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MONOALKYLTIN ORTHOSULFITES*

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SUMMARY

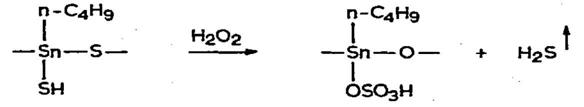
The oxidation of n-butyldithiostannonic acid with tert-butyl hydroperoxide leads to the monomeric bis(hydroxy-n-butyltin) orthosulfite which reacts readily with several organic and inorganic acids to form the corresponding substituted monoalkyltin orthosulfites. Several of these new compounds were investigated by indirect spectroscopic methods and possible structures are discussed in the light of the experimental results.

INTRODUCTION

It is known that bis(trialkyltin) sulfates may be prepared by either ester exchange reactions of trialkyltin mercaptides[1] or by reaction of sodium hydrogensulfate with bis(trialkyltin) oxides or hydroxides[2]. The preparation of organotin sulfates by the oxidation of organotin sulfides such as bis(tributyltin) sulfide or dibutyltin sulfide with aqueous hydrogen peroxide has also been reported recently[3], and a bicyclic monomeric structure implying pentacoordinated tin atoms was proposed for bis(tri-n-butyltin) sulfate, or more precisely, bis(tri-n-butyltin) orthosulfite in the solid state[4,5].

RESULTS AND DISCUSSION

While the oxidation of n-butyldithiostannonic acid with hydrogen peroxide allowed the preparation of the polymeric n-butylstannonic hydrogen sulfate[3], according to eqn. (1), we have found that its oxidation with tert-butyl hydroperoxide leads mainly to the monomeric binuclear bis(hydroxy-n-butyltin) orthosulfite by chain



$$-\underset{SH}{\overset{n\text{-}C_4H_9}{Sn}}-S- \xrightarrow{H_2O_2} -\underset{OSO_3H}{\overset{n\text{-}C_4H_9}{Sn}}-O- + H_2S\uparrow \qquad (1)$$

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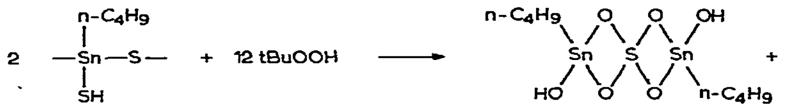
scission [eqn. (2)]. Molecular weight measurements indicate also the possible presence of small amounts of a polymeric form of this orthosulfite.



$$+\ 2\ H_2SO_4\ +\ S\ +\ 10\ H_2O\ +\ 12\ CH_2{=}C(CH_3)_2 \qquad (2)$$

The hydroxyorganotin orthosulfite reacts easily with carboxylic acids and anhydrides to form the carboxylate analogs. The hydroxyl group also reacts with sulfonic and sulfuric acids to produce the corresponding disulfonates and bis(hydrogen sulfates). In view of the oxidation reaction of n-butyldithiostannonic acid with hydrogen peroxide, it would be reasonable to assume that an unstable bis(hydrogen sulfate) is formed as an intermediate during the reaction with tert-butyl hydroperoxide. This possibility is reinforced by the fact that such a bis(hydrogen sulfate) can be prepared from the bis(hydroxy-n-butyltin) orthosulfite and sulfuric acid and that this latter compound reverts to the hydroxyorganotin orthosulfite when oxidized with tert-butyl hydroperoxide [eqn. (3)].

$$HO(C_4H_9)SnSO_4Sn(C_4H_9)OH \xrightleftharpoons[\text{t-BuOOH}]{H_2SO_4} HO_3SO(C_4H_9)SnSO_4Sn(C_4H_9)OSO_3H \qquad (3)$$

Substituted bis(alkyltin) orthosulfites are extremely hygroscopic and decompose easily when exposed to heat. They are soluble in most ketones in which their molecular weight in solution can easily be measured by osmometry.

