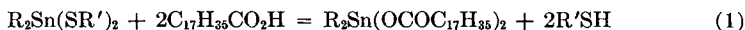


***Exchange of Carboxylate for Thiolate in Organotin Compounds
and the Mechanism of Poly(vinyl Chloride) Stabilization***

The effectiveness of alkyltin mercaptides as thermal stabilizers for poly(vinyl chloride) is well known.¹ We have described recently² the reaction between some dialkyltin dimercaptides or di(thiolcarboxylates) and hydrogen chloride, liberated during the degradation of the polymer. Long-chain aliphatic carboxylic acids and their derivatives are often used in the commercially fabricated polymer as lubricants. We considered that the stabilizer and lubricant in such systems could interact and modify the efficiency of the former.

We now report the reaction of a number of organotin stabilizers with octadecanoic acid and octadecanol. The organotin compounds were prepared by heating to reflux the organotin oxide and the mercaptan or carbothiolic acid with benzene and azeotropic distillation of the water formed in the reaction. The stabilizer-lubricant mixtures were allowed to react in the absence of solvent at 80°C for 5 min, cooled to room temperature, and dissolved in deuteriochloroform. In several cases the reaction was also carried out at 150°C for 5 min, typical processing conditions for the stabilized polymer. In each case, the organotin compound and the lubricant were mixed in the molar proportions indicated in eq. (1):



The hydroxy and thiol groups in the reaction products were detected by proton magnetic resonance spectroscopy and the hydroxy:thiol ratio was determined by integration. In the reactions of the organotin compounds III, IV, and VII (Table I) with octadecanol, any thiol resonances would have been obscured partially by other absorptions. The absence of thiols was confirmed by treating the compounds I, III, and IV with isopropanol when the thiol regions of the spectra showed no absorptions. In the same way, exchange of groups between the mercaptides VI, VIII, and IX and a weak carboxylic acid was confirmed conveniently by using benzoic acid in place of octadecanoic acid. The resonance of the hydroxyl proton was identified positively in the products of several experiments by exchange with deuterium oxide.

The efficiency of the organotin compound and octadecanoic acid or octadecanol mixtures as thermal stabilizers for PVC was determined by milling each in turn in the same molar proportion into unplasticized PVC. Discs were cut from the milled, stabilized polymer, and the rate of color formation in the discs was followed at constant temperature (190°C).³ The results are collected and compared in Table I.

The organotin carbothiolates I and II were inert toward both octadecanoic acid and octadecanol, and no differences were observed in the efficiency of stabilizer-lubricant mixtures in lines 1 and 2 or lines 4 and 5 in Table I. The thiolates III-V and VII each gave free benzenethiol on treatment with octadecanoic acid. The relative intensities of the hydroxy and thiol resonances indicated partial exchange of the sulfur ligands on tin for oxygen ligands. No exchange was observed when the thiols III, IV, and VII were treated with octadecanol. The efficiencies of the thiolate-octadecanol mixtures as PVC stabilizers, lines 7, 11, and 15 in Table I, were significantly higher than the corresponding thiolate-octadecanoic acid mixtures, lines 6, 9, and 16 in Table I. This may be explained, in part at least, by the loss of the sulfur-tin stabilizers III, IV, and VII through conversion to the less effective oxygen analogues by exchange with the lubricant when this was octadecanoic acid. The phenylthiolate (V), the benzylthiolate (VI), and the methylthioglycollates (VIII and IX) also gave the free thiols when treated with carboxylic acids. In each case, exchange of ligand groups was incomplete and the equilibrium favored the thiolate. The proportions of the components in the product mixture were dependent on the organotin thiolate used.

It has been observed previously that organotin alkoxides gave organotin thiolates on treatment with thiols under forcing conditions.⁴ We have also shown² that carbothiolic

TABLE I
Reactions Between Some Organotin Sulfur Compounds and Octadecanoic Acid or Octadecanol

