Synthesis and Mössbauer Spectra of Dimethyltin Derivatives of Monobasic Sulphonic Acids

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IN contrast to the well studied class of alkyltin carboxylates, the corresponding derivatives of sulphonic acids have not attracted much attention. Very few derivatives of alkyl- and aryl-sulphonic acids have been synthesized[1] and virtually no structural information is available. We report a novel and very simple method for the preparation of dimethyltin disulphonates of the general formula $Me_2Sn(SO_3X)_2$, where X = F, Cl, Me, Et, or CF_3. Only the SO_3Me derivative has been reported previously.

The synthesis involves the solvolysis of dimethyltin dichloride or trimethyltin chloride in the corresponding acid according to:

$$(1)\ Me_2SnCl_2 + 2HSO_3X \xrightarrow{25^\circ} Me_2Sn(SO_3X)_2 + 2HCl \quad \text{or}$$

$$(2)\ Me_3SnCl + 2HSO_3X \xrightarrow{25-60^\circ} Me_2Sn(SO_3X)_2 + CH_4 + HCl$$

Procedure (2) can be regarded as a two-step reaction, whereby HCl is evolved instantaneously on addition of the acid. The trimethyltin chloride is dissolved completely and in a slower process over 15—20 min., depending on temperature and the acid strength, methane is produced in a mildly exothermic reaction. Finally the dimethyltin disulphonate crystallizes out quantitatively and can be separated from the excess of acid either by evaporation *in vacuo* or by filtration and washing with CCl_4. The second step and the evolution of methane are only observed when an approximately twofold excess of acid over the required amount is used. At higher solvent to solute ratios the stable $Me_3Sn^+_{solv}$ cation is formed which is capable of existence in strong protonic acids. Even heating to 100° does not result in a cleavage of a tin–carbon bond.

The protolysis of a tin–carbon bond has been observed before[2,3] mainly in carboxylic acids, but the reactions reported indicate a variety of products. Generally route (2) was preferred because it yields better crystalline products and the reaction could be followed by methane evolution.

All prepared compounds are fairly high melting, non-volatile, hygroscopic, white crystalline solids, insoluble in nonpolar solvents but soluble in co-ordinating solvents, *e.g.* alcohols and ether. They undergo thermal decomposition at or slightly above the melting point.

The ^{119}Sn Mössbauer spectra were recorded and are listed together with the melting points in the Table. As can be seen, the isomer shifts δ fall in the region 1·60—1·80 mm./sec. relative to SnO_2. The quadrupole splittings Δ are very large, the value of 5·54 mm./sec. for $Me_2Sn(SO_3F)_2$ at 80° K being the largest hitherto reported value for a tin compound. With decreasing acid strength or decreasing electronegativity of X in SO_3X, the quadrupole splittings decrease slightly. All compounds show a noticeable Mössbauer effect at room temperature, with $\epsilon_{205}/\epsilon_{80}$ values in the vicinity of *ca.* 0·10. This is quite in contrast to dialkyltin dicarboxylates, where polymeric structures are doubtless present, but no room temperature effect has been observed.[4] We conclude that stronger polymeric association for the disulphonates is likely. The similarity of the Mössbauer data suggests a strong structural similarity within the group. Dimethyltin sulphate[5] also shows very similar parameters.

Mössbauer parameters of $Me_2Sn(SO_3X)_2$ *compounds*

Compound	M.p.	Method of preparation	T[°K]	δ [mm./sec.]	Δ [mm./sec.]	$\epsilon_{295}/\epsilon_{80}$
$Me_2Sn(SO_3F)_2$	253°	1 and 2	80	1·82	5·54	0·089
			295	1·77	5·41	
$Me_2Sn(SO_3CF_3)_2$	336—337°	2	80	1·79	5·51	0·129
			295	1·78	5·51	
$Me_2Sn(SO_3Cl)_2$	370—375°	1 and 2	80	1·75	5·20	0·197
			295	1·72	5·18	
$Me_2Sn(SO_3Me)_2$	312°	2	80	1·52	5·05	0·129
			295	1·54	5·03	
$Me_2Sn(SO_3Et)_2$	272^{c}	2	80	1·52	4·91	0·117
			295	1·51	4·83	
Me_2SnSO_4			80	1·611	5·003	0·577
			295	1·572	4·94	

Vibrational spectra indicate the presence of only one type of SO_3X group, judging from the number of bands in the SO_2 stretching frequency region. They are substantially lowered as compared to their position in covalent, monodentate arrangements. So is *e.g.* $\nu(SO_2)_{as}$ for $Me_2Sn(SOF_3)_2$ found at 1360 (i.r.) and 1354 (Raman), whereas the normal range is *ca.* 1510—1440 $cm.^{-1}$.[6] On the other hand, $\nu(SO_2)_{as}$ for the SO_3F^- ion is found at *ca.* 1290 $cm.^{-1}$.[7] This fact and the position and number of the remaining vibrations exclude an ionic structure with an Me_2Sn^{2+} cation, which would be also inconsistent with the Mössbauer data as well as with the observed insolubility in the parent acids. In all these compounds the SO_3X group appears to act as a bidentate bridging group.

In the tin–carbon stretching frequency region, $\nu(Sn–C)_{as}$ for the SO_3F compound is found at 576 $cm.^{-1}$ and is only i.r.-active, whereas $\nu(Sn–C)_{sym}$ at 531 $cm.^{-1}$ is only Raman-active. The mutual exclusion suggests a linear or near linear C–Sn–C arrangement. Such a molecular structure with a distorted octahedral environment for tin, and both methyl groups *trans*, can also explain the unusually large Δ values for hexaco-ordinated tin. According to Fitzsimmons *et al.*,[8] the quadrupole splitting for octahedral tin of the SnA_4B_2 type is expected to be about twice as large for a *trans*-isomer as for a *cis*-isomer, assuming the co-ordination polyhedron has axial symmetry.

A suggested structure, rationalising all observed features is shown in the Figure. The possibility of unequal tin–oxygen bond distances as found recently in the case of a bridging carboxylate group[9] can not be ruled out.

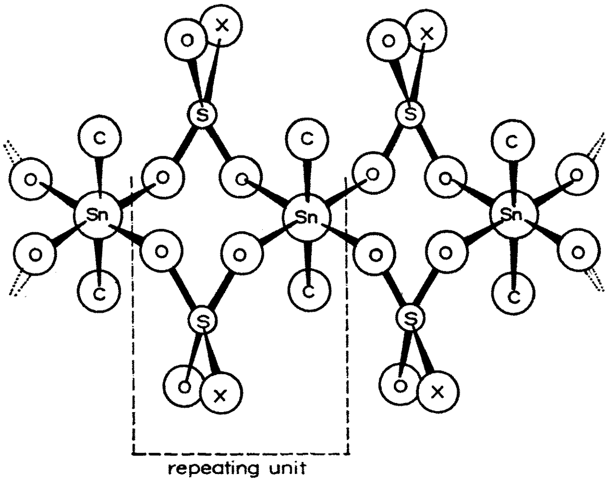

FIGURE. *Suggested structure for* $Me_2Sn(SO_3X)_2$ *compounds.*

Attempts to extend the synthetic route to diphenyl derivatives failed, due to side reactions such as further solvolysis of the Sn–C bond and attack of the aromatic ring.

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