Several of these new compounds were investigated by IR and Mössbauer spectroscopic methods. The IR spectra of the bis(alkyltin) orthosulfites show, as most n-substituted tin sulfates, the common vibrations at about 1100, 880 and 685 cm^{-1}

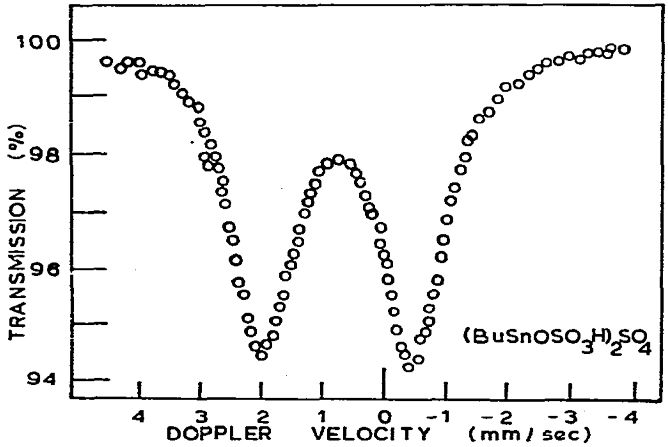
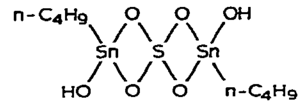
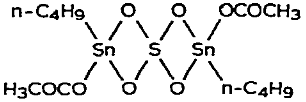
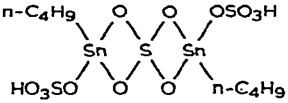
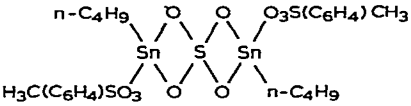
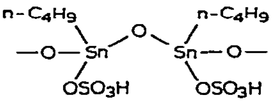
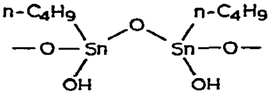
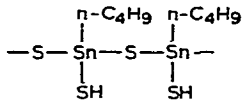


Fig. 1. Mössbauer spectrum of $(n\text{-}C_4H_9SnOSO_3H)_2SO_4$ at 84°K using a source of $BaSnO_3$ at room temperature. The isomer shift reference point is the center of a $BaSnO_3$–$BaSnO_3$ resonance spectrum at 294°K.

TABLE 1

MÖSSBAUER PARAMETERS AT 84±3°K FOR COMPOUNDS DISCUSSED IN THE TEXT

Compound		$\delta^{a,b}$ (mm/sec)	$\Delta E_Q{}^b$ (mm/sec)
(I)		0.89	2.22
(II)		0.82	2.38
(III)		0.83	2.33
(IV)		0.81	2.40
(V)		0.80	2.05
(VI)		0.71	1.59
(VII)		1.42	1.52

[a] With respect to $BaSnO_2$ at 294°K. [b] All values ±0.003 mm/sec.

which have been assigned to the stretching and deformation bands of the sulfate ion[6,7], while other minor absorptions in the 500 cm^{-1} region may be associated with the tin–hydrocarbon bond vibrations. The Mössbauer parameters for a number of the new mono-n-butyltin orthosulfites and related molecules are summarized in Table 1, and a typical resonance spectrum is shown in Fig. 1. The observed quadrupole splittings are sufficiently large to permit resolution of the two components of the hyperfine spectrum and show, as expected, that the distribution of electric charge about the metal atom lacks cubic symmetry in all of the compounds examined. The isomer shifts observed, falling in the range +0.7 to +1.4 mm/sec with respect to $BaSnO_3$, show unambiguously that all of these compounds can be considered as derivatives of Sn^{IV}, and that there is no evidence for the formation of reduced species in the synthetic procedures.

The narrow range of δ and ΔE_Q values for four bis(n-butyltin) orthosulfites suggests that these compounds are all iso-structural, and that the small differences in the isomer shift and quadrupole splitting parameters arise from steric and bonding effects of the OH, $OCOCH_3$, OSO_3H and $SO_3(C_6H_4)CH_3$ moieties, respectively. Moreover, these values are similar to those observed for other monoalkyltin complexes of electronegative ligands which impose restricted geometry on the environment of the metal atom[8], and distinct from monoalkyltin complexes such as (C_2H_5)-$Sn(O)OH$[9], $(n\text{-}C_4H_9)Sn(O)OH$ and the 8-hydroxyquinoline complexes of butyl- and phenyltin trichloride at 78°K which have been reported[9,10]. These latter four compounds have quadrupole splittings in the range +1.5 to +1.7 mm/sec; that is, comparable to $[(n\text{-}C_4H_9)Sn(O)OH]_n$ and $[(n\text{-}C_4H_9)Sn(S)SH]_n$, to be discussed below.

