The Mechanism of Stabilization of Poly(vinyl Chloride).   II.   Cleavage of Organotin Sulfur Compounds by Anhydrous Hydrogen Chloride

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Synopsis

A number of organotin compounds of the type R_nSnY_{4-n}, where R = alkyl or aryl; Y = alkylthio, arylthio or carbothiolate; and $n = 1, 2, 3$ have been prepared and treated with hydrogen chloride at 180°C in o-dichlorobenzene solution.   The organotin compounds were also tested at 190°C as thermal stabilizers for PVC.   Cleavage of tin–carbon bonds by hydrogen chloride was demonstrated in some cases by analysis of the organotin–hydrogen chloride reaction products.   The formation of monoalkyl(aryl)tin chlorides or stannic chloride, or both, in the model system was shown to correspond to a catastrophic mode of degradation in the polymer.   The use of stabilizers with fewer than two alkyl or aryl groups on tin also gave this mode of degradation.

INTRODUCTION

As a part of our investigation of the mechanism of stabilization of poly-(vinyl chloride) by organotin compounds, we wished to examine the reaction between organotin sulfur compounds (I–VIII) and anhydrous hydrogen chloride in a chlorinated hydrocarbon solvent at temperatures used in the commercial processing of stabilized PVC.   Hydrogen chloride may attack one or more tin–sulfur bonds, and tin–carbon cleavage may occur or both types of cleavage may take place together.   We have shown recently that aqueous hydrochloric acid cleaves tin–sulfur bonds under mild conditions.[1]   The relative ease of reaction was determined by the acidity of the thiol or carbothiolic product, and the nature of these products was compared with the efficiency of the organotin reactant as a PVC stabilizer.

The cleavage of tin–carbon bonds by acids, and in particular hydrogen chloride, is well documented,[2] but the cleavage of the tin–carbon bonds in an organotin–PVC system has been the subject of only a single report. Minsker and co-workers[3] treated PVC with tri-n-butylstannyl lithium and triphenylstannyl lithium to replace some of the chlorine atoms with the

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organotin groups.   They observed tin–carbon cleavage when the polymer was heated or when a solution of the modified PVC in tetrahydrofuran was treated with hydrogen chloride.

In an investigation of the thermal degradation of PVC containing di-alkyl- or diaryltin thiolates,[4] we observed in some cases a premature and sudden degradation of the polymer, with swelling, blackening, and complete loss of mechanical properties (catastrophic degradation).   This breakdown was often preceded by a blue color and was similar to the degradation caused by the presence in the polymer of strong Lewis acids, such as zinc chloride or stannic chloride.   The time under thermal stress required for catastrophic degradation of the PVC was short when the stabilizer contained the alkyl or aryl groups that were shown to cleave rapidly from tin in previous work on the attack by halogens or acids on the corresponding tetraorganotin compounds.[2,6]   Alkyl groups that were slow to cleave from tetralkyltins gave stabilizers which did not promote rapid catastrophic degradation.   The importance of nucleophilic assistance in the electrophilic cleavage of carbon–tin bonds has been suggested by previous work.[6,7] o-Dichlorobenzene is a solvent of low nucleophilicity; it is probably similar to PVC in this respect, and it was chosen partly on this basis as a solvent for the present study.

We report here an investigation of the attack of anhydrous hydrogen chloride on some organotin sulfur compounds in o-dichlorobenzene at $180°C$. Compounds with one, two, and three alkyl or aryl groups were used, and the organotin reaction products were analyzed by alkylation with an excess of Grignard reagent and subsequent estimation by gas–liquid chromatography.   The same organotin compounds were evaluated as PVC stabilizers. Octadecanol and octadecanoic acid were used as lubricants in the stabilized polymer, and the effect of these compounds on the model reaction was also examined.

Although the model system described here provides a valuable medium for convenient examination of some reactions that may occur in an organotin-stabilized polymer, the results obtained cannot be applied directly to the more complex polymer system without modification.   However, model compound studies linked closely to investigations on the polymer will provide the most useful results.

EXPERIMENTAL

Reaction Between Di(phenylthio)di-*n*-butyltin and Hydrogen Chloride

Di(phenylthio)di-*n*-butyltin (0.5 g) was dissolved in o-dichlorobenzene (5 ml), and the solution was introduced into a reaction tube fitted with a gas inlet and reflux condenser.   A slow stream of dry hydrogen chloride was passed into the solution which was heated to reflux on an oil bath. The reflux and the passage of hydrogen chloride was continued for 1 hr. The hydrogen chloride stream was the replaced by nitrogen for 15 min, and heating was discontinued.   The reactions between other organotin compounds and hydrogen chloride were carried out in the same way.

