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THE INFLUENCE OF THE ORGANIC GROUPS ON THE EFFECTIVENESS OF ORGANOTIN bis (ISOOCTYL THIOGLYCOLATES) AS THERMAL STABILIZERS FOR PVC

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Abstract—A series of dialkyl- and diaryl-tin bis (isooctyl thioglycolate)s were prepared and their ability to inhibit the thermal degradation of PVC examined. There were no simple correlations between electronic and steric effects of the tin-bound organic groups and stabilizer activity. Some of the less effective substituted-alkyltin and aryltin compounds were shown to be susceptible to Sn—C bond cleavage by hydrogen chloride.

INTRODUCTION

Many of the organotin compounds currently in use for the stabilization of PVC against thermal decomposition are dialkyltin bis(isooctyl thioglycolate)s*, $R_2Sn(SCH_2COOC_8H_{17}-i)_2$ R = Me, *n*Bu or n-C_8H_{17}. Considerable progress has been made in understanding the mechanism of stabilization [1, 2] and the function of the thioglycolate residues is reasonably clear [3]. The present work is concerned with the effect of variations in the organic groups R on the stabilizer efficiency. By synthesizing a range of alkyl- and aryl-tin bis(isooctyl thioglycolate)s showing various electronic and steric effects and examining their stabilizing ability under standard conditions, it was hoped that further information would be obtained on the mechanism of stabilization.

RESULTS AND DISCUSSION

Most of the organotin stabilizers were prepared by standard methods summarized in Eqns (I)–(III).

$$4RMgX + SnCl_4 \rightarrow R_4Sn + 4MgXCl \qquad (I)$$

$$(X = Cl, Br \text{ or } I)$$

$$R_4Sn + SnCl_4 \rightarrow 2R_2SnCl_2 \qquad (II)$$

$$R_2SnCl_2 + 2NaSCH_2COOC_8H_{17}-i \rightarrow R_2Sn(SCH_2COOC_8H_{17}-i)_2 + 2NaCl \qquad (III)$$

Tetra *o*-fluorophenyltin was obtained using *o*-fluorolithiobenzene (from *o*-bromofluorobenzene and *n*-butyllithium–TMED complex). Heating equimolar amounts of tetrakis (trimethylsilylmethyl)tin and tin(IV) chloride gave only Tris (trimethylsilylmethyl)tin chloride. However, the diiodide was obtained by heating the tetrakis compound with iodine. Dibenzyltin dichloride and bis(2-ethoxycarbonylethyl)tin dibromide were prepared by direct reaction between tin metal and, respectively, benzyl chloride [4] and ethyl 3-bromopropanoate [5]. All the dihalides were purified by standard methods and some of the new compounds characterized as 2,2'bipyridyl adducts. Reaction(III) generally gave the required products in good yield but prolonged heating of bis(*o*-methoxyphenyl)-tin dichloride with sodium isooctyl thioglycolate in methanol gave bis(*o*-methoxyphenyl)tin bis(methyl isooctylthioglycolate) instead of the required product. (The powerful catalytic effect of the *o*-methoxyphenyltin compounds in promoting transesterification with the solvent has been discussed elsewhere [6]). The compounds tested as PVC stabilizers are shown in Table 1; they are all oils which decomposed on attempted distillation.

PVC was treated with 2% of each stabilizer as well as plasticizer and lubricant in a hot roll mill and the resulting sheet aged in an oven at 195° with samples being withdrawn at intervals and examined for colour development. Scrutiny of the specimens and the data in Table 1 show that there was little to choose between the very effective di-*n*-alkyltin compounds from methyl to octyl. This group includes several compounds in commercial use and all are highly successful in inhibiting discolouration. Even after 90 min at 195°, several of the brown samples retain some transparency. Introducing the branched *t*-butyl groups effects a dramatic fall in stabilizing power and after only 30 min the sample is a darker colour than any of the *n*-alkyl analogues after 90 min. Simple electronic effects do not explain why the *t*-butyltin compound is less effective than the *n*-alkyltins. Although replacement of one hydrogen by methyl in going from R=Me to R=Et effects a marginal improvement; replacement by the more powerful donor trimethylsilyl group in $R{=}Me_3SiCH_2$ give a much poorer stabilizer. However, replacement of a methyl hydrogen by electron-withdrawing bromine or phenyl in $R{=}BrCH_2$ and $PhCH_2$ gives even less effective compounds. Inferior stabilization again results if the electronegative substituent is placed in the β-position e.g. $R{=}PhCH_2CH_2$. Steric considerations may be more important, though here also no simple correlation exists and isopropyltin compounds are very effective [7].