In conjunction with the IR data summarized above and the available physicochemical properties of the monoalkyltin orthosulfites, the Mössbauer data summarized in Table 1 lead to a self-consistent structural view of these compounds which envisages a tetradentate orthosulfite moiety acting as a bridging group between two metal atoms each of which has a significant distortion from T_d symmetry. The magnitude of this distortion, which is reflected primarily in the ΔE_Q parameter, arises both from small differences in the electron withdrawing power of the OX group, as well as its stereochemical requirements. In this context, the largest quadrupole splitting is observed for the *p*-toluenesulfonate complex, and the smallest for the hydroxy complex, while these have the smallest and largest isomer shift, respectively, of the sulfate derivatives. This observation is consistent with the postulate that the field gradient of the charge distribution about the metal atom—which is reflected in the ΔE_Q parameter—is principally due to an imbalance in the *p*-electron population. Starting with an sp^3 hybrid set of four bonding orbitals used in the metal atom in its σ-interaction with its nearest neighbor atom environment, the difference in the electron withdrawing power (electronegativity) of the Sn–C bond compared to the Sn–OS and Sn–OX gives rise to an imbalance in the relative amount of *s* and *p* character used in this interaction. By Bent's postulates[11], as the electronegativity of the OX moiety increases, the Sn–C interaction will increase in the relative amount of *s* character and the Sn–OX interaction will increase in the relative amount of *p* character, thus leading to an increase in the quadrupole splitting. At the same time, increasing electronegativity of the OX group will withdraw increasing charge from the metal atom, leading to a decrease in the isomer shift value which is observed. While these systematics are influenced to some small extent by the differences in stereochemical requirements of the OX group which may exert a small influence on the C–Sn–O bond angles, this is presumably not a major perturbation since the stereochemical requirements of the four membered O–Sn–O–S ring assures a large accessible area for the positioning of the remaining two bonds. On this basis, the present data suggest an order of electron withdrawing power of the OX group in these compounds as follows:

$$OH < OSO_3H < OCOCH_3 < SO_3(C_6H_4)CH_3$$

this order being reflected in both of the parameters extracted from the Mössbauer spectroscopic data.

The influence of the restrictive geometry imposed by the four membered O–Sn–O-ring is illustrated by the Mössbauer data for the oxy-bridged polymers [Table 1, compounds (V) and (VI)], both of which show significantly smaller quadrupole splittings than the sulfate homologues having the same OX group.

Although some of this change in the quadrupole splitting (compared to the sulfate bridged complexes) may be due to the difference in electron donor-acceptor properties of the O-bridged moiety compared to the SO_4-bridged group, the small change observed in the isomer shift of the former, compared to the latter, suggests that this is a minor effect, and that the major contribution to the change in the quadrupole splitting results from the change in stereochemistry. It should be noted that in the O-bridged species, a smaller isomer shift is observed for the hydroxy complex, compared to the OSO_3H complex, but insufficient data are available at the present time to afford a more detailed explanation of this observation.

Finally, it is interesting to note that the largest isomer shift—and hence the largest *s*-electron density at the ^{119}Sn nucleus—is recorded for n-butyldithiostannonic acid, the thio homologue of compound (VI) in Table 1. This observation can be accounted for qualitatively by the lesser electronegativity of the bridging sulfur atom and the SH group, compared to a bridging oxygen and the OH group, and hence a greater covalency in the metal–ligand interaction. This difference in electronegativity and bond length may also account for the easy formation of the tetrameric cage structure of mono-n-butyltin sulfide from n-butyldithiostannonic acid[12] while n-butylstannonic acid leads invariably to polymeric structures. Nonetheless, the available data are too limited to provide a more quantitative discussion of the observed results.