Detection of Organotin Chlorides in the Reaction of Organotin Thiolates with Anhydrous Hydrogen Chloride

By Gas–Liquid Chromatography. The crude reaction mixture from the last experiment was purged with nitrogen to remove hydrogen chloride, and the products were separated by gas–liquid chromatography on a 5-ft stainless steel column packed with 10% SE30 on Celite. Di-n-butyltin dichloride was detected together with thiophenol. Di(phenylthio)dimethyltin was treated with hydrogen chloride as in the previous experiment and then subjected to GLC analysis. Dimethyltin dichloride, methyltin trichloride, and thiophenol were detected. Interference was observed between dimethyltin dichloride and thiophenol.

Di(phenylthio)diphenyltin and phenylthiotriphenyltin gave diphenyltin dichloride and phenyltin trichloride in each case together with thiophenol.

Tri(benzylthio)-n-butyltin gave n-butyltin trichloride and benzylmercaptan, although mutual interference was observed. This interference made the direct quantitative estimation of organotin chlorides difficult. It was convenient to determine these compounds as the tetraorganotin derivatives after reaction with the Grignard reagent as described below.

By Complex Formation. The reaction mixture from the treatment of di(phenylthio)di-n-butyltin with hydrogen chloride was purged with nitrogen to remove hydrogen chloride and an excess of 2,2-dipyridyl in ether was added. The white precipitate of the complex $Bu_2^nSnCl_2(bipy)$ was collected by filtration and identified by melting point and mixed melting point with an authentic sample. Bu^nSnCl_3, Me_2SnCl_2, and Ph_2SnCl_2 from the appropriate reactions formed complexes with bipyridyl in the same way.

Reactions of Alkyltin Thiolates with Grignard Reagent

Dimethyltin dithiobenzoate was dissolved in anhydrous ether, and an excess of n-butylmagnesium bromide was added. The reaction mixture was allowed to stand at room temperature for 30 min and was analyzed for tetraalkyltin compounds by gas–liquid chromatography. Only di-n-butyldimethyltin was detected. A similar reaction with tri(phenylthio)-methyltin gave only tri-n-butylmethyltin.

Detection and Analysis of the Organotin Chlorides in the Model Experiments

Attempts to detect the organotin chlorides by gas–liquid chromatography were unsuccessful. The method of Jitsu et al.[8] was adopted, in which the chlorides were detected and analyzed as tetra(organo) tin compounds.

A solution of n-propylmagnesium chloride was prepared from n-propyl chloride (39.3 g, 0.5 mole) and magnesium (12.2 g, 0.5 mole) in ether (200 ml). Ether was then added to give a final volume of 250 ml. The n-propylmagnesium chloride solution (25 ml) was added slowly to the o-dichlorobenzene solution of the reaction product from the reaction of hydrogen chloride on di(phenylthio)di-n-butyltin. After 30 min at room temperature, the excess n-propylmagnesium chloride was decomposed by the

TABLE I
Products from the Reaction of Some Organotin Compounds with
Dry Hydrogen Chloride in o-Dichlorobenzene at 180°C

Organotin compound	R' of R'MgX	Reaction products, %				GLC Column temp., °C
		R_3SnCl	R_2SnCl_2	$RSnCl_3$	$SnCl_4$	
MeSn(SPh)$_3$ (I)	Bu[a]	—	—	100	0	206
MeSn(SPh)$_3$ + C$_{18}$H$_{37}$OH[a]	Bu^n	—	—	90	10	206
Me$_2$Sn(SPh)$_2$ (II)	Bu^n	—	100	0	0	206
Me$_2$Sn(SPh)$_2$ + C$_{18}$H$_{37}$OH[a]	Bu^n	—	95	5	0	206
Me$_2$Sn(SCOPh)$_2$ (III)	Bu^n	—	85	10	5	206
Me$_2$Sn(SCOPh)$_2$ + C$_{18}$H$_{37}$OH[a]	Bu^n	—	85	15	0	206
Pr$_2^i$Sn(SCH$_2$Ph)$_2$ (IV)	Bu^n	—	100	0	0	206
Pr$_2^i$Sn(SCH$_2$Ph)$_2$ + C$_{17}$H$_{35}$CO$_2$H[a]	Bu^n	—	95	5	0	206
Bu^{n}Sn(SCH$_2$Ph)$_3$ (V)	Pr^n	—	—	100	0	202
Bu$_2^n$Sn(SPh)$_2$ (VI)	Pr^n	—	100	0	0	202
Ph$_3$SnSPh (VII)	Pr^n	0	70	25	5	235
Ph$_3$SnSPh + C$_{18}$H$_{37}$OH[a]	Pr^n	0	40	35	25	235
Ph$_2$Sn(SPh)$_2$ (VIII)	Pr^n	—	25	70	5	235
Ph$_2$Sn(SPh)$_2$ + C$_{18}$H$_{37}$OH[a]	Pr^n	—	10	55	35	235
Ph$_2$Sn(SPh)$_2$ + C$_{17}$H$_{35}$CO$_2$H[a]	Pr^n	—	0	0	100	235

