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PREPARATION AND SPECTROSCOPIC STUDIES OF DIORGANOTIN OXYCARBONATES

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Summary

The synthesis, ^{119m}Sn Mössbauer and infrared spectra of a series of diorganotin oxycarbonates of the type, $(R_2Sn)_2OCO_3 \cdot nH_2O$, where R = Me, Et, Ph, $n = 0$; R = Pr, Bu, Oct, $n = 1$, are reported.

Structures are proposed for these compounds in the solid state, on the basis of their spectroscopic data.

Introduction

Although the bis(triorganotin) carbonates, $(R_3SnO)_2C{:}O$, have been well characterised and studied spectroscopically [1–4], there have been very few investigations of the corresponding diorganotin derivatives. The preparation of dimethyltin carbonate, Me_2SnCO_3, by the reaction of dimethyltin dichloride with silver carbonate in methanol [5] or with potassium carbonate in water [6] has been reported, but later studies have shown [7] that this product is likely to be the oxycarbonate, $(Me_2Sn)_2OCO_3$. The same workers claimed [7] the synthesis of diphenyltin oxycarbonate, $(Ph_2Sn)_2OCO_3$, by the reaction of diphenyltin dichloride with cesium carbonate in methanol solution at ambient temperature.

Our interest in the diorganotin oxycarbonates has recently arisen because of their possible involvement as intermediates in the environmental degradation [8] of bis(tributyltin) carbonate in wood [9], and their possible industrial utility as light stabilisers for rigid PVC [10].

In this paper, we describe the results of a reinvestigation of the synthesis of diphenyltin oxycarbonate and report the preparation of a series of four new dialkyltin oxycarbonates, $(R_2Sn)_2OCO_3$. The structures of these compounds in the solid state are discussed in terms of their ^{119m}Sn Mössbauer and infrared spectral data.

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Experimental

Preparation of $(R_2Sn)_2OCO_3$*, where R = Me, Et or Ph*

Equimolar (0.005 mol) aqueous solutions of the dimethyl- or diethyl-tin dichloride and potassium carbonate were mixed, with stirring, at room temperature. The products, which precipitated immediately, were filtered off, washed with water, and obtained, after drying in air at room temperature, as fine white, free-flowing powders. Diphenyltin oxycarbonate was prepared in the same way as the higher dialkyltin oxycarbonates, as detailed below.

Preparation of monohydrates, $(R_2Sn)_2OCO_3 \cdot H_2O$*, where R = Pr, Bu or Oct*

Owing to the low solubility of diphenyltin dichloride and the higher dialkyltin dichlorides in water, their oxycarbonates were prepared in methanol solution, using cesium carbonate [7] as the source of carbonate ion.

In a typical synthesis, the appropriate diorganotin dichloride (0.005 mol) in methanol was added dropwise to a stirred methanolic solution of an equimolar (0.005 mol) quantity of cesium carbonate at room temperature. The white precipitate, which formed immediately, was filtered off and transferred to a beaker of distilled water. The white precipitate was stirred vigorously in the water for 10–15 min to remove the cesium chloride, which was co-precipitated with the diorganotin oxycarbonate during the reaction. The purified product was filtered off and allowed to dry in air at room temperature.

The melting points and analytical data for the products are shown in Table 1.

Infrared measurements

Infrared spectra were obtained as Nujol mulls, or as potassium bromide discs, on a Grubb-Parsons Spectromaster Mark I or a Perkin–Elmer 599 infrared spectrophotometer. The asymmetric carbonyl stretching frequencies for the compounds are recorded in Table 2.

TABLE 1

ANALYTICAL DATA AND MELTING POINTS FOR DIORGANOTIN OXYCARBONATES, $(R_2Sn)_2OCO_3 \cdot nH_2O$

R	*n*	Analysis (Found (calcd.) (%))			M.p. (°C)
		C	H	Sn	
Me	0	15.66 (16.04)	3.21 (3.21)	64.1 (63.6)	> 300
Et	0	24.52 (25.12)	4.68 (4.65)	55.0 (55.4)	> 300
Pr	1	31.12 (30.95)	5.90 (5.95)	48.5 (47.2)	> 300
Bu	1	36.58 (36.43)	6.85 (6.79)	43.5 (42.5)	> 300
Oct	1	50.87 (50.51)	8.86 (8.93)	31.2 (30.4)	103
Ph	0	47.10 (48.23)	3.53 (3.21)	37.6 (38.3)	> 300

TABLE 2

^{119m}Sn MÖSSBAUER PARAMETERS, AT 295 AND 80 K, AND ASYMMETRIC CARBONYL STRETCHING FREQUENCIES FOR DIORGANOTIN OXYCARBONATES

