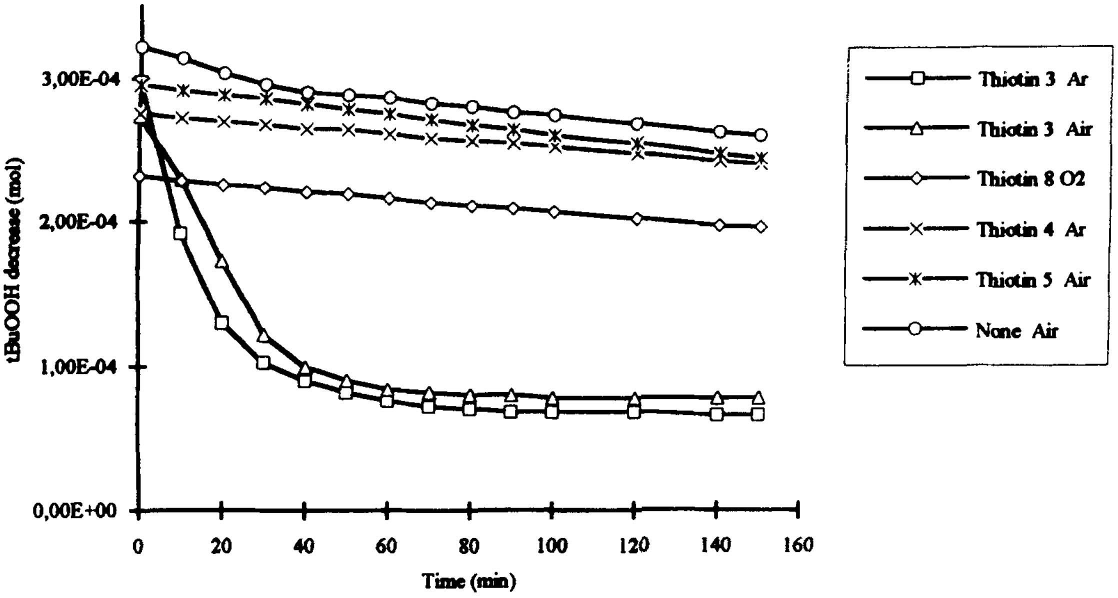


Figure 2 Disappearance of t-BuOOH, in presence of thio-organotin compounds, in trimethylcyclohexane, under a controlled atmosphere.

viz:

1: 2.3–2.4
2: 2.0–2.4
3: 2.8–3.0

^{119}Sn NMR analysis of **1** and **2** show that they are, in fact, very complex mixtures including oligomers and polymers. In consequence it is difficult to draw a conclusion from the observed stoichiometry in the case of compounds containing the "Sn(S)" functional group. However, the stoichiometry of **3** could be considered meaningful. On these bases, it seems difficult to assign, for this compound, a behavior similar to that suggested for a homologous derivative by Scott.[8] Such a stoichiometry does not seem possible for the two first steps proposed by Scott and the third corresponds to a catalytic degradation process.

Since 1,1,3,3,5,5-hexabutyl-1,3,5-tristanna-2,4,6-cyclotrithiane **6** appears as a good model molecule for "sulfur bridge" (i.e. Sn–S–Sn linkage), it was synthesized according to the published literature,[11] which indicated that differentiation between the trimer and the polymer was made on the basis of a liquid state for the polymer and a solid state for the trimer. In our hands, numerous experiments, under described experimental conditions or under very different ones, never led to a solid. However, ^{119}Sn NMR of the products indicated only one type of tin atom, a fact in agreement with a cyclic structure. In any case, whether cyclic or a linear structure, is involved the sulfur bridge is present. The reaction of this compound with t-butyl hydroperoxide (Fig. 1) shows a very weak efficiency for the degradation of hydroperoxides. On this basis, it seems that the sulfur bridge cannot be considered as the single moiety responsible for the efficiency of compounds **1** and **3**.

Although the order of reactivity of the organotin compounds with t-butyl hydroperoxide is the same as their efficiency in the stabilization of polyolefins,[12] it seems presently too early to attribute their stabilizing properties to reactions with hydroperoxides.