[a] 0.3 g of a poly(vinyl chloride) lubricant added.

addition of methanol (10 ml). The filtered solution was reduced in volume to 2 ml. The gas phase chromatogram obtained from a 5-ft column showed only the presence of di-n-butyldi-n-propyltin. The peak was identified by comparison with a chromatogram obtained by treating di-n-butyltin chloride with n-propylmagnesium chloride as above.

The products of the reaction between the other organotin sulfur compounds and hydrogen chloride were similarly analyzed using the Grignard reagent. Table I records the results and some experimental details.

Evaluation of Organotin Compounds as Thermal Stabilizers for PVC

The organotin sulfur compounds were tested as stabilizers for PVC by milling each in turn (2×10^{-3} mole) into 100 g of PVC resin and 0.5 g of lubricant. The rate of color formation in polymer discs at constant temperature was followed.[9] Table II lists the time taken for the discs to degrade catastrophically (blue-black color suddenly appearing) or for the discs to degrade noncatastrophically to a dark-brown color, at 190°C. Table II also lists the results for several organotin sulfur compounds not listed in Table I but which cause catastrophic degradation.

Detection and Analysis of the Organotin Chlorides in Degraded PVC

Phenylthiotriphenyltin (5 g) was milled with PVC (50 g) and stearic acid (0.5 g) at 150°C for 5 min. Discs from the milled polymer were degraded at 180°C for 4.5 hr, and 2 g of polymer was then extracted with tetra-

TABLE II
Catastrophic and Noncatastrophic Degradation of PVC Stabilized with Organotin
Compounds and in the Presence of Several Lubricants at 190°C

Organotin compound	Lubricant	Time to complete degradation, min	
		Catastrophic	Non-catastrophic
MeSn(SPh)$_3$ (I)	C$_{17}$H$_{35}$CO$_2$H	30	—
Me$_2$Sn(SPh)$_2$ (II)	C$_{17}$H$_{35}$CO$_2$H	—	40
Me$_2$Sn(SPh)$_2$ (II)	C$_{18}$H$_{37}$OH	—	45
Me$_2$Sn(SPh)$_2$ (II)	liquid paraffin	—	45
Me$_2$Sn(SCOPh)$_2$ (III)	C$_{17}$H$_{35}$CO$_2$H	—	40
Pr$_2^i$Sn(SCH$_2$Ph)$_2$ (IV)	C$_{17}$H$_{35}$CO$_2$H	—	40–45
Pr$_2^i$Sn(SCH$_2$Ph)$_2$ (IV)	C$_{18}$H$_{37}$OH	—	45
Pr$_2^i$Sn(SPh)$_2$ (IX)	C$_{17}$H$_{35}$CO$_2$H	30–30	—
Pr$_2^i$Sn(SPh)$_2$ (IX)	liquid paraffin		40
Bu^{n}Sn(SCH$_2$Ph)$_3$ (V)	C$_{17}$H$_{35}$CO$_2$H	30–35	—
Bu^{n}Sn(SCH$_2$Ph)$_3$ (V)	none	30–35	—
Bu$_2^n$Sn(SPh)$_2$ (VI)	C$_{17}$H$_{35}$CO$_2$H	—	40
Bu$_2^n$Sn(SPh)$_2$ (X)	C$_{18}$H$_{37}$OH	—	45
Bu$_2^t$Sn(SCH$_2$Ph)$_2$ (XI)	C$_{18}$H$_{37}$OH	35	—
Bu$_2^t$Sn(SCH$_2$Ph)$_2$ (XI)	C$_{17}$H$_{35}$CO$_2$H	25–30	—
Ph$_3$SnSPh (VII)	C$_{17}$H$_{35}$CO$_2$H	20–25	—
Ph$_2$Sn(SCOPh)$_2$ (XII)	C$_{17}$H$_{35}$CO$_2$H	15	—
(p-MeO,C$_6$H$_4$)$_2$Sn(SCOPh)$_2$ (XIII)	C$_{17}$H$_{35}$CO$_2$H	10	—
Sn(SPh)$_4$ (XIV)	C$_{17}$H$_{35}$CO$_2$H	10	—
Bu$_2^t$Sn(SCOPh)$_2$ (XV)	C$_{17}$H$_{35}$CO$_2$H	—	40
Ph$_2$Sn(SPh)$_2$ (VIII)	C$_{18}$H$_{37}$OH	35–40	—
Ph$_2$Sn(SPh)$_2$ (VIII)	C$_{17}$H$_{35}$CO$_2$H	25	—