Compound	80 K		295 K		ν_{as}(CO) (cm^{-1})
	δ (mm s^{-1})	Δ (mm s^{-1})	δ (mm s^{-1})	Δ (mm s^{-1})	
$(Me_2Sn)_2OCO_3$	1.12(5)	3.24(5)	1.01(1)	2.98(1)	1510
			1.10	3.24[a]	1510[a]
$(Et_2Sn)_2OCO_3$	1.23(5)	3.32(5)	1.46(9)	3.03(9)	1495
$(Pr_2Sn)_2OCO_3\cdot H_2O$	1.20(5)	3.06(5)	[b]	[b]	1510
$(Bu_2Sn)_2OCO_3\cdot H_2O$	1.20(5)	3.02(5)	[b]	[b]	1510
$(Oct_2Sn)_2OCO_3\cdot H_2O$	1.24(5)	3.14(5)	[b]	[b]	1505
$(Ph_2Sn)_2OCO_3$	0.93(1)	1.97(1)	1.02(5)	2.29(5)	1514
$(Ph_2Sn)_2OCO_3$			0.97 1.16	2.29[a] 3.93[a]	1510[a]

[a] Ref. 7. [b] Very weak spectra obtained.

Mössbauer spectra

^{119m}Sn Mössbauer spectra were obtained using a constant acceleration microprocessor spectrometer (from Cryophysics Ltd., Oxford) with a 512-channel data store. A 15mCi Ba^{119m}SnO$_3$ source was used at room temperature and samples were packed in perspex discs. Spectra were recorded at 80 K, using a liquid nitrogen cryostat, and at room temperature, and fitted with Lorentzian functions by a least squares fitting programme [11].

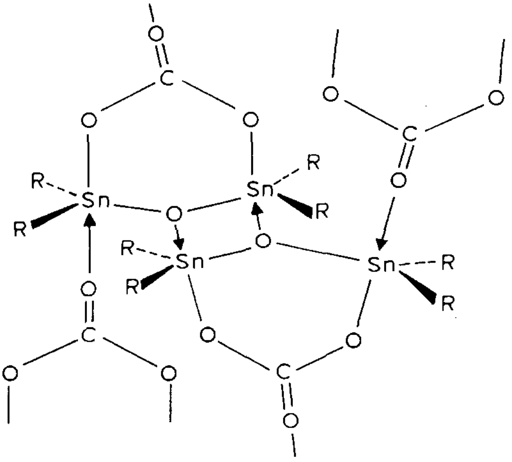
The values of the isomer shift (δ) and the quadrupole splitting (Δ) parameters for the diorganotin oxycarbonates are in Table 2. The isomer shift values are quoted relative to $BaSnO_3$.

Results and discussion

The diorganotin oxycarbonates are high melting, insoluble materials, which display room temperature ^{119m}Sn Mössbauer spectra. These properties are indicative of polymeric structures in the solid state. Additionally, the low carbonyl infrared stretching frequencies (1495–1515 cm^{-1}) observed for the compounds (Table 2) are in accord with bridging carbonate groups [7].

The similarity of the Mössbauer parameters for the dialkyltin oxycarbonates suggest that they all adopt the same structure in the solid state, and the quadrupole splitting values (3.0–3.3 mm s^{-1}) are typical of those associated with a trigonal bipyramidal tin atom geometry, in which the two alkyl groups are occupying equatorial positions [12]. Hence, the compounds probably possess a polymeric structure I, containing intermolecularly bridging carbonate groups and four-membered Sn_2O_2 rings, as proposed by Goel et al. for the dimethyltin derivative [7].

The Mössbauer parameters for diphenyltin oxycarbonate (Table 2) are also consistent [13,14] with equatorial R groups and trigonal bipyramidal coordination at tin, as in structure I, c.f. Ph_2Sn(sal-*N*-2-OC_6H_4), which shows δ 0.99, Δ 2.19 mm s^{-1} [13]. Goel et al. [7] reported that $(Ph_2Sn)_2OCO_3$ gave a four line Mössbauer spectrum, the parameters for the inner doublet being in good agreement with our



(I)

values (Table 2). We find that, if the product is not washed effectively with water after precipitation from methanol, it shows a similar four line Mössbauer spectrum (δ 1.00(3), Δ 2.26(3) mm s^{-1}; δ 1.16(5), Δ 3.82(5) mm s^{-1}), and it is therefore likely that the larger quadrupole split doublet is due to an ionic diphenyltin impurity, in which the tin atom is occupying an octahedral *trans*-R_2SnX_4 geometry, e.g. $\{Ph_2SnCl_4\}^{2-}$, which shows [15] δ 1.44, Δ 3.80 mm s^{-1}.

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