

Mechanism of Stabilization of Poly(vinyl Chloride).

I. The Cleavage of Organotin Compounds by Aqueous Hydrochloric Acid

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Synopsis

A number of organotin compounds with the general formula R_nSnY_{4-n} where R = alkyl and aryl, Y = thiolate, carbothiolate, and carboxylate, and $n = 0, 1, 2, 3$ were cleaved with aqueous hydrochloric acid to give the corresponding organotin chlorides and thiols, carbothiolic acids or carboxylic acids. The organotin salts were also evaluated as thermal stabilizers for PVC, and their efficiency was compared with the nature of the aqueous acid cleavage products.¹

Introduction

Organotin compounds containing alkyl- or arylthio groups have been used since 1960 as thermal stabilizers for poly(vinyl chloride) (PVC).² They offer advantages in retaining efficiency at high processing temperatures, they show good compatibility with the resin, and color formation is gradual after the initial period of stabilization. These compounds inhibit the degradation by mechanisms which are not well understood,³ and it appears that there are several ways in which they may be active.⁴

The early suggestion that organotin compounds acted as scavengers for hydrogen chloride, by analogy with metal soap stabilizers, has now been questioned.⁵

It has also been proposed⁶ that degradation proceeded through a radical mechanism and that it was terminated by alkylation of a polymer radical with dibutyltin diesters. As an alternative, the work of Frye and others⁵ indicated that ester groups were retained in the polymer in preference to alkyl groups and that the esters were introduced by replacement of chlorine at active sites on the polymer. Onozuka⁷ has confirmed that organotin stabilizers react with model compounds which represent the active chlorine atoms on allylic and tertiary sites in the polymer chain. Two groups of investigators^{8,9} have demonstrated the substitution of mercaptides from organotin sulfur compounds into allylic chlorides, and evidence for the importance of the intermediate $R_2Sn(Cl)Y$ was obtained.⁸ Allylic rear-

rament was also observed,⁹ and elimination of hydrogen chloride from the model was shown to compete with substitution.⁸

The reaction half-lives for the loss of chlorine from an allylic model compound in the presence of a stabilizer have been correlated with efficiency of the stabilizer in PVC.⁸ Organotin thiolates and carbothiolates are highly reactive and may combine with other components of the degrading polymer system in addition to reactive sites on the polymer chain.¹⁰ It has been shown that organotin compounds of general formula R_2SnY_2 react with the hydrogen chloride liberated by the polymer,^{5,11} and we report an investigation of the products that may be formed in the reaction of compounds containing one, two, three, or four tin-sulfur bonds with hydrogen chloride under mild aqueous conditions. These conditions provide a convenient system for a preliminary examination of tin-sulfur bond cleavage although they do not represent a model for the polymer. An approximate model for the stabilizer-hydrogen chloride interaction in PVC is described in the succeeding paper.

EXPERIMENTAL

Typical syntheses of the new compounds used in this investigation are described below (see also Table I).

S-Acetyl-3-thiol-3-phenylpropionic Acid. Cinnamic acid (44.4 g, 0.3 mole) and thioacetic acid (50% in acetic acid, 45.8 g, 0.3 mole) were added to azobisisobutyronitrile (1.0 g) and the mixture was warmed to initiate the exothermic reaction. The mixture was cooled periodically to moderate the reaction. Finally, the reaction mixture was heated for 1 hr on the steam bath. The product was crystallized from benzene to give S-acetyl-3-thiol-3-phenylpropionic acid (57.1 g, 85%), mp 95–96°C (lit. 95–96°C).¹²

Dimethyltin Di(thiobenzoate) (II), Method a. Aqueous sodium thiobenzoate (10 ml, 5*M*) was stirred with dimethyltin dichloride (5.50 g, 25

TABLE I
Preparation, Physical Characteristics, and Microanalyses
for Some Organotin Compounds

