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STUDY ON TRIORGANOSTIBINE SULFIDE AND ITS COMPLEXES

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INTRODUCTION

In the course of our study on organoantimony compounds we have found that pentavalent compounds containing formally Sb–S single bonds are easily reduced to the trivalent state[1]. However, $(CH_3)_3SbS$ is a fairly stable crystalline substance which forms a novel complex, $(CH_3)_2SnCl_2 \cdot 2\,(CH_3)_3SbS$[2], and is markedly different from polymeric amorphous $(C_6H_5)_3SbO$[3]. In this paper we wish to report on the reactions of triorganostibine sulfides with some tin(IV) compounds and the behavior of four novel complexes, $R_2SnX_2 \cdot 2\,(CH_3)_3SbS$ ($R = CH_3$, C_2H_5; $X = Cl$, Br), in chloroform solution.

EXPERIMENTAL

Preparation of triorganostibine sulfide

$(CH_3)_3SbS$ was prepared by the reaction between trimethylstibine oxide and H_2S in methanol and purified by recrystallization from methanol: m.p. 176° (dec.). (Found: C, 18.33; H, 4.59. C_3H_9SSb calcd.: C, 18.11; H, 4.56%.) Mol.wt. found osmometrically in C_6H_6 at 25°: 204, 198, 210, at concentrations 0.17, 0.22 and 0.29% w(sample)/w(solvent), respectively; in $CHCl_3$ at 25°: 210, 208 at concentrations 0.54 and 0.98% w/w, respectively; calcd. for monomer: 199.

R_3SbS ($R = C_2H_5$, C_6H_{11}) were prepared by the reaction of R_3SbBr_2 with hydrated Na_2S in methanol and purified by recrystallization from petroleum ether or methanol. $(C_2H_5)_3SbS$: m.p. 119–120° (reported[4]: 118°); $(C_6H_{11})_3SbS$: m.p. 144° (reported[4]: 144°). Mol. wt. found osmometrically in $CHCl_3$ at 25°: 419, 427 at concentrations 0.37 and 1.00% w/w, respectively; calcd. for $(C_6H_{11})_3SbS$, mol. wt.: 403.

Reactions of $(CH_3)_3SbS$ and $(C_6H_{11})_3SbS$ with tin(IV) compounds

All the reactions were carried out by mixing the both compounds in various mole ratios in methanol, acetone or chloroform and the results are summarized in Table 1.

Complexes, $R_2SnX_2 \cdot 2\,(CH_3)_3SbS$, were isolated in the manner described in our previous paper[2]. They were also obtained by dissolving in mole ratios 3:3:1 of $(CH_3)_3SbS$, $(CH_3)_3SbX_2$ and $(R_2SnS)_3$ in the above solvents. For example, $(CH_3)_3SbS$ (2 g), $(CH_3)_3SbCl_2$ (2.4 g) and $[(CH_3)_2SnS]_3$ (1.8 g) were dissolved in 150 ml of chloroform. After evaporating the solvent, $(CH_3)_2SnCl_2 \cdot 2\,(CH_3)_3SbS$ was obtained

TABLE 1

REACTIONS OF R_3SbS AND TIN(IV) COMPOUNDS IN METHANOL, ACETONE OR CHLOROFORM

Tin(IV) chloride[a]	*$(C_6H_{11})_3SbS$*	*$(CH_3)_3SbS$*	*Tin(IV) chloride*[a]	*$(C_6H_{11})_3SbS$*	*$(CH_3)_3SbS$*
R_3SnCl			*R_2SnCl_2*		
R = n-C_4H_9	—[b]	—	R = n-C_4H_9	—	—
n-C_3H_7	—	—	n-C_3H_7	Ex	—
C_2H_5	—	—	C_2H_5	Ex	Complex
CH_3	—	—	CH_3	Ex	Complex
C_6H_5	Ex[c]	Ex	C_6H_5	Ex	Ex
n-$C_4H_9SnCl_3$	Ex	Ex	$SnCl_4$	Ex	Ex

[a] The results obtained with bromide are quite similar to those of chloride. [b] — = starting materials are recovered. [c] Ex = exchange reaction.

