On the Metallo-organic Compounds. XII. Dialkyltin Sulphide R_2SnS (or tri-thio-anhydro-tris-dialkylstanne-dithiol $(R_2SnS)_3$).

By Taichi HARADA.

(Received March 31, 1942.)

In the previous papers⁽¹⁾ the author described that dialkyltin halide and the diacetate combined with dialkyltin oxide in the ratio 1:3 to form the complex compounds.

$$[R'OSnR_2OSnR_2OSnR_2OR'\cdot SnR_2X_2]$$

(where R′ represents the alkyl radical or hydrogen of the solvent alcohol or water) and

$$R_2\underline{SnOSnR_2OSnR_2O}\cdot SnR_2(CH_3COO)_2$$

The formation of $R'OSnR_2OSnR_2OSnR_2OR'$ and $\underline{SnR_2OSnR_2OSnR_2O}$ in the compounds may be regarded as the condensation product of three molecules of $R_2Sn(OR')(OH)$ formed previously by the interaction of R_2SnO with R′OH under a given condition. It is pointed out, therefore, that tri-anhydro-tris-dialkylstanne-diol is the product formed by the elimination of one molecule of water from di-anhydro-tris-dialkylstanne-diol $H(R_2SnO)_3OH$. The correctness of this assumption is supported further by the results of molecular weight determination of

$[((C_2H_5)_2SnO)_3\cdot Sn(C_2H_5)_2(CH_3COO)_2]$⁽¹⁾ and also of

$[(CH_3)_2SnO\cdot Sn(CH_3)_2(CH_3COO)_2]$

described below. The latter compound is very slightly soluble in such organic solvents as alcohol, benzene, naphthalene, etc., but fairly soluble when they are hot; hence the molecular weight of this compound was determined in naphthalene by its freezing-point method.

In a concentrated solution the determination gives a value which indicates that the compound is in a trimolecular form while as the solution becomes dilute the value decreases to a certain extent, indicating dissociation; that is, at 2.906, 1.672 and 1.396% concentrations the depressions were 0.113, 0.113 and 0.128°C. respectively. As these figures give molecular weights of 1268, 882 and 763 respectively (Calcd. for the trimolecular one

$$[((CH_3)_2SnO\cdot Sn(CH_3)_2(CH_3COO)_2)_3],\ \text{M.W., } 1925.$$

Therefore, dialkyltin oxide might have the six-membered hetero-cyclic structure:

$$R_2\underline{SnOSnR_2OSnR_2O}\ .$$

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(1) T. Harada, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **35** (1939), 290; **36** (1939), 497; **38** (1940), 146.

It is difficult, however, to determine the molecular weight of the compound owing to its insolubility in all solvents.

Dialkyltin sulphide resembles dialklytin oxide in the type of reactions and in its constitution: that is, the compound is regarded as one wherein the oxygen is replaced by sulphur, and therefore, many similarities might be expected to exist between them. Contrary to the insolubility of the former, the latter is soluble in certain organic solvents. We expected that the result of the molecular weight determination of the sulphide will give a notion regarding the structure of the oxide. For this purpose the present investigation was carried out.

Recently Kotscheschkow(2) obtained dimethyltin sulphide as a precipitate by saturating the aqueous solution of dimethyltin dichloride with hydrogen sulphide. The nature of the compound, however, is not disclosed except the melting point 148°C.

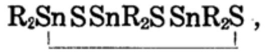
Dialkyltin sulphide is easily prepared by treating dialkyltin dihalide with KSH in absolute alcohol saturated with H_2S, therefore, the reaction may be represented as follows:

$$R_2SnX_2 + 2\,KSH = R_2SnS + SH_2 + 2\,KX.$$

Both dimethyltin sulphide and diethyltin sulphide are colourless crystals, and the former melts at 149°C., the latter at 24°C. These compounds are also formed when the dialkyltin dihalide is treated with Na_2S in boiling alcohol according to the reaction:

$$R_2SnX_2 + Na_2S = R_2SnS + 2\,NaX.$$

The compound reacts with a strong mineral acid such as hydrochloric acid for example, producing the dialkyltin dihalide with evolution of hydrogen sulphide. The structure of these sulphides must be represented as the six-membered hetero-cyclic one



$$R_2Sn\,S\,SnR_2S\,SnR_2S\ ,$$

since the molecular weight determination in benzene and in naphthalene becomes three times the mono-molecular one. Therefore, the structure of the dialkyltin oxide $(R_2SnO)_3$ in

$$[(R_2SnO)_3 \cdot SnR_2(OAC)_2]$$

must be represented in a similar way. However, the sulphide has no tendency to combine with the corresponding dihalide or diacetate to form a complex compound as in the oxide. This is expected to be unlike the nature of oxygen which makes them able to extend secondary valencies producing complex compounds.