EXPERIMENTAL

The Mössbauer effect measurements were carried out in transmission geometry using a constant acceleration spectrometer of the type described earlier[13,14], in conjunction with a $Ba^{119m}SnO_3$ source at room temperature. Samples were mounted as thin layers of microcrystalline powders in standard copper sample holders and attached to the copper cold finger of a liquid nitrogen cooled cryostat fitted with mylar windows. Where necessary, hygroscopic samples were mounted in sample holders in an inert atmosphere, and immediately cooled to liquid nitrogen temperature. Sample temperatures were monitored by means of a calibrated thermocouple and remained constant within $\pm 1°$ during the 10 to 20 h data acquisition time. Spectrometer calibration was effected using 0.8 mil NBS 99.99% pure iron foil and a $Pd(^{57}Co)$ source at room temperature and subsequent data analysis used NBS hyperfine splitting values. All isomer shift values are reported with respect to the centroid of a room temperature $BaSnO_3$–$BaSnO_3$ spectrum, such data being directly comparable within the quoted experimental error ($\pm$0.003 mm/sec), to the SnO_2 isomer shift reference point used in the earlier literature. Data reduction was effected from manual plots of the data using the numerical methods described earlier[15]. The

IR spectra were obtained at room temperature using KBr wafers (Perkin–Elmer 337 grating spectrophotometer).

Bis(hydroxy-n-butyltin) orthosulfite

A solution of 27 g of tert-butyl hydroperoxide in 50 ml of toluene was added dropwise to a refluxing suspension of 12 g of n-butyldithiostannonic acid in 50 ml of toluene. The reaction mixture was maintained at reflux until 4.5 ml of water were collected in a trap and the evolution of isobutene had subsided. The reaction product was filtered, washed with carbon disulfide and purified by reprecipitation from 2-butanone with n-hexane. Upon drying, a quantitative yield (11.8 g) of bis(hydroxy-n-butyltin) orthosulfite, an off white amorphous powder melting with decomposition at 275°, was obtained. (Found: C, 20.86; H, 4.03; O, 17.81; S, 6.75; Sn, 49.92; mol.wt., 580. $C_8H_{20}O_6SSn_2$ calcd.: C, 20.63; H, 4.03; O, 17.77; S, 6.88; Sn, 50.97%; mol.wt., 476.) IR (cm^{-1}): 3300 s, 2850 s, 1650 w, 1450 w, 1325 m, 1320 vs, 1150 s, 1040 vs, 950 s, 870 w, 685 m, 640 m, 625 m, 500 s.

Bis(acetoxy-n-butyltin) orthosulfite

To a refluxing suspension of 4.8 g of bis(hydroxy-n-butyltin) orthosulfite in 50 ml of toluene was added 0.7 g of glacial acetic acid. The reaction was monitored by IR until disappearance of the absorption band characteristic of the hydroxyl group. The water of condensation, amounting to 0.8 ml, was collected in a trap and 5.1 g of bis(acetoxy-n-butyltin) orthosulfite was filtered from the solvent, washed with n-hexane and vacuum dried, m.p. 192–196° decompn. (Found: C, 24.38; H, 4.40; O, 20.99; S, 5.91; Sn, 40.38; mol.wt., 577. $C_{12}H_{24}O_8SSn_2$ calcd.: C, 25.47; H, 4.27; O, 22.62; S, 5.66; Sn, 41.96%; mol.wt., 566.) IR (cm^{-1}): 3005 m, 2900 vs, 2870 s, 1570 vs, 1435 vs, 1255 s, 1150 s, 1040 vs, 980 s, 730 s, 690 m, 600 w, 560 w, 465 m.

Bis(p-toluenesulfoxy-n-butyltin) orthosulfite

A solution of 3.5 g of *p*-toluenesulfonic acid in 20 ml of anhydrous alcohol was added dropwise to a refluxing suspension of 4.8 g of bis(hydroxy-n-butyltin) orthosulfite in 100 ml of benzene. The reaction mixture was kept at reflux until 0.8 ml of water had been condensed. Filtration of the mixture in a glove box, under N_2, yielded 7.1 g of a fine amorphous white powder, extremely hygroscopic and melting with decomposition at 110°. (Found: C, 32.57; H, 4.16; O, 21.02; S, 11.96; Sn, 29.78; mol.wt., 847. $C_{22}H_{32}O_{10}S_3Sn_2$ calcd.: C, 33.44; H, 4.08; O, 20.25; S, 12.17; Sn, 30.04%; mol.wt., 790.) IR (cm^{-1}): 2930 m, 1450 w, 1375 w, 1150 vs, 1110 s, 1040 m, 1005 m, 810 w, 685 m, 616 w, 565 m.

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