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MECHANISM OF THERMAL STABILIZATION OF PVC BY ORGANOTIN COMPOUNDS: SCAVENGING OF CHLORINE ATOMS

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Summary

Organotin compounds, R_2SnX_2 ($X = OCOR'$, SR''), effective in the thermal stabilization of PVC are shown to react with chlorine atoms by substitution of X groups at the tin atom.

Introduction

The thermal degradation of PVC is a complex reaction involving a number of reaction pathways. One process, first proposed by Winkler [1], which has been shown to be important by a number of workers [2,3] is a radical mechanism involving chain-carrying chlorine atoms. It is now readily accepted that chlorine atom initiators are generated in the induction period which precedes decomposition [4]. The possibility that non-radical processes [5] may also be involved in the degradation is emphasised.

An organotin stabilizer of the type R_nSnX_{4-n} ($n = 1,2$) delays the decomposition of PVC by various means including exchange of X groups with allylic chlorine atoms *, absorption of hydrogen chloride and generation of HX compounds which can add to double bonds. Another possible role for the stabilizer is that of scavenger for chlorine atoms and the present paper is concerned with this type of reaction.

Results and discussion

Evacuated quartz tubes containing solutions of the organotin compounds in carbon tetrachloride were irradiated with UV light. Volatile products were

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* Unpublished results [6] indicate that these allylic chlorine atoms are produced during an induction period and are unlikely to be present before degradation begins.

TABLE 1

PRODUCTS OBTAINED FROM THE PHOTOCHEMICAL DECOMPOSITION OF CARBON TETRACHLORIDE IN THE PRESENCE OF ORGANOTIN COMPOUND (% relative abundance)

	$Bu_2Sn(OAc)_2$	$Bu_2Sn(OCOC_2H_5)_2$	$Bu_2Sn(SEt)_2$
But-1-ene	5.8	16.7	7.3
Chloroform	9.8	36.8	23.3
RCOOH	35.9	40.0	—
CCl_3CCl_3	44.6	3.3	4.6
EtSH	—	—	7.0
EtSSEt	—	—	51.8
Bu_2SnCl_2	[7.5] [a]	[9.0] [a]	[12.0] [a]

[a] % yield.

SCHEME 1

$$CCl_4 \xrightarrow{UV} Cl^{\bullet} + CCl_3^{\bullet}$$

$$Cl^{\bullet} + Bu_2Sn(OCOCH_3)_2 \rightarrow Bu_2Sn(OCOCH_3)Cl + CH_3COO^{\bullet}$$

$$Cl^{\bullet} + Bu_2Sn(OCOCH_3)Cl \rightarrow Bu_2SnCl_2 + CH_3COO^{\bullet}$$

$$CH_3COO^{\bullet} + Bu_2Sn(OCOCH_3)_2 \rightarrow CH_3COOH + CH_3CH_2\dot{C}HCH_2SnBu(OCOCH_3)_2$$

$$CCl_3^{\bullet} + Bu_2Sn(OCOCH_3)_2 \rightarrow CHCl_3 + CH_3CH_2\dot{C}HCH_2SnBu(OCOCH_3)_2$$

$$CH_3CH_2\dot{C}HCH_2SnBu(OCOCH_3)_2 \rightarrow CH_3CH_2CH{=}CH_2 + Bu\dot{S}n(OCOCH_3)_2$$

$$2CCl_3^{\bullet} \rightarrow CCl_3CCl_3$$

identified by combined gas chromatography/mass spectroscopy and dibutyltin dichloride was isolated. The relative abundance of the volatile products and the yields of dibutyltin dichloride are shown in Table 1.

A reasonable mechanism for the reaction involving dibutyltin diacetate which accounts for the products obtained is shown in Scheme 1 (similar mechanisms are applicable to the dipropionate and the dithiolate). The richest sources of hydrogen are the butyl groups and earlier work [7] has shown that these are attacked in the β-position by trichloromethyl radicals to give but-1-ene. It is possible that the chlorine atoms also abstract hydrogen from the butyl groups to give hydrogen chloride which could then react by a polar mechanism to give dibutyltin dichloride and acetic acid. However, this is unlikely to be a major reaction pathway as no hydrogen chloride was detected and the amounts of dibutyltin dichloride obtained would require larger amounts of butene to be produced. It has been shown previously [8] that alkyltin carboxylates react with t-butoxyl radicals but, in that case, substitution occurred at tin with elimination of the alkyl group rather than the carboxyl residue.

Chlorine atoms were also generated by heating a solution of *N*-chlorosuccinimide in cyclohexane. In this case dibutyltin diacetate was essentially unchanged with only traces of dibutyltin dichloride being obtained. The principal products were chlorocyclohexane, hydrogen chloride and a small amount of acetic acid. In this system the cyclohexane is a much more efficient hydrogen donor than the organotin compound and the dominant reaction is chlorination of the alkane solvent. Although considerable hydrogen chloride is produced it does not interact strongly with the organotin compound supporting the view that, in the carbon tetrachloride reaction, the dibutyltin dichloride is formed by a radical substitution.

In contradiction of tentative inferences drawn before this work was completed [9] we now conclude that organotin stabilizers, R_2SnX_2, could complete successfully with the polymer for chlorine atoms in degrading PVC and that this would be an effective stabilization process.