TABLE 2

TRIMETHYLSTIBINE SULFIDE COMPLEXES, $R_2SnX_2 \cdot 2\ (CH_3)_3SbS$

R	*X*	*M.p. (°C)*	*% C found (calcd.)*	*% H found (calcd.)*	*% X found (calcd.)*	*% S found (calcd.)*	*Mol. wt.*[a] *found/concentration*[b]	
CH_3	Cl	147–147.5	15.98 (15.56)	3.93 (3.92)	11.25 (11.48)		Toluene:	647/0.23, 666/0.49, 647/0.55, 661/0.75
							DMF:	263/0.61, 259/1.02, 315/1.88, 363/2.41
							$CHCl_3$:	308/0.72, 294/1.24, 323/2.07
							Calcd.:	617
	Br	123–124	13.84 (13.60)	3.25 (3.42)	22.99 (22.62)	8.84 (9.08)	Toluene:	740/0.24, 756/0.41
							$CHCl_3$:	339/0.45, 343/0.99
							Calcd.:	706
C_2H_5	Cl	122–123	18.80 (18.61)	4.36 (4.37)	9.90 (9.93)		Toluene:	660/0.24, 665/0.49, 663/0.74
							$CHCl_3$:	280/0.38, 301/1.01
							Calcd.:	645
	Br	121	16.41 (16.35)	3.54 (3.84)	21.92 (21.76)	8.49 (8.73)		

[a] At 65°C in toluene and DMF, at 25°C in $CHCl_3$. [b] [w(sample)/w(solvent)] × 10^2.

as colorless crystals: yield, 6.1 g (98 %). Properties of the complexes are shown in Table 2. They are soluble in polar solvents but almost insoluble in non-polar solvents.

Sulfur–halogen exchange reactions were confirmed by isolating the reaction products: SnS_2, $RSnS_{3/2}$, $(R_2SnS)_3$ or $(R_3Sn)_2S$ and R'_3SbX_2. For example, triphenyltin chloride (7.7 g, 0.02 mole) in 50 ml of acetone was added to $(CH_3)_3SbS$ (2 g, 0.01 mole) in 50 ml of methanol. The clear solution was concentrated on a water bath to give colorless crystals. The insoluble part in 50 ml of benzene was recrystallized from acetone to give 2.1 g (88 %) of trimethylantimony dichloride, m.p. 224°

(dec.). (Found: Sb, 51.34. $C_3H_9Cl_2Sb$ calcd.: Sb, 51.21 %.) From the benzene solution 7.0 g (96 %) of bis(triphenyltin) sulfide was obtained; m.p. 140.5–141.5° (reported[5]: 141.5–143°). When triphenyltin chloride and trimethylstibine sulfide were treated in 1 : 1 mole ratio, the same exchange products and the excess of trimethylstibine sulfide were obtained. Similarly, the reaction products were isolated almost quantitatively in the exchange reactions shown in Table 1.

Infrared spectra

The infrared spectra in the 4000–400 cm^{-1} region were recorded using Hitachi EPI-2G spectrophotometer and in the 400–100 cm^{-1} region using Hitachi FIS-1 spectrophotometer both equipped with gratings. In the 4000–400 cm^{-1} region the spectra in the solid state were determined as mulls in nujol or hexachlorobutadiene, but in solution they were measured in chloroform or bromoform. The spectra from 400 to 100 cm^{-1} were measured as paraffin paste of low melting point.

Molecular weight determinations

Molecular weights were determined at 25° or 65° using Mechrolab Model 302 vapor pressure osmometer.

NMR spectra

The NMR measurements were made at room temperature (20°) and at selected temperatures from 35° down to −40° in $CHCl_3$ and CH_2Cl_2 with a Japan Electron Optics JNM-3H-60 spectrometer operating at 60 Mc/sec. Through these experiments tetramethylsilane was used as an internal standard.

X-ray powder patterns

The X-ray powder patterns were obtained using Geiger-flex made by Rigaku-Denki Co. Ltd.