Experimental. Dimethyltin sulphide or tri-thio-anhydro-tris-dimethyltin-dithiol: Dimethyltin diiodide was treated with KSH in absolute alcohol saturated with H_2S, then the solution of the mixture was

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(2) *Ber.* **56** (1933), 1661.

extracted with ether after the addition of water. On evaporation of ether, colourless crystals were formed, m.p., 149°C.

(2) Dimethyltin diiodide was dissolved in absolute alcohol and was treated with Na_2S by heating until the solution indicated to be neutral or alkaline. The solvent was evaporated and a large amount of water was added. In this way a white substance separated out. The substance was extracted with ether. On evaporation of the solvent after filtration, a crystalline compound was formed which was identical with the compound formed by method I. Dimethyltin sulphide is difficultly soluble in hot alcohol but easily soluble in ether, benzene, naphthalene, etc.

Anal. Subs., 0.2749: SnO_2, 0.2288, $BaSO_4$, 0.3558.
Subs., 0.4430: SnO_2, 0.3701, $BaSO_4$, 0.5522.
Calcd. for C_4H_6SnS, Sn and S, 65.65 and 17.73.
Found: Sn, 65.66, S, 17.78, Sn, 65.77, S, 17.35.

(1) M.W. of the Subs. in Benzene (Cryoscopic Method)

Subs.	Conc. (%)	ΔT	C_6H_6(c.c.) at 20°	Obs. M.W.
0.7566 …………	5.191	0.505	25	543
" …………	3.309	0.315	40	543

(2) M.W. of the Subs. in Naphthalene (Cryoscopic Method)

Subs.	Conc. (%)	ΔT	$C_{10}H_8$ (g.)	Obs. M.W.
0.9208 …………	4.403	0.610	19.99	541
" …………	3.262	0.430	27.31	541
" …………	2.705	0.355	33.12	542

Calcd. for $(CH_3)_2$ SnS, M.W., 180.8 and for $((CH_3)_2SnS)_3$, M.W., 542.4.

Diethyltin sulphide or tri-thio-anhydro-tris-diethyltin-dithiol: Diethyltin dibromide was treated with Na_2S in absolute alcohol. Then water was added; a heavy liquid separated out. The liquid was extracted with ether. The ethereal solution was dried with anhydrous Na_2SO_4, then the solvent ether was removed in the usual way. In this way an impure amber coloured liquid was obtained. It was purified by vacuum distillation (b.p., $219–221^{8mm}$, m.p. 24°C.). Its specific gravity was found to be 1.7264 at 35°C. The compound reacts with a strong acid, e.g. hydrochloric acid, forming the acid derivative with evolution of hydrogen sulphide. Diethyltin sulphide is soluble in ordinary organic solvent such as ether, benzene, etc. and insoluble in water.

Anal. Subs., 0.3964: SnO_2, 0.2862, $BaSO_4$, 0.4322.
Calcd. for $C_4H_{10}SnS$:Sn and S, 56.85 and 15.35.
Found; Sn, 56.87 and S, 14.98.

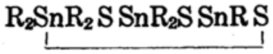
M.W. of the Subs. in Benzene (Cryoscopic Method)

Subs.	Conc. (%)	ΔT	C_6H_6(c.c.) at 20°	Obs. M.W.
0.7065	3.115	0.256	25	615
"	2.245	0.180	35	625
"	1.755	0.140	45	625

Calcd. for $(C_2H_5)_2SnS$, M.W., 208.8 and for $((C_2H_5)_2SnS)_3$ M.W., 626.5.

Summary.

Dialkyltin sulphide has been prepared by treating dialkyltin dihalide with KSH in absolute alcohol, saturated with hydrogen sulphide. The six-membered hetero-cyclic structure



$$R_2SnR_2S\,SnR_2S\,SnR\,S$$

and the term tri-thio-anhydro-tris-dialkylstanne-dithiol are suggested for the compound from the results of the molecular weight determination.

The Institute of Physical and Chemical Research,
Komagome, Hongo, Tokyo.