Compound no.	Melting point (or boiling point), °C	Method of preparation	Found		Calculated	
			C, %	H, %	C, %	H, %
III	(174–176 at 0.6 mm)	b	51.3	5.8	51.3	5.7
X	70.5–71.5	b	54.1	5.9	53.9	6.0
XI	58–59	b	45.9	4.6	45.8	4.6
VIII	108–109	a	52.7	5.6	52.1	5.6
XVIII	92–93	a	51.6	4.4	51.1	4.1
XIX	(172–176 at 0.4 mm)	c	49.5	3.8	49.5	3.9
XII	89.5–90.5	b	50.8	5.8	50.8	5.7
XIII	59–60	b	52.2	6.1	52.8	6.1
XIV	132–133	b	53.3	6.0	53.0	6.0

mmole) in ether (100 ml) for 1 hr. The ether layer was separated and dried. The product was obtained by removal of the ether and crystallization from benzene–light petroleum as a colorless solid (9.1 g, 86%), mp 135.5–137°C.

ANAL. Found: C, 45.8%; H, 3.6%. Calcd for $C_{16}H_{16}O_2S_2Sn$: C, 45.4%; H, 3.8%.

Di-*n*-butyltin Di(thiobenzoate) (VII), Method b. Di-*n*-butyltin oxide (12.43 g, 0.05 mole) and thiobenzoic acid (14.0 g, 0.1 mole) were heated under reflux in benzene (100 ml) for 1 hr with removal of water by azeotropic distillation. The reaction mixture was cooled and filtered, and the benzene was removed from the filtrate under reduced pressure. Crystallization of the product from light petroleum gave di-*n*-butyltin di(thiobenzoate) (18.0 g, 71%), mp 55–56°C.

ANAL. Found: C, 52.4%; H, 5.6%; Calcd for $C_{22}H_{28}O_2S_2Sn$: C, 52.1%; H, 5.6%.

Di(phenylthio)diphenyltin (VI), Method c. Diphenyltin dichloride (6.88 g, 20 mmoles) and benzenethiol (4.4 g, 40 mmoles) were dissolved in ether (30 ml) and benzene (20 ml). The solution was saturated with ammonia gas for 30 min. The precipitated ammonium chloride was collected by filtration and the solvents removed from the filtrate. Crystallization from light petroleum gave di(phenylthio)diphenyltin (9.2 g, 94%), mp 64–65°C (lit. 65°C).¹³

Tin Tetra(thiobenzoate) (XXI). Phenylstannic acid (2.29 g, 10 mmoles) thiobenzoic acid (4.2 g, 30 mmoles) and benzene (50 ml) were heated to reflux for 1 hr with removal of the water formed by azeotropic distillation. The solution was cooled and filtered, and the benzene was removed from the filtrate under vacuum. The product, tin tetra(thiobenzoate) (2.0 g, 40%), was crystallized from benzene–light petroleum, mp 145–6°C.

ANAL. Found: C, 50.2%; H, 3.1%. Calcd for $C_{28}H_{20}O_4S_4Sn$ requires: C, 50.4%; H, 3.0%.

Tin Dichloride Dithiobenzoate. Stannic chloride (2.60 g, 10 mmoles) and thiobenzoic acid (5.6 g, 40 mmoles) were dissolved in benzene, and nitrogen was passed through the solution for 30 min to remove the hydrogen chloride formed in the reaction. The product (5.1 g, 76.5%) was obtained as yellow needles after crystallization from benzene–light petroleum, mp 185.5–186.5°C.

ANAL. Found: C, 36.6%; H, 2.4%. Calcd for $C_{14}H_{10}Cl_2O_2S_2Sn$: C, 36.2%; H, 2.2%.

Titration of Thiolates and Carbothiolates with Iodine Solution.^{14,15} The thiolato-organotin compound (0.1–1.0 g) was weighed out into a suitable flask and dissolved in diethyl ether (10 ml), and 0.4*M* aqueous hydrochloric acid (10 ml) was added. The liberated thiol was titrated with 0.1*M* aqueous iodine solution in potassium iodide. The equivalence point was

TABLE II
Cleavage of Some Organotin PVC Stabilizers with Aqueous Hydrochloric Acid