hydrofuran (50 ml) at room temperature for 24 hr. The filtered solution was reduced in volume to 10 ml on the rotary evaporator and was treated with n-propylmagnesium chloride and analyzed by GLC as described above for the model experiments. The products characterized were diphenyltin dichloride (~5%), phenyltin trichloride (~5%), and tin(IV) chloride (80%). Di(phenylthio)diphenyltin was milled with PVC, degraded and analyzed as described in the previous experiment to give phenyltin trichloride (~5%) and tin(IV) chloride (90%).

Typical syntheses of the new compounds used in this investigation are described below.

Bis(4-methoxyphenyl)tin Di(thiobenzoate). Tetrakis(4-methoxyphenyl)tin (2.75 g, 5 mmole) and thiolbenzoic acid (1.4 g, 10 mmole) were mixed and heated on a steam bath for 20 min. The product was dissolved in benzene (5 ml) and precipitated by the addition of excess light petroleum. The dried crystals weighed 2.4 g (79%), mp 149–150°C.

ANAL. Found: C, 55.3%; H, 4.1%. Calcd for C$_{28}$H$_{24}$O$_4$S$_2$Sn: C, 55.4%; H, 4.0%.

Di(phenylthio)di(tert-butyl)tin. Di-t-butyltin dihydroxide (2.67 g, 10 mmole), benzenethiol (2.2 g, 20 mmole), and benzene (50 ml) were heated

at reflux for 1 hr. The water formed was removed by azeotropic distillation. The reaction mixture was then cooled and filtered, and the benzene was removed from the filtrate. Recrystallization from light petroleum gave di(phenylthio)di(*tert*-butyl)tin (3.38 g, 75%), mp 78–9°C.

ANAL. Found: C, 49.5%; H, 3.8%; Calcd for $C_{20}H_{28}S_2Sn$: C, 49.5%; H, 3.9%.

The same preparative method was used for the compounds in Table III.

TABLE III
Microanalytical Results for Some Organotin Compounds

Organotin compound	Found, %		Calculated, %	
	C	H	C	H
$Pr_2{}^iSn(SCH_2Ph)_2{}^a$	52.8	6.2	53.2	6.3
$Bu^nSn(SCH_2Ph)_3{}^a$	55.1	5.5	55.1	5.4
$Bu_2{}^tSn(SCH_2Ph)_2{}^b$	55.0	6.6	55.1	6.7
$Me_2Sn(SCH_2Ph)_2{}^a$	49.1	5.0	48.6	5.1

a Liquid.
b Solid, mp 50–51°C.

Phenylthiotriphenyltin,[10] *di(phenylthio)dimethyltin,*[11] *di(phenylthio)di-(n-butyl)tin,*[12] *di(benzylthio)di(n-butyl)tin,*[12] *diphenyltindi(thiobenzoate),*[13] *di-(benzylthio)diphenyltin,*[14] *tetra(phenylthio)tin,*[15] *tri(phenylthio)methyltin,*[1] *di-methyl di(thiobenzoate),*[1] *di(phenylthio)diphenyltin,*[1] *di(phenylthiodi(isopro-pyltin,*[1] and *di*(tert-*butyl)tin di(thiobenzoate)*[1] were prepared as described previously.

DISCUSSION

The results in Table I show that cleavage of both tin–carbon and tin–sulfur bonds in alkyltin thiolates and carbothiolates took place when the organotin compounds were heated in *o*-dichlorobenzene in the presence of dry hydrogen chloride. Compounds with one, two, or three carbon–tin bonds each showed cleavage of the organic groups, and this suggests that the reaction is general under these conditions. The yields of cleavage products were dependent on the nature of the organic groups attached to tin. Similar sequences have been reported[6,16] for the halodemetallation of mixed tin tetraalkyls in solvents of low nucelophilicity. The addition of a compound of potentially high nucleophilic character, such as octadecanol or octadecanoic acid, to the model system caused an increase in the rate of cleavage of the tin–carbon bonds. It has been shown that alcohols and acids may offer nucleophilic assistance to the cleavage of tin–carbon bonds,[6,16] and the two PVC lubricants probably participated in the same way. Octadecanoic acid was more effective than octadecanol in this respect. Methyl–tin cleavage was observed for the thiobenzoate (III) but not for the thiolate (II) (Table I), and this suggests that the thiobenzoic acid, formed initially from the ester (III), facilitated the subsequent cleavage of the carbon–tin bonds.

