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Stabilization of PVC by Organotin Compounds

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ABSTRACT

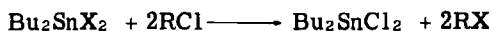
Stabilizers, R_2SnX_2 , react with allylic chlorine atoms during the induction period and also absorb HCl to give XH molecules which add to double bonds. Changes in R which facilitate Sn-C bond cleavage are unfavorable, but γ -carbonyl groups are beneficial.

I would like to present a brief review of some of the work we have carried out recently on stabilization of PVC by organotin compounds. For the stabilization of PVC the period of empiricism is over, and new stabilizers should be developed on a rational basis.

Although some use of monoalkyltin compounds has been made, the archetypal organotin stabilizer has the formula R_2SnX_2 , and dibutyltin di(isooctylthioglycollate) is a common example. These stabilizers are extremely efficient in inhibiting the thermal decomposition of PVC and could only have been developed by empirical methods. During the last few years we have gained much knowledge of the chemistry of stabilization. Though we do not know all the details, we know enough to base future stabilizer design on theoretical principles.

EXCHANGE REACTIONS

Since metal soaps effect exchange reactions between fatty acid residues and chlorine atoms, it seemed likely that organotin compounds might undergo similar reactions. Frye et al. [1] obtained some evidence for this, showing that PVC films absorbed radioactivity when heated in air with Bu_2SnX_2 compounds having labeled X groups. At the time there was no evidence that these organotin compounds would react with chlorohydrocarbons, but subsequent work has shown that reactions of the type



do occur, at least when RCl is a tertiary or an allylic chloro compound [2, 3]. It now seems that the latter is the most important initiation site in PVC [4]. We heated PVC with $\text{Bu}_2\text{Sn}({}^{35}\text{SBU})_2$ under vacuum, since we consider this approximates most closely to the conditions used in industrial processing, and obtained quite different results [5, 6] (Fig. 1). Instead of the level of radioactivity reaching a maximum value in 1-2 hr as had been observed by Frye, there was a slow uptake of radioactivity during an induction period which terminated

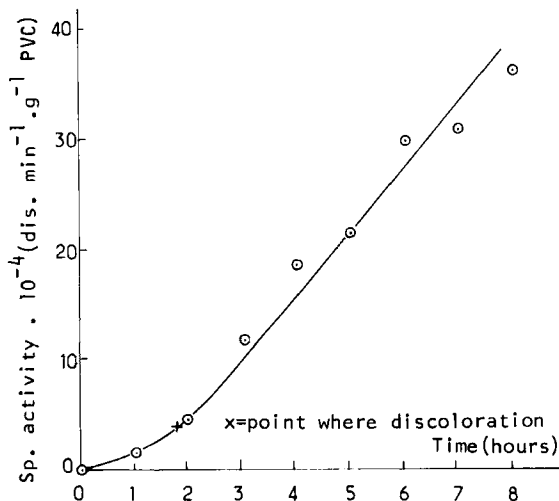


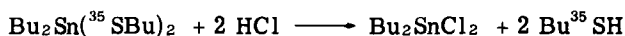
FIG. 1. Uptake of radioactivity of PVC heated at 180°C with $\text{Bu}_2\text{Sn}({}^{35}\text{SBU})_2$ in vacuo.

after about 2 hr when the polymer began to discolor. The specific activity of the PVC then increased at a constant rate and continued to do this long after the 8-hr period shown in Fig. 1.

We consider that during the induction period the stabilizer functions in a preventative way by exchanging allylic chlorine atoms with the X groups of Bu_2SnX_2 to give more stable structures. We can calculate from the amount of radioactivity absorbed from the stabilizer at the end of the induction period the approximate number of allylic chlorine atoms in the polymer; the value obtained is 3 per 100 polymer molecules.

ABSORPTION OF HYDROGEN CHLORIDE

At the end of the induction period, hydrogen chloride is evolved, and the stabilizer then assumes a healing role. The thiol liberated by the reaction



adds to the double bonds in the degrading polymer. Evidence for this was obtained by degrading virgin polymer and then treating it with the labeled thiol Bu^{35}SH . Not only was the color discharged, but the uptake of radioactivity was similar to that observed in the experiment with labeled stabilizer. Of the organotin thiolates used in stabilization the alkyl thioglycollates are particularly effective. Is this because ROCOCH_2SH adds more efficiently to double bonds than simple thiols? It is a reasonable assumption that additions to degraded PVC would be by a radical mechanism, and our knowledge of such reactions suggests that thioglycollate addition would be more effective. Although few quantitative data are available, the chain transfer constants for addition of thiols to styrene (Table 1) support this view.