Reactant	Products	Yield of thiol or carbo- thiolic acid, %	Efficiency of Reactant as PVC stabilizer ^a	t_1 , min ^b	t_2 , min ^c
Me ₂ Sn(SPh) ₂ (I)	Me ₂ SnCl ₂ + PhSH	99	very good	15	40
Me ₂ Sn(SCOPh) ₂ (II)	Me ₂ SnCl ₂ + PhCOSH	98	good	10	40
Pr ₂ Sn(SPh) ₂ (III)	Pr ₂ SnCl ₂ + PhSH	99	very good	10	40
Bu ₂ Sn(SCH ₂ Ph) ₂ (IV)	Bu ₂ SnCl ₂ + PhCH ₂ SH	99	very good	20	40
Bu ₂ Sn(SPh) ₂ (V)	Bu ₂ SnCl ₂ + PhSH	99	very good	15	40
Ph ₂ Sn(SPh) ₂ (VI)	Ph ₂ SnCl ₂ + PhSH	99	very good	10	20
Bu ₂ Sn(SCOPh) ₂ (VII)	Bu ₂ SnCl(SCOPh) + PhCOSH	93	good	10	40
Bu ₂ Sn(SCOPh) ₂ (VIII)	Bu ₂ SnCl(SCOPh) + PhCOSH	99	good	15	40
Ph ₂ Sn(SCOPh) ₂ (IX)	Ph ₂ SnCl(SCOPh) + PhCOSH	99	good	10	15
Bu ₂ Sn(SCO-C ₆ H ₄ - <i>p</i> -Me) ₂ (X)	Bu ₂ SnCl(SCO-C ₆ H ₄ - <i>p</i> -Me) + <i>p</i> -Me-C ₆ H ₄ -COSH	84	good	10	40
Bu ₂ Sn(SCO-C ₆ H ₄ - <i>m</i> -Cl) ₂ (XI)	Bu ₂ SnCl(SCO-C ₆ H ₄ - <i>m</i> -Cl) + <i>m</i> -Cl-C ₆ H ₄ -COSH	80	good	10	40
Bu ₂ Sn(OCOCH ₂ SPh) ₂ (XII)	Bu ₂ SnCl ₂ + PhSCH ₂ CO ₂ H	0	poor	5	25
Bu ₂ Sn(OCOCH ₂ SCH ₂ Ph) ₂ (XIII)	Bu ₂ SnCl ₂ + PhCH ₂ SCH ₂ CO ₂ H	0	poor	5	25
Bu ₂ Sn[OCOCH ₂ CH(Ph)SCOMe] ₂ (XIV)	Bu ₂ SnCl ₂ + MeCOSH(Ph)CH ₂ CO ₂ H	0	poor	5	30
Pr ₂ SnSPh (XV)	Pr ₂ SnCl + PhSH	99	poor	10	30
Bu ₂ SnSPh(XVI)	Bu ₂ SnCl + PhSH	98	poor	5	25
Ph ₂ SnSPh (XVII)	Ph ₂ SnCl + PhSH	99	fair	10	25
Bu ₂ Sn(SCOPh) ₂ (XVIII)	Bu ₂ SnCl ₃ + PhCOSH	99	good	10	35
MeSn(SPh) ₂ (XIX)	MeSnCl ₃ + PhSH	99	very good	15	30
Sn(SCOPh) ₄ (XXI)	SnCl ₄ + PhSH	99	poor	10	10
SnCl ₂ (SCOPh) ₂ (XXII)	SnCl ₄ + PhCOSH	87	poor	5	15
	SnCl ₄ + PhCOSH	99	poor	10	10

^a Overall assessment.

^b Time at initial discoloration.

^c Time at blackening.

determined using a soluble starch indicator or the first yellow color of the iodine. In some cases, a slight yellow color was visible even at the equivalence point, but this could be distinguished from the iodine color. Table II lists the reactants and products obtained.

Evaluation of Compounds as Stabilizers for PVC. PVC resin (Corvic D 55/9) (100 g), stearic acid (0.5 g), and organotin compound (2 mmoles) were blended together and then milled for 5 min at 145–150°C on a two-roll mill. The polymer was removed as a sheet. Discs were cut from the sheet and heat aged in closed aluminum cylinders contained in a thermostat at 190°C.¹⁶ Color formation in the discs was assessed at short-time intervals, and the results were recorded in Table III on a comparative basis.