Table II shows the results obtained when PVC, stabilized by a number of organotin compounds, was thermally degraded. Two modes of degradation were observed, catastrophic and noncatastrophic (see above). Stabilizers (I, V, VII, and VIII) with one, two, or three organic groups on tin were associated with catastrophic degradation. Reference to Table I confirms that each of these compounds was cleaved predominantly to a mono-alkyltin or aryltin trichloride, or to stannic chloride or to a mixture of both in the model system. The time to catastropic degradation for polymer stabilized with the thiolate VIII was shortened by 10–15 min when octadecanoic acid replaced octadecanol as the lubricant. A similar effect was observed with stabilizer XI. It may be seen from Table I that under model conditions, tin–carbon cleavage in the thiolate (VIII) was facilitated when octadecanoic acid replaced octadecanol in nucleophilic assistance to bond cleavage.

Thus, it is clear that the formation of tin tri- or tetrachlorides in the model system is paralleled by factors that cause the catastrophic degradation of PVC. The simplest explanation of these observations is that tin tri- or tetrachlorides are formed in the polymer. This explanation has been tested by isolation of the organotin products from samples of catastrophically degraded polymer. The stabilizers VII and VIII each gave tin tetrachloride as the principal product together with small proportions of the trichloride in each case and the dichloride from VII, confirming extensive tin–carbon bond cleavage in PVC.

When replacement of organic groups on tin by chlorine did not go below R_2SnCl_2 (II, IV, and VI), or when not more than 10% $RSnCl_3$ and 5% $SnCl_4$ were formed (III, IV with octadecanoic acid), normal degradation was observed when the polymer was stabilized with these compounds. However, when breakdown of the stabilizer gave 25% or more of $RSnCl_3$ together with 5% or more of $SnCl_4$ (I, V, VII, VIII), then catastrophic degradation of the polymer occurred. The operation of additional factors in the polymer that cause catastrophic degradation cannot be excluded by these observations.

The following sequence may be drawn up to show the relative yields of tin–carbon bond cleavage products in o-dichlorobenzene from the diorganotin compounds II, III, IV, VI, and VIII: phenyl > isopropyl > methyl > n-butyl. The times for degradation of PVC stabilized with the diorganotin compounds II, III, IV, VI, VIII, IX, X, XI, XII, XIII, and XV increased in the order p-anisyl < phenyl < t-butyl < isopropyl < methyl < n-butyl. These are basically inductive sequences, and the similarity between the two reinforces the suggestion that the factors which contribute to carbon–tin cleavage in the model system are important in lowering the efficiency of the organotin stabilizer in PVC.

Polymer samples, with a representative selection of the stabilizers from Table II, were degraded thermally at 180°C, the temperature used in the model investigation. The results confirmed that the course of degradation paralleled that observed at 190°C, although the useful lifetime of the samples was doubled.

The practical importance of the cleavage reaction lies in the beneficial effects found when both monoalkyl and dialkyltin compounds were present as stabilizers in a PVC system.[17] The monoalkyltin imparted excellent resistance to discoloration of the polymer, but caused early catastrophic degradation, a phenomenon to be avoided in processing equipment. The dialkyltin compound imparted longer-term stability. Good dialkyltin stabilizers gave efficient resistance to discoloration for 15–20 min at 190°C, and the advantages of monalkyltin compounds were not significant within this time. It is useful to have present in the polymer a diorganotin stabilizer which suffers slow tin–carbon bond cleavage to form the monoalkyltin trichloride with its advantages, but still allows the polymer to degrade normally. A close approach to this ideal situation was found by using dimethyltin and diisopropyltin compounds to stabilize PVC against thermal degradation at 190°C. The claims of U.S. Pat. 3,507,827[18] appear to have been based upon this reaction. The patent claimed a stabilizer system which imparted resistance to early discoloration in the polymer when thermally stressed to a temperature greater than 180°C (350°F). Alkyl, cycloalkyl, and dicycloalkyltin compounds were specifically claimed.

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