Turning to the aryltins, although less effective than the alkyl compounds, diphenyltin bis(isooctyl thiogly-

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* The term "isooctyl" derives from a commercial available mixture of C_8 alcohols in which 2-ethylhexanol predominates.

Table 1. Organotin bis(isooctyl thioglycolate)s, $R_2Sn(SCH_2COOC_8H_{17}-i)$ tested as thermal stabilizers for PVC. 2% of stabilizers introduced using hot mill. Samples then aged at 195°

R	Time for first perceptible colour (min)	Time for sample to become black or dark brown (min)
Me	50	80
Et	60	80
Pr	40	90
Bu	40	70
t-Bu	20	30
C_8H_{17}	40	70
Me_3SiCH_2	20	50
$PhCH_2$	20	30
$BrCH_2$	0*	0*
$PhCH_2CH_2$	20	50
$EtOCOCH_2CH_2$	20	40
Ph	20	50
p-$MeOC_6H_4$	10	10
p-$PhOC_6H_4$	10	10
p-ClC_6H_4	10	30
p-$CF_3C_6H_4$	10	40
o-$MeOC_6H_4$†	20	20
o-$PhOC_6H_4$	20	40
o-FC_6H_4	20	30
No stabilizer	0*	0*

* Discolouration had occurred during milling.

† Corresponding times for bis(*o*-methoxyphenyl)tin bis(methyl thioglycolate) 10, 20.

colate) does inhibit discolouration. The remaining entries in Table 1 show that substitution in either the ortho or para positions by electron-donating or electron-withdrawing groups reduced the stabilizer activity. The marked loss of activity on going from R=alkyl → Ph → *p*-$MeOC_6H_4$ is paralleled by increasing ease of fission of Sn—C bonds by protic acids. The latter proceeds by electrophilic attack of a proton on the tin bound carbon atom [8].

Most of the results in Table 1 can be explained in terms of an increased tendency of some compounds to undergo Sn—C fission by hydrogen chloride envolved during the degradation. Although reaction (IV) normally occurs during stabilization [1]

$$R_2Sn(SCH_2COOC_8H_{17}-i)_2 + 2HCl \longrightarrow R_2SnCl_2 + 2i\text{-}C_8H_{17}OCOCH_2SH \quad \text{(IV)}$$

if it were accompanied by Sn—C fission, the powerfully prodegradant Sn(IV) chloride would be produced [9, 10]. To test this idea, some representative stabilizers were treated with excess dry hydrogen chloride at ~180°. The results are given in Table 2 from which it is clear than an efficient dialkyltin compound does not undergo Sn—C fission. The less effective phenyl-, *o*-methoxyphenyl, benzyl and ethoxycarbonylethyl–tin compounds show partial cleavage of tin carbon bonds, while one of the worst stabilizers, bis(*p*-methoxyphenyl) tin bis(isooctyl thioglycolate), was entirely converted to tin (IV) chloride under the same conditions. The *o*-methoxyl and especially the *o*-phenoxyl compounds are markedly better stabilizers than the corresponding *p*-substituted derivatives. This may be due to steric hindrance to fission of the Sn—C bond.

These results show that the nature of the tin-bound organic group exerts a profound effect on the stabilizing efficiency of organotin bis(isooctyl thioglycolate)s. All of the compounds examined, except the bis(bromomethyl)tin compound, have stabilizing activity with the di(*n*-alkyl)tin compounds being most effective. The principal reason for the reduced stabilizer activity in the aryl- and substituted alkyltins appears to be that these compounds are susceptible to carbon-tin bond cleavage by hydrogen chloride, a reaction which produces the prodegradant tin (IV) chloride.