The decomposition products

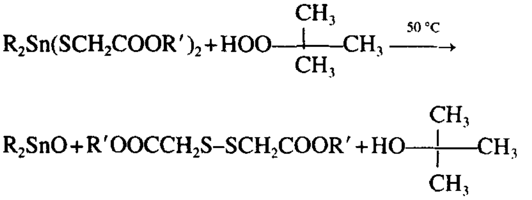
In order to facilitate the analysis and identification of the products of the most reactive thio-organotins, we decided to replace trimethylcyclohexane by cyclohexane (since the reaction does not involve free-radical species, their behavior should be similar) and the high-molecular-weight organotins by lighter ones (with the stearyl thioglycolate and thiodecyl groups replaced respectively by methyl thioglycolate and thiobutyl groups).

Dibutyldimethoxycarbonylmethanethiyltin (7)

Although the graphs describing the disappearance of t-BuOOH are not superposable (Fig. 3), the stoichiometries observed for compound **3** in trimethylcyclohexane, or **7** in trimethylcyclohexane or cyclohexane, are not very different. This fact confirms the validity of the change of solvent for an easier analysis.

The reactions of t-BuOOH with **7** in cyclohexane with molarities 0.125 M and 0.0375 M have shown the formation of significant quantities of t-butanol and dimethoxycarbonylmethyl disulfide $(SCH_2CO_2Me)_2$ (**9**), as well as traces of acetone and small quantities of two other unidentified products. The compounds have been identified by comparison with reference samples by GLC or GLC–MS. Several experiments were run in cyclohexane and in neat reactants (in order to minimize losses during the elimination of cyclohexane), but in all cases the measurements did not allow a complete balance of t-butoxyl group (1 mol of t-butanol is formed by reference with the thio-organotin compound and $\frac{1}{3}$ mol by reference with t-BuOOH) and methyl thioglycolate (the thioglycolate moiety of the disulfide represents two-thirds of the initial quantity in reaction). After elimination of these compounds, a heavier derivative was isolated. It was most probably dibutyltin oxide since, when reacted with hydrogen chloride, it gave dibutyltin dichloride which further reacted with propylmagnesium bromide to yield dibutyldipropyltin (identified by GLC in comparison with a reference sample).

This quantitative study, in conjunction with the preceding kinetic data, allows choice to be made between Scott[8] and Wirth's[9] proposals. Our results (stoichiometry and main reaction products) agree with Wirth's conclusions (Eqn [4]).



$$R_2Sn(SCH_2COOR')_2 + HOO\!-\!\underset{CH_3}{\overset{CH_3}{C}}\!-\!CH_3 \xrightarrow{50\,°C} R_2SnO + R'OOCCH_2S\!-\!SCH_2COOR' + HO\!-\!\underset{CH_3}{\overset{CH_3}{C}}\!-\!CH_3$$

[4]

It is interesting to note that the reaction temperature for our study was closer to that used by Wirth (50 °C) than that used by Scott (60–80 °C). Thus, we attempted to extend our studies over a wider temperature range. At 70 °C the reaction was so violent that we limited ourselves to 60 °C. The results showed that the reaction products are the same at 60 and 40 °C: disulfide, t-butanol and dibutyltin oxide (identified, after derivatization, as dibutyldipropyltin).