RESULTS AND DISCUSSIONS

As shown in Table 1, the products vary with tin(IV) compounds employed and the complex formation is observed only in the reactions of $(CH_3)_3SbS$ with $(CH_3)_2SnX_2$ and $(C_2H_5)_2SnX_2$. This indicates that R_3SbS is fairly reactive as a ligand and is markedly different from R_3PS which has been reported to form a stable complex, $SnX_4 \cdot 2\,R_3PS$[6].

Infrared spectra of $R_2SnX_2 \cdot 2\,(CH_3)_3SbS$ in the solid state

The infrared bands of $(CH_3)_3SbS$ were assigned by referring to the spectra of $(CH_3)_3SbX_2$[7], R_3PS[8] and R_3AsS[9], and the relevant frequencies are summarized in Table 3. Since this compound is monomeric in solution as described in the experimental part, a strong band at about 430 cm^{-1} is reasonably assigned to $\nu(Sb{=}S)$. As is shown in Table 4, this band shifts to the lower frequency side by about 30 cm^{-1} in complexes, $R_2SnX_2 \cdot 2\,(CH_3)_3SbS$. This is quite analogous to $SnX_4 \cdot 2\,R_3PS$[6], $(C_6H_5)_3PS \cdot ICl$[8], $ZnI_2 \cdot 2\,(CH_3)_3PS$[10] and $HgI_2 \cdot (C_6H_5)_3PSe$[11], and indicates the coordination through sulfur to tin atom.

TABLE 3

IR FREQUENCIES OF R_3SbS (900–100 cm^{-1} REGION, IN cm^{-1})

R = CH₃ Solid[a]	*R = CH₃* Solution[b]	*R = C₂H₅* Solid[a,c]	*Assignment*
855 s	838 s		CH_3–(Sb) rock.
785 w	774 w		
		706 s	CH_2–(Sb) rock.
555 s	551 s	529 m	Sb–C deg. str.
531 m	531 m	506 s	Sb–C sym. str.
431 s	433 s	421 s	Sb=S str.
180 m			C_3Sb def.
149 s			

[a] Mulls in nujol or hexachlorobutadiene, or paste of paraffin with low melting point. [b] Measured in $CHCl_3$ or $CHBr_3$ down to 400 cm^{-1}. [c] Measured down to 400 cm^{-1}.

TABLE 4

IR FREQUENCIES OF $R_2SnX_2 \cdot 2\,(CH_3)_3SbS$ IN THE SOLID STATE[a] (900–100 cm^{-1} REGION, IN cm^{-1})

R = CH₃		*R = C₂H₅*		*Assignment*
X = Cl	*X = Br*	*X = Cl*	*X = Br*	
850 s	845 s	852 s	850 s	CH_3–(Sb) rock.
794 (sh.)	792 (sh.)	792 w	792 w	
781 s	779 s			CH_3–(Sn) rock.
		688 m	688 m	CH_2–(Sn) rock.
561 s	558 s	559 m	557 m	Sb–C deg. str.
(561)	555 s	529 (sh.)	522 (sh.)	Sn–C antisym. str.
529 s	524 s	533 m	529 m	Sb–C sym. str.
?	?	476 vw	472 vw	Sn–C sym. str.
402 s	401 s	401 s	401 s	Sb=S str.
		370 w		
		291 w	289 w	C–C–Sn def.
		280 w	281 (sh.)	
230 s	232 m	202 s	220 m	Sn–S str.
(230)		(202)		Sn–Cl str.
	162 m		142 m	Sn–Br str.
138 s	130 s	160 m	120 s	C_3Sb def.
		118 s		
(138)	(130)	(118)	(120)	C_2Sn def.

[a] Mulls in nujol or hexachlorobutadiene, or paste of paraffin with low melting point. ( ): Values considered to be overlapped.