Line no.	Reactant (leaving group)	Reagent (replacing group)	Temperature, °C	PMR resonances δ^a ppm		Intensity ratio (OH:SH)	Extent of replacement, %	Efficiency of reactant-reagent mixture as stabilizer for PVC	t^b	t^c
				SH	OH					
1	$\text{Me}_2\text{Sn}(\text{SCOPh})_2$ (I)	$\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$	80, 150	—	11.04	—	0	good	15	40
2		$\text{C}_{18}\text{H}_{37}\text{OH}$	80, 150	—	2.08	—	0	good	15	40
3		Pr^iOH	80	—	2.03	—	0	—	—	—
4	$\text{Bu}^n\text{Sn}(\text{SCPh})_2$ (II)	$\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$	80, 150	—	1.87	—	0	good	15	40
5		$\text{C}_{18}\text{H}_{37}\text{OH}$	80, 150	—	11.08	—	0	good	15	40
6	$\text{Me}_2\text{Sn}(\text{SPh})_2$ (III)	$\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$	80, 150	3.43	10.94	5.5	18	very good	10	40
7		$\text{C}_{18}\text{H}_{37}\text{OH}$	80	—	4.87	—	0	excellent	10	50
8		Pr^iOH	80	—	2.06	—	0	—	—	—
9	$\text{Bu}^n\text{Sn}(\text{SPh})_2$ (IV)	$\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$	80	3.40	11.03	5.0	20	very good	10	40
10		$\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$	150	3.40	11.07	6.0	17	very good	10	40
11		$\text{C}_{18}\text{H}_{37}\text{OH}$	80	—	2.03	—	0	excellent	10	45
12		Pr^iOH	80	—	2.45	—	0	—	—	—
13	$\text{Bu}^n\text{Sn}(\text{SPh})_2$ (V)	$\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$	150	3.4	11.15	7.5	13	good	10	25
14	$\text{Me}_2\text{Sn}(\text{SCH}_2\text{Ph})_2$ (VI)	PhCO_2H	25	1.71	9.38	4.0	25	—	—	—
15	$\text{Bu}^n\text{Sn}(\text{SCH}_2\text{Ph})_2$ (VII)	$\text{C}_{18}\text{H}_{37}\text{OH}$	80	—	3.87	—	0	very good	10	50
16		$\text{C}_{17}\text{H}_{35}\text{CO}_2\text{H}$	80	1.95	10.20	(5) ^c	(20) ^c	good	15	40
17	$\text{Me}_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{Me})_2$ (VIII)	PhCO_2H	25	2.0	9.95	3.6	28	—	—	—
18	$\text{Ph}_2\text{Sn}(\text{SCH}_2\text{CO}_2\text{Me})_2$ (IX)	PhCO_2H	25	1.95	10.30	2.4	42	—	—	—

^a PMR chemical shift measured downfield from internal TMS.

^b See experimental section; in units of minutes.

^c Approximate value.

acids are liberated only partially when dialkyltin di(carbothiolates) are titrated in the presence of the strong acid aqueous hydrochloric acid. On the other hand, thiols (weaker acids than carbothiolic acids) were formed quantitatively from the corresponding dialkyltin dithiolates and hydrochloric acid. In the present work, the low acidities of the thiols in the organotin compounds III-IX explains the reactivities of the latter toward octadecanoic acid and benzoic acid. The failure of the esters I and II to react with the same carboxylic acid is due to the higher acidity of the carbothiolic acid.

The results reported here provide an explanation in chemical terms for the empirically observed "incompatibility" between organotin stabilizers and some of the lubricants used in the commercial formulation of rigid PVC.

All of the new compounds prepared gave satisfactory elemental analyses and showed the expected infrared and PMR absorption spectra.

Experimental

The organotin compounds were prepared by standard methods and were characterized by microanalysis, infrared, and PMR spectroscopy as parts of other investigations.⁵

Interaction Between Lubricants and Organotin Stabilizers. Octadecanol or octadecanoic acid (2 mmoles) and the thioorganotin compound (2 mmoles) were mixed intimately and fused together at 80°C (or 150°C) for 5 min. The cooled samples were dissolved in deuteriochloroform (0.5 ml) and allowed to stand at room temperature for 10 min before PMR analysis on a Jeolco Model C 60HZ (60 MHz) instrument. In the cases where benzoic acid was used, the thio-organotin compound (2 mmoles) was dissolved in deuteriochloroform (0.5 ml) containing benzoic acid (2 mmoles).

Evaluation of stabilizer efficiency. The organotin stabilizer, containing 2 mg atom tin, was mixed with PVC (Corvic D55/9, 100 g) and the lubricant (0.5 g) and fused on a two-roll mill at 150°C. Milling was continued for 5 min after fusion. Test discs (14 mm in diameter and 1 mm thick) were cut from the cooled hide and heated between aluminum platens in standard tubes at the thermostat temperature of 190°C.³ Samples were removed at intervals and the colors were compared with those obtained from a parallel determination using a standard stabilizer and which was carried out at the same time. The times at initial discoloration (t_1) and at blackening (t_2) were noted and are recorded in Table I.

The authors thank Messrs. Robinson Bros. Ltd., for the financial support of this work and for a research studentship to M.H.

References

1. F. Chevassus and R. de Brautells, *Stabilization of Poly(vinyl Chloride)*, Edward Arnold, London, 1963.
2. B. W. Rockett, M. Hadlington, and W. R. Poyner, *J. Polym. Sci.*, **B9**, 371 (1971).
3. Int. Org. Standardization, R. 305, 1963.
4. D. Sukahani, V. D. Gupta, and R. C. Mehrotra, *J. Organometallic Chem.*, **7**, 85 (1967).
5. M. Hadlington, Ph.D. Thesis, The Polytechnic, Wolverhampton, England, 1972.

B. W. ROCKETT
M. HADLINGTON

Department of Physical Sciences
The Polytechnic
Wolverhampton, England

W. R. POYNER

Messrs. Robinson Bros. Ltd.
Ryders Green
West Bromwich, England

Received February 14, 1972
Revised June 13, 1972