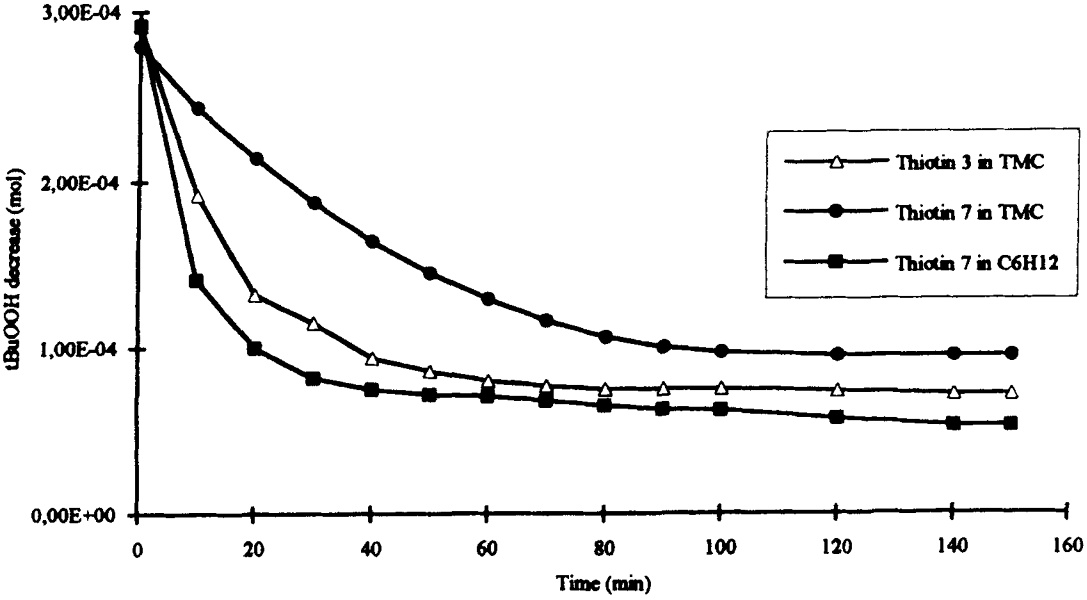


Figure 3 Disappearance of t-BuOOH, in presence of thio-organotin compounds, in solvents, under an air atmosphere. TMC, trimethylcyclohexane.

Further oxidation of the disulfide is certainly possible but did not occur significantly between 40 and 60 °C in the presence of the thiotin derivative. It appears that t-butyl hydroperoxide is more reactive towards the organometallic reagent than towards the disulfide.

Taking into account the facile formation of disulfide by oxidation of mercaptans with peroxyl derivatives, observed in the case of t-BuOOH with methyl thioglycolate, it is tempting to explain the formation of **9** by Eqns [5] and [6], which agree with the stoichiometry found.

$$\mathrm{Bu_2Sn(SCH_2CO_2Me)_2 + 2\ t\text{-}BuOOH \rightarrow Bu_2Sn(OOt\text{-}Bu)_2 + 2\ HSCH_2CO_2Me} \quad [5]$$

$$\mathrm{t\text{-}BuOOH + 2\ HSCH_2CO_2Me \rightarrow t\text{-}BuOH + H_2O + (SCH_2CO_2Me)_2} \quad [6]$$

Di-t-butylperoxydibutyltin was reported previously by Davies and co-workers,[13] and isolated with difficulty due to its high water sensitivity. Considering the formation of water during the oxidation of the thiol, it is not surprising that it was not observed in our experiment.

BuSn(S)SBu

Because of the violent nature of the reaction, the hydroperoxide was added very slowly with a syringe pump at the rate of 1.1 ml h^{-1} at 30 °C, and subsequently the reaction mixture was heated at 40 °C during 15 min. Separation and analyses of the products indicated.

(1) a t-BuOOH/BuSn(S)SBu stoichiometry around 3.4 : 1;
(2) an almost complete transformation of hydroperoxide into t-butanol;
(3) the formation of Bu_2S_2 (as a mixture with other products which did not allow a precise quantitative evaluation); and
(4) the formation of a residue which, after reaction with propylmagnesium bromide, essentially gave butyltripropyltin (identified by comparison with a reference sample). Analysis gave a formula $(C_{4.16}H_{11}O_{3.3}S_{0.75}Sn)_n$ which, taking into account the identified compounds, corresponds to $BuSn(C_{0.16}H_2O_{3.3}S_{0.75})$. Thus, several Sn–S bonds have been replaced by Sn–O bonds but the residue still contains a nonnegligible amount of sulfur. Although most of the sulfur bound to the butyl group was recovered as disulfide, we could not identify the transformation product of the sulfur bridge. Part of it could remain in the residue in a more or less oxidized form.

Considering the difficulties of identifying the heavy products and the imprecise structure of the compounds containing a sulfur bridge, it did not appear reasonable to continue the product-analysis approach. However, the reactivity of the thio-organotin compounds with t-BuOOH at higher temperatures has been examined by means of the DSC technique.[14]

In conclusion, this work has shown the high reactivity of compounds containing a sulfur bridge towards t-butyl hydroperoxide. Di(thioalkyl)dibutyltin compounds appear to be slightly less reactive; tri(thioalkyl) and tetrakis(thioalkyl)tins are weakly reactive. The reactions, conducted at 40 °C with model compounds, essentially led to t-butanol, dialkyl disulfide and alkyltin oxide.