In R_3SbS the estimated frequencies* for a pure single and double antimony-sulfur bonds are 337 and 483 cm^{-1}, respectively. The small shift of the absorption band on complex formation suggests that the coordination through sulfur to tin

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* From the calculation using Gordy's rule[12], force constants corresponding to a single and a double antimony–sulfur bond, 1.70 × 10^5 and 3.48 × 10^5 dynes/cm, respectively, were obtained. Zingaro *et al.*[4] calculated by using the same value, 3.48 × 10^5 dynes/cm, however, their result, the frequency at 131 cm^{-1} for ν(Sb=S), is not reasonable.

atom is fairly weak and the additional π-bonding on the Sb–S bond still remains. The Sn–S stretching vibration arising from complex formation is expected to appear at lower frequency than that in $[(CH_3)_2SnS]_3$. Thus, the bands observed at 232–202 cm^{-1} may be associated with the Sn–S stretching modes of these complexes. The Sn–C symmetric stretching band is not observed in the spectra of $(CH_3)_2SnX_2 \cdot 2\ (CH_3)_3SbS$, for the band is usually weak and may be obscured by the strong Sb–C symmetric stretching band at about 530–520 cm^{-1}.

Behavior of the complex in solution

As is shown in Table 2, complexes are dissociated in polar solvents, such as DMF or $CHCl_3$, but not in toluene. The infrared spectrum of $(CH_3)_2SnCl_2 \cdot 2\ (CH_3)_3SbS$ in $CHCl_3$ shown in Table 5 is markedly different from that in the solid state, and can be interpreted straightforwardly as a superimposed spectrum of $(CH_3)_3SbS$, $(CH_3)_3SbCl_2$ and $[(CH_3)_2SnS]_3$. A similar result can be deduced from Table 5 with the bromide.

The proton NMR spectrum of $(CH_3)_2SnCl_2 \cdot 2\ (CH_3)_3SbS$ in $CHCl_3$ is shown in Fig. 1, together with that of $(CH_3)_3SbS$. Three sharp singlets observed at 7.66, 8.44 and 9.12 ppm [$J(^{117}Sn–CH_3)$ 58.8 cps; $J(^{119}Sn–CH_3)$ 61.5 cps] of which the intensity ratio is about 3 : 3 : 2 are satisfactorily assigned to methyl protons of $(CH_3)_3$-

TABLE 5

IR FREQUENCIES OF $R_2SnX_2 \cdot 2\ (CH_3)_3SbS$ AND RELATED COMPOUNDS IN $CHCl_3$ (600–300 cm^{-1} REGION, IN cm^{-1})

(I) $(CH_3)_2SnCl_2 \cdot 2\ (CH_3)_3SbS$ (II) $(CH_3)_2SnBr_2 \cdot 2\ (CH_3)_3SbS$ (III) $[(CH_3)_2SnS]_3$ (IV) $(CH_3)_3SbS$ (V) $(CH_3)_3SbBr_2$ (VI) $(CH_3)_3SbCl_2$

(I)	*(II)*	*(III)*	*(IV)*	*(V)*	*(VI)*	*Assignments*
571 m					572 m	Sb–C deg. str.
	566 m			566 m		Sb–C deg. str.
551 s	552 s		551 m			Sb–C deg. str.
540 s	541 s	541 m				Sn–C antisym. str.
530 s	531 s		531 m			Sb–C sym. str.
517 s	517 s	517 m				Sn–C sym. str.
433 vs	433 vs		433 s			Sb=S str.
363 vs	362 vs	363 s				Sn–S–Sn antisym. str.
326 s	326 s	326 m				Sn–S–Sn sym. str.

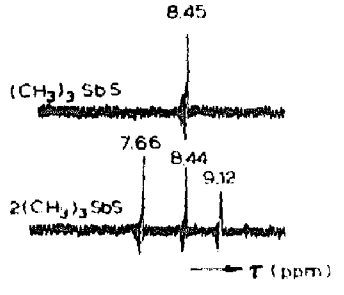

Fig. 1. Proton NMR spectra of $(CH_3)_3SbS$ and $(CH_3)_2SnCl_2 \cdot 2\ (CH_3)_3SbS$ at 60 Mc/sec in $CHCl_3$ at 20

$SbCl_2$[13], $(CH_3)_3SbS$ and $[(CH_3)_2SnS]_3$[14], respectively. This spectrum does not markedly change at temperatures from +35° down to −40°. A mixture of $(CH_3)_3SbS$ and $(CH_3)_2SnCl_2$ in mole ratio 2 : 1 in $CHCl_3$ also showed the same spectrum. The other three complexes gave quite analogous results in $CHCl_3$ or CH_2Cl_2 solution. However, as is shown in Fig. 2, the X-ray powder patterns of $(CH_3)_2SnX_2 \cdot 2\ (CH_3)_3SbS$ can not be understood as a mixture of these three components.