DISCUSSION

Estimation of Thiols

Cleavage of the tin–sulfur bond of alkylthiotrimethyltin compounds by bromine to give trimethyltin bromide and the disulfide was reported by Abel and Brady.¹⁵ They describe a similar quantitative reaction with iodine and mention that titration with standard iodine solutions may be used to estimate some organotin–sulfur compounds. No experimental details were given, nor were the limitations of the method defined. Peach¹⁴ used iodine in carbon tetrachloride for the nonaqueous titration of di- and tri-alkyltin thiolates. Satisfactory results were obtained for trialkyltin thiolates but not for dialkyltin thiolates. The results of only four titrations were reported.

In the present paper, we have examined the cleavage of the tin–sulfur bonds in thio-organotin compounds, a reaction which also takes place, but under different conditions, in the polymer (see succeeding paper). This was done by shaking the organotin thiolate in ether with dilute aqueous hydrochloric acid. The quantitative estimation of the thiol liberated was achieved by titration with aqueous iodine. The quantitative nature and wide range of our results as compared with the observations of Peach¹⁴ and the partial cleavage observed with other organotin thiolates demonstrates that we are not in fact cleaving the tin–sulfur bond by iodine. Cleavage of tin–sulfur bonds by aqueous hydrochloric acid was also demonstrated in this study by gas–liquid chromatography. Also, our method is applicable to organotin thiolates of all degrees of alkylation.^{14,15}

Cleavage of Tin–Sulfur Bonds by Aqueous Acid

Table II shows three distinct modes of reaction between the organotin sulfur compounds and hydrochloric acid. The first, and most usual, mode was the quantitative, or near-quantitative, replacement of the carbothiolic ester or thioalkyl groups by chlorine in compounds I–VI and XV–XXII to give the corresponding organotin chloride and free thiol or carbothiolic acid.

TABLE III
Relative Abundance (%) of Mass-Spectral Ions (^{120}Sn)
of some Dialkyltin Chloride Thiobenzoates^a

Fragment	$\text{Me}_2\text{SnCl}(\text{SCOPh})$		$\text{Bu}^n_2\text{SnCl}(\text{SCOPh})$	
	<i>m/e</i> ratio	%	<i>m/e</i> ratio	%
$[\text{M}-\text{R}]^+$	307	2.7	349	28.4
$[\text{M}-\text{R}-\text{SCOAr}]^+$	170	2.4	212	48.4
$[\text{M}-\text{Cl}]^+$	287	1.4	371	1.9
$[\text{R}_2\text{SnCl}_2]^+$	220	2.7	304	3.2
$[\text{RSnCl}_2]^+$	205	100	247	48.4
$[\text{R}_2\text{SnCl}]^+$	185	44	276	0 ^b
$[\text{RSn}]^+$	135	3.9	177	4.8
$[\text{SnCl}]^+$	155	56	155	100

^a $\text{R}_2\text{SnCl}(\text{SCOAr})$.

^b Possibly obscured by another fragment.

The second mode of reaction was characterized by the loss of one carbothiolic ester residue from the dialkyltin thiobenzoates (VII–XI) to give the corresponding chloride thiobenzoates. In some cases, the dialkyltin chloride thiobenzoate was synthesized and characterized by mass spectrometry. The identity of the ionic fragments produced in the mass spectrometer, as identified by their mass/charge ratios, are listed in Table III.

Tin tetra(thiobenzoate) (XXI) was intermediate between these two modes. The titration in fact indicated the loss of seven carbothiolic ester residues from two moles of the carbothiolate (XXI). Although no attempt was made to isolate a product, the formation of a binuclear complex containing one carbothiolic ester group seems to be the most likely explanation for this behavior. The third group of compounds (XII–XIV) did not give thiols or carbothiolic acids with aqueous hydrochloric acid.