EXPERIMENTAL

Analytical instrumentation

NMR

^1H NMR was run on a Hitachi–Perkin-Elmer R24 spectrometer at 60 MHz, in CCl_4 or $CDCl_3$, with tetramethylsilane as internal standard. ^{119}Sn NMR was run on a Bruker AC200 spectrometer at 74.5 MHz, fitted with an Aspect 3000 computer, in C_6D_6, with tetramethyltin as internal standard.

MS

The spectra were obtained on a VG MS.16F spectrometer, coupled with an Intersmat IGC 121 M chromatograph.

GLC

Delsi 1200 FL chromatographs, flame ionization and filled columns, or Varian 3300, flame ionization, capillary columns with a Varian 4400 recorder–integrator were used.

Reagents and products

Butyl mercaptan (BuSH), dibutyltin dichloride (Bu_2SnCl_2), dibutyltin oxide (Bu_2SnO), t-butyl hydroperoxide (t-BuOOH) and dibutyl disulfide (BuSSBu) were purchased from Aldrich. The hydroperoxide, provided in water solution, was extracted with pentane and the organic solution was dried on magnesium sulfate. The solvent was evaporated under reduced pressure (Rotavapor) at room temperature. 1,3,5-Trimethylcyclohexane was purchased from Fluka.

The thiotin compounds **1–5** and **8**, as well as butyltin trichloride ($BuSnCl_3$) and methyl thioglycolate, were kindly provided by the Groupement de Recherche de Lacq (Elf–Atochem).

$(Bu_2SnS)_3$ (6)[11]

A mixture of dibutyltin oxide (12.45 g, 0.05 mol) and $Na_2S,9H_2O$ (12 g, 0.05 mol) in 200 ml water and 10 ml ethanol was stirred at room temperature for 2 h. Then, acetic acid (10 ml) was added and the mixture stirred again for 2 h. After decantation the organic phase was dried and evaporated. A pale yellow oil was obtained and used without further purification after checking by ^{119}Sn NMR [δ (ppm) 129.5, s).

$Bu_2Sn(SCH_2CO_2Me)_2$ (7)

Dibutyltin dimethoxide, $Bu_2Sn(OMe)_2$ (14.75 g, 0.05 mol), obtained from dibutyltin dichloride and sodium methanolate, was slowly added to methyl thioglycolate, $HSCH_2CO_2Me$ (10.6 g, 0.1 mol). The reaction was very exothermic. The methanol formed was eliminaterd under reduced pressure and the residue dissolved in 100 ml pentane. After filtration the solution was evaporated under reduced pressure. The product was obtained as a transparent oil (90% yield) which was used without further treatment.

^{1}H NMR, δ(ppm): 3.7, 3H, s; 3.35, 2H, s; 0.7–1.8, 18H, m. ^{119}Sn NMR, δ(ppm): 81.14.

$(SCH_2CO_2Me)_2$ (9)[15]

t-Butyl hydroperoxide (9 g, 0.1 mol) was added to methyl thioglycolate (21.2 g, 0.2 mol) and the mixture was stirred for 30 min at room temperature and 2 h at 60 °C. After elimination of all volatile compounds at 40 °C under reduced pressure (1 h), the disulfide was used without further purification.

^{1}H NMR (δ, ppm): 3.7, 3H, s; 3.6, 2H, s. MS: M^+ (80%); $(MeOCOCH_2)_2S^+$ (98%); $MeOCOCH_2SSCH_2^+$ (70%); $MeOCO^+$ (61%).

$BuSn(S)SC_4H_9$ (10)

Into a 500-ml three-necked flask containing 21 ml water, $BuSnCl_3$ (28.3 g, 0.1 mol) was slowly added while refrigerating the reactor with ice water. Then, 50 ml toluene was poured in before the addition, by means of a syringe, of butyl mercaptan (9 g, 0.1 mol). To this solution, strongly stirred, was added 21 ml of a 20% solution of sodium hydroxide in water. The mixture was heated at 70 ° C for 40 min. After cooling at 50 °C, $Na_2S,9H_2O$ was added (24 g, 0.1 mol) and the mixture was heated at 60 °C for 90 min. The cooled mixture was decanted and 100 ml ether was added before it was washed to neutrality, dried on magnesium sulfate and the solvent was evaporated off under reduced pressure. A yellow oil was obtained which showed a very complex ^{119}Sn NMR spectrum with multiple lines between 120 and 150 ppm. It must be noted that the ^{119}Sn NMR spectra of the other sulfur-bridged compounds **1** and **2** showed similarly from very complex patterns of oligomers and polymers, respectively from 110 to 150 and from 68 to 122 ppm.