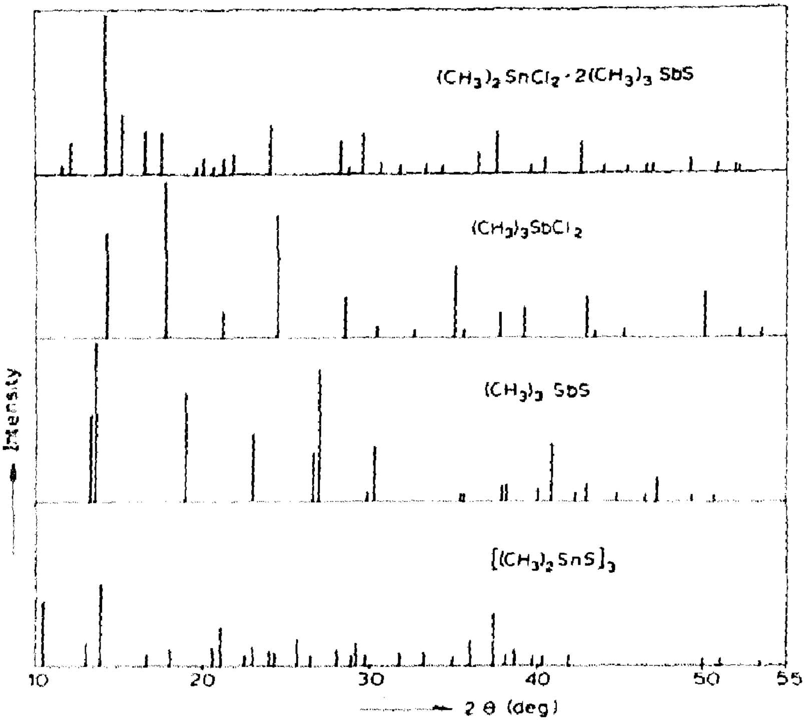

Fig. 2. X-ray powder patterns of $(CH_3)_2SnCl_2 \cdot 2\ (CH_3)_3SbS$ and its related compounds.

From these findings, it can be concluded that these complexes change into the three species in $CHCl_3$. However, since these complexes can be prepared from polar solvents such as $CHCl_3$, CH_3CN, DMF etc., the following equilibrium should exist in them.

$$R_2SnX_2 \cdot 2\ (CH_3)_3SbS \rightleftarrows (CH_3)_3SbS + (CH_3)_3SbX_2 + \tfrac{1}{3}(R_2SnS)_3$$

SUMMARY

The results of the reaction of $(CH_3)_3SbS$ with tin(IV) compounds can be classified into three types: recovery of the reactants, complex formation and sulfur-halogen exchange. The complexes, $R_2SnX_2 \cdot 2\ (CH_3)_3SbS$, were obtained only in limited cases ($R = CH_3, C_2H_5$; $X = Cl, Br$). These complexes exist as a monomeric species in toluene, but in $CHCl_3$ it was confirmed by IR and NMR measurements that these change into three species, $(CH_3)_3SbS$, $(CH_3)_3SbX_2$ and $[(CH_3)_2SnS]_3$. Since the complexes can also be prepared from the mixture of these three in $CHCl_3$, the presence of the following equilibrium has been suggested.

$$R_2SnX_2 \cdot 2\ (CH_3)_3SbS \rightleftarrows (CH_3)_3SbS + (CH_3)_3SbX_2 + \tfrac{1}{3}(R_2SnS)_3$$

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