EXPERIMENTAL

Tetraalkyl- and tetraaryltin compounds

The following compounds were made by standard procedures. (*p*-$MeOC_6H_4)_4Sn$, m.p. 132–134.5°; (lit. [11] 134.8°), (*p*-$ClC_6H_4)_4Sn$; m.p. 195–197°; (lit. [12] 197–198°), (*p*-$CF_3C_6H_4)_4Sn$; m.p. 147–148°; (lit. [13] 150–150.7°), *n*-Pr_4Sn; b.p. 52–54°/0.7 mm; (lit. [14] b.p. 116°/13 mm), $(Me_3SiCH_2)_4Sn$; b.p. 87–90°/0.01 mm; (lit. [15] b.p. 94°/0.2 mm), (*p*-$PhOC_6H_4)_4Sn$; m.p. 171–173°; (lit. [16] 171°), $(PhCH_2CH_2)_4Sn$; purified by column chromatography n_D^{25} 1.5909 (Found, C, 70.9; H, 6.7. $C_{32}H_{36}Sn$ calc.: C, 71.3; H, 6.7% (lit. [17] b.p. 288°/12 mm), (*o*-$MeOC_6H_4)_4Sn$; m.p. 173–175; (lit. [18] 172–173°).

Tetrakis (o-*fluorophenyl*)*tin*

To a stirred solution containing 1,2-bis dimethylamino) ethane (7.44 g, 0.68 mol) and *n*-butyllithium (4.10 g, 0.064 mol) in hexane under nitrogen at −78° was added *o*-bromofluorobenzene (11.2 g, 0.064 mol) in ether (80 cm^3) during 15 min. Stirring and cooling were maintained for a further 15 min and stannic chloride (4.17 g, 0.016 mol) in

Table 2. Reaction between organotin bis(isooctyl thioglycolate)s, $R_2Sn(SCH_2COOC_8H_{17})_2$, and excess hydrogen chloride in refluxing *o*-dichlorobenzene (b.p. 179°)

Starting material	Reaction products
R =	
Bu	Bu_2SnCl_2
Ph	Ph_2SnCl_2, $PhSnCl_3$, $SnCl_4$
p-$MeOC_6H_4$	$SnCl_4$
o-$MeOC_6H_4$	(*o*-$MeOC_6H_4)_2SnCl_2$, *o*-$MeOC_6H_4SnCl_3$, $SnCl_4$
$PhCH_2$	$(PhCH_2)_2SnCl_2$, $PhCH_2SnCl_3$, $SnCl_4$
$EtOCOCH_2CH_2$	$(EtOCOCH_2CH_2)_2SnCl_2$, $EtOCOCH_2CH_2SnCl_3$, $SnCl_4$

benzene (50 cm^3) added and the mixture allowed to reach room temperature. Hydrolysis and conventional isolation gave, after recrystallization (benzene/light petroleum) colourless crystals (3.0 g, 38%) m.p. 136–138° (Found: C, 58.35; H, 3.45. $C_{24}H_{16}F_4Sn$ calc.: C., 57.8, H, 3.2%).

Dialkyl- and diaryltin dihalides

The following compounds were made by standard proprocedures. $(n\text{-}Pr)_2SnCl_2$ m.p. 79–80°; (lit. [19] 79.5–80.5), $(t\text{-}Bu)_2SnCl_2$; m.p. 40–41°; (lit. [20] 42–43°), $(PhCH_2)_2SnCl_2$; m.p. 161°; (lit. [4] 163–164°), $(EtOCOCH_2CH_2)_2SnBr_2$; m.p. 99–100° (lit. [5] 99–101.5°), $(BrCH_2)_2SnBr_2$; m.p. 85.5–87°; (lit. [21] 87°), $(p\text{-}MeOC_6H_4)_2SnCl_2$; m.p. 81.5–83°; (lit. [22], 76°), $(p\text{-}ClC_6H_4)_2SnCl_2$; m.p. 82–83°; (lit. [23], 88°), $(o\text{-}PhOC_6H_4)_2SnCl_2$; m.p. 97–98°; (lit. [24] 98–99°), $(o\text{-}MeOC_6H_4)_2SnCl_2$; m.p. 113–114.5° (lit. [25] 113°).