Reactions of t-BuOOH with thiotin compounds

Into a 20-ml flask, 3×10^{-4} mol t-BuOOH, 1×10^{-4} mol thiotin compound, 6 ml 1,3,5-trimethylcyclohexane and 6.5×10^{-4} mol undecane (internal standard) were introduced. The mixture was stirred and maintained in a thermostated bath at 40 °C.

The disappearance of t-BuOOH was monitored by GLC (filled column, 10% OV 225 on Aeropak; oven, 70 °C; injector, 110 °C; detector, 155 °C; vector, 20 ml min^{-1} N_2).

In the case of experiments needing argon or oxygen bubbling, the reaction mixtures were initially degassed. A weak and steady stream of gas bubbles (7–10 ml min^{-1}) was maintained throughout the experiment.

Identification of decomposition products

From $Bu_2Sn(SCH_2CO_2Me)_2$ (7)

Compound **7** (4 g, 0.01 mol) and t-BuOOH (2.7 g, 0.03 mol) were stirred and heated at 40 °C for 40 min. After cooling, the volatile products were gathered under vacuum in a trap maintained at liquid nitrogen temperature. GLC analysis (capillary column, DB210, 25 m; oven, 5 min at 40 °C followed by programming from 40 to 200 °C, 8 °C min^{-1}; vector, 1 ml min^{-1} N_2) allowed the identification of t-BuOH as well as traces of unreacted t-BuOOH. The remaining solid was washed three times with 20 ml ether and the ether solution was dried on magnesium sulfate and evaporated under reduced pressure: a liquid residue was obtained and analyzed by

GLC–MS (filled column, Carbowax 10% 20M, 3 m; oven, programmed from 100 to 200°C, 4 °C min^{-1}; source, 200 °C). The observed fragmentation was in all points similar to that of a disulfide [$(MeOCOCH_2S)_2$] sample. A 2 g portion of the solid residue, washed and dried under vacuum, were treated with 20 ml of a 50% HCl solution in water, under stirring, for 2 h. The mixture was then extracted with 100 ml ether and the organic phase, washed to neutrality, was dried over magnesium sulfate. After filtration and evaporation under reduced pressure 1.5 g of yellow solid was obtained. This solid was treated with 20 ml of a 1 M solution of propylmagnesium bromide in ether. After hydrolysis, decantation, drying and solvent evaporation, 1 g of a colorless liquid was obtained. It was identified by GLC (capillary column, DB1, 2 m; oven, programmed from 50 to 200 °C, 4 °C min^{-1}) as dibutyldipropyltin by comparison with an authentic sample prepared similarly from 1 g of pure Bu_2SnCl_2.[16]

From BuSn(S)SBu (10)

To 3.38 g (11.3 mmol) of **10**, 4.58 g (50.8 mol) of t-BuOOH was added at room temperature through a syringe pump. At the end of the addition the mixture was heated at 40 °C for 15 min and then cooled down. The volatile compounds (2.67 g) were trapped, under reduced pressure, at liquid nitrogen temperature. GLC analysis showed that they were mainly t-BuOH and traces of t-BuOOH. The residue was a yellow oil which, kept in solution with 50 ml ether, slowly gave a yellow precipitate. After filtration and Soxhlet extraction with ether, the analysis of the residue (two independent analyses) gave: C, 20.62, 21.12; H, 4.87, 4.46; O, 20.61, 19.07; S, 9.38, 9.44; Sn, 46.16, 44.62%. The evaporation of the extraction solvent yielded 1.55 g of a liquid for which MS showed exactly the pattern of Bu_2S_2.[17] The solid was finally treated by an excess of propylmagnesium bromide (1 M in ether) and gave an alkylated product whose retention time (GLC: capillary column, DB1, 25 m; 50–200 °C; 4 °C min^{-1}) was identical to that of a sample of $BuSn(C_3H_7)_3$[16] synthesized from $BuSnCl_3$ and a solution of Grignard reagent.

Acknowledgements The authors thank Elf–Atochem and Elf–Atochem North America for funding this research and the Conseil Régional d'Aquitaine for its participation in the purchase of part of the necessary equipment. They dedicate this work to the memory of Dominique Rancèze.

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