The important stabilizing reaction which occurs between stabilizer and hydrogen chloride has not been fully studied. When a dibutyltin dicarboxylate reacts with hydrogen chloride at 180°C , no Sn-C bond cleavage was observed [10], but subsequent work on other stabilizers has shown that Sn-C bonds can be attacked [11]. In order to obtain more information about these reactions we have been studying the stabilizing abilities of a series of compounds, $\text{R}_2\text{Sn}(\text{SCH}_2\text{COOC}_8\text{H}_{17})_2$, in which systematic changes are made in the group R [12]. PVC containing the stabilizer is aged at 195°C and the time for complete discoloration (i.e., for the sample to become uniformly black or dark brown) is recorded. Some preliminary results of this work are shown in Table 2. The best stabilizers are those compounds in which

TABLE 1. Chain Transfer Constants for Thiols with Styrene at 60°C

Thiol	Chain transfer constant
t-Bu SH	4 ^a
CH ₃ (CH ₂) ₁₁ SH	19 ^a
CH ₃ (CH ₂) ₄ SH	20 ^b (at 6.25°C)
EtOCH ₂ CH ₂ CH ₂ SH	21 ^a
BuSH	22 ^c
EtOCOCH ₂ SH	58 ^a

^aData of Gregg et al. [7].

^bData of Smith [8].

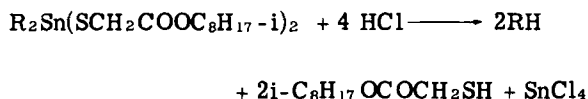
^cData of Walling [9].

TABLE 2. Approximate Time for Complete Discoloration of PVC Containing 2% of Stabilizer R₂Sn(SCH₂COOC₈H₁₇-1) heated at 195°C

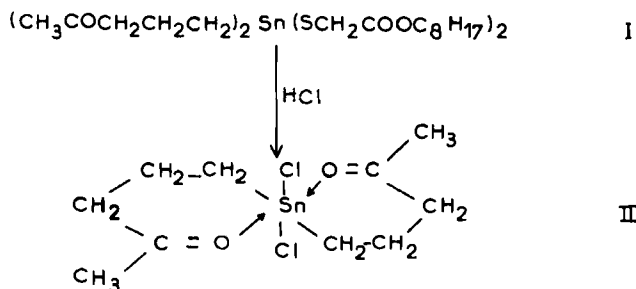
R	Time (min)
CH ₃	90
CH ₃ CH ₂	90
CH ₃ CH ₂ CH ₂ CH ₂	70
CH ₃ (CH ₂) ₇	70
C ₆ H ₅ CH ₂	40
BrCH ₂	0
C ₆ H ₅	60
p-CH ₃ OC ₆ H ₄	10

R = alkyl, the effectiveness tending to decrease as the alkyl chain is lengthened. Introduction of electron withdrawing groups in the α -position reduces the stabilizing action, this being particularly striking where R = BrCH₂. The diphenyl compound is reasonably effective, but introduction of the electron-releasing p-methoxyl group markedly reduces the stabilizing action. It is known that α -substituted alkyl groups are particularly prone to Sn-C bond cleavage. Similarly phenyl-tin-bonds, more particularly p-methoxyphenyl-tin bonds,

undergo ready fission with hydrogen chloride. For effective stabilization, all of the tin compound should be converted to the relatively weak Lewis acid R_2SnCl_2 . If both Sn-S and Sn-C bonds are attacked, the final product will be stannic chloride, which is a powerful Lewis acid catalyst for dehydrochlorination and the compound will be a poor stabilizer:



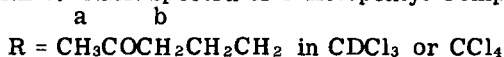
Although organotin dichlorides are relatively weak dehydrochlorination catalysts, their presence in PVC is undesirable. We attempted to prepare a stabilizer, $R_2Sn(SCH_2COOC_8H_{17}-i)_2$, in which the Lewis acidity of the ensuing dichloride would be masked by incorporating donor centers into the R groups [13, 14]. We prepared the compound where R = 4-ketopentyl and obtained spectroscopic evidence that the keto groups are free in the stabilizer but are coordinated to tin in the dichloride.



The IR spectra show that the carbonyl group in II occurs at 1680 cm^{-1} , a position characteristic of coordinated CO groups but it is displaced to 1705 cm^{-1} in $(CH_3COCH_2CH_2CH_2)_2SnCl_2 \cdot 2,2'$ -bipyridyl when the coordinating positions are taken up by the more powerfully donating nitrogen atoms of 2,2'-bipyridyl. In compound I, the carbonyl bands are masked by the carboxylate absorptions, but the NMR spectra (Table 3) show quite clearly that the ketone groups are free in I and coordinated in II. When I was incorporated into PVC it was shown to be more than twice as effective in stabilization than dibutyltin di(isooctyl thioglycollate).

To summarize, exchange reactions at the few reactive chlorine sites with X groups on tin are important. The stabilizer must be able

TABLE 3. NMR Spectra of 4-Ketopentyl Compounds



Ketopentyl compound	τ (ppm)	
	a	b
RH	7.97	7.68
R ₂ SnCl ₂	7.74	7.23
R ₂ SnCl ₂ ·2,2'-bipyridyl	7.89	7.42
R ₂ Sn(SCH ₂ COOC ₈ H ₁₇ -i) ₂	7.93	7.52

to absorb HCl by Sn-X bond cleavage only; where XH is a thiol, the ease with which it can add to double bonds seems to be important, though we should note that most of these additions occur after color formation. Although we still have much to learn, direct application of present knowledge can lead to improved stabilizers as in the case of the 4-ketopentyl compounds.

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