*Bis(*p*-trifluoromethylphenyl)tin dichloride*

Tetrakis(*p*-trifluoromethylphenyl)tin (3.49) g and stannic chloride (1.30 g) were heated for 4 hr at 180–185°. After crystallization from light petroleum the product was obtained as colourless crystals: (2.80 g, 54%) m.p. 80.5–82° (Found: C, 35.0; H, 1.6; $C_{14}H_8F_6Cl_2Sn$ calc.: C, 35.0; H, 1.7%). Treatment with 2,2′-bipyridyl gave the 1:1 adduct as colourless crystals (79%) m.p. 255–257° (Found: C, 45.5; H, 2.5; N, 4.6. $C_{24}H_{16}F_6Cl_2N_2Sn$ calc.: C, 45.3; H, 2.5; N, 4.4%).

*Bis(*p*-phenoxyphenyl)tin dichloride*

This was prepared by the above method in 47% yield and had m.p. 61–63° (Found: C, 54.6; H, 3.3; $C_{24}H_{18}Cl_2O_2Sn$ calc.: C, 54.6; H, 3.4%). The 2,2′-bipyridyl adduct obtained in 58% yield had m.p. 199–201° (Found: C, 59.5; H, 3.7; N, 3.95. $C_{34}H_{26}Cl_2N_2O_2Sn$ calc.: C, 59.7: H, 3.8; N, 4.1%).

Bis(2-phenylethyl)tin dichloride

This was prepared by the same method in 70% yield and had m.p. 58–59.5° (Found: C, 48.0; H, 4.6; $C_{16}H_{18}Cl_2Sn$ calc.: C, 48.0; H, 4.5%). The 2,2′-bipyridyl derivative (59% yield) had m.p. 202–204° (Found: C, 56.5; H, 5.0; N, 5.2. $C_{26}H_{26}Cl_2N_2Sn$ calc.: C, 56.15; H, 4.7; N, 5.0%).

*Bis(*o*-fluorophenyl)tin dichloride*

Prepared by the same method (29% yield) m.p. 67–69° (Found: C, 38.4;, H, 2.2. $C_{12}H_8Cl_2F_2Sn$ calc.: C, 37.9; H, 2.1%).

Attempted preparation bis(trimethylsilylmethyl)tin dichloride

Heating a mixture of tetrakis(trimethylsilylmethyl)tin (4.67 g, 0.01 mol) and stannic chloride (2.61 g, 0.01 mol) for 7 hr at 185–190° gave a brown solid from which, by repeated crystallization from light petroleum, was obtained tris(trimethylsilylmethyl)tin chloride (1.5 g, 27%) m.p. 94.5–96 (lit. [26] 94–96°) (Found: C, 34.5; H, 7.7. $C_{12}H_{33}ClSi_3Sn$ calc.: C, 34.7; H, 8.0%).

Bis(trimethylsilylmethyl)tin diiodide

A mixture of iodine (2.54 g, 0.01 mol and tetrakis(trimethylsilylmethyl)tin (2.34 g, 0.005 mol) was sealed in an evacuated Carius tube and heated for 12 hr at 170–190°. The product was distilled under reduced pressure to give a yellow oil (2.26 g) which slowly solidified m.p. 32–35° (lit. [27] 34.6–35.4°) (Found: C, 17.3; H, 3.7. $C_8H_{22}I_2Si_2Sn$ calc.: C, 17.6; H, 4.1%).

Dialkyl- and diaryltin isooctylthioglycolates

The following procedure is typical. Diphenyltin dichloride (5.16 g, 0.015 mol) in dry benzene (200 cm^3) was added to a stirred refluxing solution containing sodium (0.69 g, 0.03 mol) and isooctylthioglycolate (6.12, 0.03 mol) in dry methanol (50 cm^3). Stirring and refluxing were continued for 4 hr; the precipitated sodium chloride was removed (filtration and centrifuging); evaporation of the solvent under reduced pressure gave the product as a yellow oil (9.12 g, 90%), n_D^{20} 1.5410 (lit. [28] $n_D^{25} = 1.5448$). Attempted distillation under reduced pressure caused decomposition. (Found; C. 56.5; H, 7.4. $C_{32}H_{48}O_4S_2Sn$ Calc.: C, 56.6; H, 7.1%). All of the compounds in Table 3 were prepared by the same method except where noted below.