Experimental

Infrared spectra were measured using a Perkin—Elmer 325 spectrophotometer, Nujol mulls were used for solids and liquid samples were recorded as neat films. Nuclear magnetic resonance spectra were recorded using a Perkin—Elmer R12 (60 MHz) instrument. GLC/mass spectra were obtained using an AEI MS 30 mass spectrometer integrated with a Pye-Unicam 104 gas chromatograph by courtesy of the U.L.I.R.S. service at Queen Elizabeth College.

Analar carbon tetrachloride was dried with calcium chloride and fractionally distilled under nitrogen using a column packed with "Dixon" stainless steel gauze rings, a middle fraction (b.p. 76.5°C) was collected, no impurities could be detected by GLC. Cyclohexane (600 cm^3) was added in small portions to a mixture of concentrated nitric acid (35 cm^3) and concentrated sulphuric acid (40 cm^3) and the mixture stirred. The cyclohexane was separated, washed with water, dried over calcium chloride and fractionally distilled through a column packed with "Dixon" rings, a middle fraction b.p. 81°C was collected.

Photochemical reaction between dibutyltin diacetate and carbon tetrachloride

Dibutyltin diacetate (10.00 g) added to a quartz tube as 10% w/w solution in carbon tetrachloride; after degassing (3 times) the tube was sealed at $<10^{-4}$ mmHg. The tube was irradiated 8 cm from a Hanovia medium pressure mercury lamp for 24 h, a fan being used to keep the temperature of the tube at 20°C. A small sample of the contents was removed and the remainder (87.08 g) was distilled at $<10^{-4}$ mmHg and condensed using liquid nitrogen cooling giving 78.45 g of volatile material. To the residue (8.35 g) in light petroleum (50 cm^3) was added a 4% solution of 2,2'-bipyridyl in light petroleum from a burette until precipitation was complete giving the dibutyltin dichloride-bipyridyl complex (1.309) from which by treatment with mercuric chloride [10] was obtained pure dibutyltin dichloride (0.65 g 7.5%) m.p. 38—39°C (lit. [11] m.p. 39.5—40°C) (Found: C, 32.0; H, 6.2. $C_8H_{18}Cl_2Sn$ calcd.: C, 31.6; H, 6.0%).

The volatile products were analysed by GLC (mixed injection) and by combined GLC/mass spectroscopy and were identified as butene (*m/e* 56, 41) chloroform (*m/e* 87, 85, 83, 47, 35), acetic acid (*m/e* 60, 45, 43), and hexachloroethane (*m/e* 203, 201, 199, 166, 164, 119, 117, 94, 47, 37, 36, 35). The retention times in minutes were C_4H_8 0.63, CCl_4 2.00, $CHCl_3$ 3.63, CH_3COOH 10.63^a and C_2Cl_6 11.13^a (flow rate 30 cm^3 min^{-1}, column temperature 65°C, ^{a} column temperature increased from 65 to 175°C at 12° min^{-1}).

Essentially the same results were obtained when dibutyltin dipropionate was used, except that the yield of dibutyltin dichloride was 9% and the retention times in minutes of the volatile products were: C_4H_8 0.60, CCl_4 1.30, $CHCl_3$ 1.80, C_2Cl_6 13.60, C_2H_5COOH (*m/e* 74, 59, 57, 45) 24.30, (Flow rate 30 cm^3 min^{-1}, column temperature 100°C). When dibutyltin bis(ethanethiolate) replaced the dicarboxylates the yield of dibutyltin dichloride was 12% and ethanethiol and diethyl disulphide were obtained. Retention times (min), C_4H_8 0.63; C_2H_5SH (*m/e* 62, 47, formula confirmed by accurate mass measurements) 1.25; CCl_4 2.25; $CHCl_3$ 3.19; $C_2H_5SSC_2H_5$ (*m/e* 122, 94, 79, 66, 61, 60, 45) 14.13; C_2Cl_6 28.00 (flow rate 30 cm^3 min^{-1}, column temperature 68°C). The relative abundances of all the volatile products are shown in Table 1.

Thermal reaction between dibutyltin diacetate and N-chlorosuccinimide

A glass tube containing *N*-chlorosuccinimide (3.00 g, 0.022 *M*), dibutyltin diacetate (3.51 g, 0.010 *M*), cyclohexane (50 cm^3) and benzoyl peroxide was degassed, sealed at $<10^{-4}$ mmHg and heated at 100°C for 24 h. The solid succinimide (2.19 g) was filtered off and purified by crystallisation from ethanol when it had m.p. 123—125°C (lit. [12] m.p. 126°C) (Found: C, 48.7; H, 5.2; N, 14.8. $C_4H_5O_2N$ calcd.: C, 48.5, H, 5.1; N, 14.1%). Vacuum distillation of the filtrate gave a volatile fraction (29.26 g) and left a residue (3.30 g), the residue in light petroleum gave only a trace of precipitate with 2,2'-bipyridyl and its IR and ^1H NMR spectra were identical with those of dibutyltin diacetate. The volatile material contained free hydrogen chloride and was shown by combined GLC/mass spectrometry to consist of unchanged cyclohexane (*m/e* 84, 69, 56, 55, 43, 42, 41) chlorocyclohexane (*m/e* 83, 82, 67, 55, 54, 41) and acetic acid, the percentage relative abundance of the latter two components being respectively 92.6, 7.4%.

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