The organotin compounds (I–XXII) were also evaluated as stabilizers for PVC by milling each in turn into the polymer and following the rate of color formation in polymer discs at constant temperature.¹⁶ These results are recorded on a comparative basis in Table II. The results suggest that the reactivity of an organotin thiolate or carbothiolic ester toward aqueous hydrochloric acid may be a measure of its efficiency as a heat stabilizer for PVC. Care must be taken in the interpretation of the results in Table II, since the efficiency of a given stabilizer is governed, to some extent, by the number of alkyl groups attached to tin, and aqueous hydrochloric acid at room temperature provides a different medium from PVC at elevated temperatures. Consideration of the dialkyltin mercaptides (I, III–VI) and the carbothiolate (II) shows that these compounds are completely and rapidly cleaved by hydrochloric acid and they are also very good stabilizers for PVC. The diorganotin carbothiolates (VII–XI) are degraded partially to the corresponding organotin carbothiolate chlorides and are less effective stabilizers. The organotin carboxylates (XII–XIV) were poor stabilizers and did not yield free thiols with aqueous hydrochloric acid.

The thermal degradation of PVC affords hydrogen chloride, and it is probable that the stabilizer reacts quickly with the acid under these conditions. The confirmation of both tin-sulfur and tin-carbon bond cleavage in organotin-stabilized PVC is discussed in the following paper. Enough hydrogen chloride is liberated in the first few minutes of milling or fabricating PVC at 190–200°C in the presence of 1–2% of stabilizer to decompose all of the stabilizer.^{17,19} The intact stabilizer is therefore active only on the early stages of the lifetime of the polymer. The active species in stabilizing the polymer will then be the acid cleavage products of the organotin compound. These are the thiol or carbothiolic acid and, in the case of the dialkyltin compounds, the dialkyltin dichloride, the dialkyltin carbothiolate chloride, or the dialkyltin thiolate chloride. The last-named compounds have been proposed previously as active species in stabilization by Klemchuk.⁸

Our work supports the suggestion that similar compounds will be formed from organotin carbothiolic esters and PVC during degradation. However, evidence presented by Klemchuk⁸ is indirect and requires the formation of the intermediate from alkyl chlorides and organotin thiolates or carboxylates in the absence of hydrogen chloride. Recently, the dialkyltin carboxylate chlorides have been isolated from the reaction of alkyl chlorides and dialkyltin carboxylates.⁹ The possibility that the intermediate arose from reaction between dialkyltin dichloride and dialkyltin dicarboxylate was not excluded. We have now shown that it can arise, in part at least, from the dialkyltin carbothiolates and hydrochloric acid.

The above generalization may be extended empirically to the trialkyltin mercaptides (XV–XVIII), the monoalkyltin mercaptide (XIX), and the carbothiolate (XVIII). The extension is only empirical because the effects of the organotin residue and of the product organotin chloride on the polymer may vary within this group of compounds (I–XXII). Thus, it has been shown that the acceptor strengths and the activity as degradation catalysts of organotin chlorides R_nSnCl_{4-n} vary with the value of n . The trialkyltin halides are very weak acceptors, while stannic chloride is a powerful acceptor and strongly catalyzes degradation. The trialkyltin mercaptides (XV–XVIII), while giving a quantitative yield of thiol in aqueous hydrochloric acid, give less thiol on a molar basis than the corresponding dialkyltin mercaptides and are less efficient stabilizers for PVC. Conversely, the monoalkyltin mercaptide (XIX) and tri(thiobenzoate) (XVIII) release more thiol in aqueous acid and are, at least for the first 20 min or so, better stabilizers than the corresponding dialkyltin compounds. Although the stannic derivatives (XX–XXI) released more thiol with hydrochloric acid on a molar basis than the corresponding diorganotin compounds, such as the mercaptide (I) and the carbothiolate (II), they were not good stabilizers for PVC. This is presumably because the advantages of the extra available thiol is offset by the Lewis acid effect of the stannic chloride by-product that promotes degradation of the polymer. The chloride carbothiolate (XXII) yields only two moles of free carbothiolic acid and stannic chloride. It was

ineffective as a stabilizer for PVC. The free thiol or carbothiolic acid may be effective as a stabilizer through addition to olefinic groups in the polymer chains by a free-radical¹⁸ or ionic^{19,20} mechanism. We have shown in separate experiments²¹ that mixtures of thiols and dibutyltin dichloride act as PVC stabilizers, although they are less effective than the corresponding dibutyltin mercaptides.

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