Table 3. Dialkyl- and diaryltin bis(isooctyl thioglycolate)s*†‡

R in $R_2Sn(SCH_2COOC_8H_{17}\text{-}i)_2$	% Yield	n_D^{20}
Me	86	1.5071
Et	90	1.5045
n-Pr	93	1.5090
t-Bu	87	1.5164
Me_3SiCH_2§	60	1.5120
$PhCH_2$	87	1.5330
$BrCH_2$‖	93	1.5030
$PhCH_2CH_2$	41	1.5203
$EtOCOCH_2CH_2$‖	44	1.5080
Ph	90	1.5410
p-$MeOC_6H_4$	92	1.5584
p-$PhOC_6H_4$	73	1.5840
p-ClC_6H_4	94	1.5625
p-$CF_3C_6H_4$	90	1.5188
o-$MeOC_6H_4$	78	1.5576
o-$PhOC_6H_4$	96	1.5748
o-FC_6H_4	89	1.5520

* Made from the organotin dichlorides unless otherwise noted.

† Although made from pure organotin dihalides, all these products were crude and were not purified before being tested as PVC stabilizers.

‡ The compounds R = *n*-Bu and R = *n*-C_8H_{17} were kindly donated by Messers Albright & Wilson Ltd and were used as supplied.

§ Made from the corresponding diiodide.

‖ Made from the corresponding dibromide.

*Bis(*o*-methoxyphenyl)tin bis(methyl thioglycolate)*

Bis(*o*-methoxyphenyl)tin dichloride (4.04 g, 0.01 mol) in dry benzene (60 cm^3) was added to a refluxing, stirred solution of sodium (0.46 g, 0.02 mol) and isooctyl thioglycolate (4.09 g, 0.02 mol) in dry methanol (50 cm^3). After stirring for 20 hr at reflux temperature, the mixture was treated as above to give the organotin bis (methyl thioglycolate) as a pale yellow oil (4.5 g, 83%), n_D^{20} 1.6090. The N.M.R. spectrum showed a multiplet (aromatic protons) 2.30–3.20 τ, singlet ($CH_3OC_6H_4$), 6.30 τ, singlet ($S—CH_2—COO$) 6.75 τ. Absence of broad multiplet absorption in the 8.00–9.40 τ region (shown by all the $R_2Sn(SCH_2COOC_8H_{17})_2$ compounds) indicated the absence of the isooctyl group. An additional singlet at 6.55 τ of the same intensity as the methoxyl signal showed the presence of the extra methyl (ester) group (Found: C. 44.2; H, 4.4. $C_{20}H_{24}O_6S_2Sn$ calc.: C, 44.2; H, 4.5%).

*Bis(*o*-methoxyphenyl)tin bis(isooctyl thioglycolate)*

The reaction time in the above experiment was reduced from 20 to 0.5 hr. The oily product then showed the N.M.R. absorption bands expected for the isooctyl group in the region 8.10–9.30 τ but the singlet assigned to the ester methyl group at 6.55 τ was absent (Found: C, 52.7: H, 7.2 $C_{34}H_{52}O_6S_2Sn$ calc.: C, 55.2, H, 7.1%). Attempts to purify were unsuccessful.

Evaluation of organotin bis(isooctyl thioglycolates) as thermal stabilizers for PVC

Poly(vinyl chloride (10.00 g Corvic D 65/CX a suspension polymer supplied by ICI Plastics Division), organotin bis(isooctyl thioglycolate) (0.20 g), silicone oil (0.05 g) and diisooctyl phthalate (4.00 g) were mixed mechanically on a rollamixer for 20 hr. Milling for 6–8 min at 185–190° in a RAPRA micro-mill generated a film, thickness 1.5 mm, pieces of which were heated for various periods at 195° in a specially modified oven. A dibutyltin bis(isooctyl thioglycolate) standard was included with each test to ensure reproducibility of conditions.

Reaction between diphenyltin bis(isooctyl thioglycolate) and hydrogen chloride

Over a period of 2 hr an excess of anhydrous hydrogen chloride (4.65 g, 0.13 mol was passed through a solution of diphenyltin bis(isooctyl thioglycolate) (1.70 g, 0.03 mol) in *o*-dichlorobenzene (50 cm^3) which was boiling under reflux. Unreacted HCl was removed by passing dry N_2 and the solution examined by thin layer chromatography on silica gel using chloroform/acetic acid (12:1) for development. The tin compounds found, together with the results for identical experiments carried out with other organotin bis(isooctyl thioglycolate)s, are shown in Table 2.

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