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PREPARATION AND PROPERTIES OF TRIORGANOANTIMONY THIOGLYCOLATES AND GLYCOLATES

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SUMMARY

Triorganoantimony thioglycolates and glycolates, $R_3Sb(XCH_2COO)$ ($R = CH_3$, cyclo-C_6H_{11} or C_6H_5; $X = S$ or O) were prepared from the reactions of triorganoantimony dialkoxides with thioglycolic and glycolic acid, respectively. From the molecular weight, IR and PMR spectroscopic investigations, the following conclusions were obtained:

(1). $R_3Sb(XCH_2COO)$ ($R =$ cyclo-C_6H_{11} or C_6H_5; $X = S$ or O) is monomeric in $CHCl_3$ solution, and the COO group is bound to the Sb atom by an ester-type linkage. In the solid state, only the compound, $(C_6H_5)_3Sb(SCH_2COO)$, appears to have a structure similar to that in solution.

(2). A monomer–dimer equilibrium exists for trimethylantimony glycolate in $CHCl_3$ solution at room temperature; at higher concentrations the dimer predominates. Below about −15°, only the dimeric species is observed over a wide concentration range. The structure (B) was proposed for this dimeric species by means of a PMR measurement at −38°.

INTRODUCTION

In general, pentavalent triorganoantimony compounds containing Sb–S single bonds are thermally unstable. For example, trimethylantimony dimercaptides could not be isolated from the reactions of trimethylantimony diethoxide with mercaptans, since the expected compounds readily decomposed to trimethylstibine and the disulfide[1] as shown below.

$$(CH_3)_3Sb(OC_2H_5)_2 + 2\,RSH \rightarrow (CH_3)_3Sb + RSSR + 2\,C_2H_5OH$$

$$(R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ C_6H_5 \text{ or } HOCH_2CH_2)$$

However, we could isolate a series of fairly stable compounds[1] which contain Sb–S bonds, such as $(CH_3)_3Sb(SCOCH_3)_2$ and $(CH_3)_3Sb(SCOC_6H_5)_2$.

Here, we wish to report on the isolation of triorganoantimony thioglycolates and glycolates, $R_3Sb(XCH_2COO)$ ($R = CH_3$, cyclo-C_6H_{11} or C_6H_5; $X = S$ or O). The structures of these compounds, with the exception of trimethylantimony thioglycolate, will be discussed on the basis of molecular weight and spectral measurements. Trimethylantimony thioglycolate, $(CH_3)_3Sb(SCH_2COO)$, appeared to decompose during the spectral measurements.

EXPERIMENTAL

Materials

R_3SbBr_2 (R=cyclo-C_6H_{11} or C_6H_5) was prepared by bromination of R_3Sb, which was prepared by the Grignard method. The glycolic and thioglycolic acids were of reagent-grade quality.

Preparation of $R_3Sb(XCH_2COO)$ (R=cyclo-C_6H_{11} or C_6H_5; $X=S$ or O)

$$R_3SbBr_2+2\ NaOCH_3+HXCH_2COOH \rightarrow R_3Sb(XCH_2COO)+2\ NaBr+2\ CH_3OH$$

A benzene solution of (cyclo-$C_6H_{11})_3SbBr_2$ (4.62 g, 8.7 mmole) was added to $NaOCH_3$ (0.4 g of Na dissolved in excess methanol), and the mixture was stirred for 30 min. The precipitate of NaBr was filtered off, and to the filtrate thioglycolic acid (0.92 g, 10 mmole) was added. After evaporation of the solvent under reduced pressure, the solid obtained was recrystallized from ethanol to give colorless crystals of (cyclo-$C_6H_{11})_3Sb(SCH_2COO)$ in a nearly quantitative yield. The other three compounds were prepared in a similar manner.

Preparation of $(CH_3)_3Sb(XCH_2COO)$ ($X=S$ or O)

$$(CH_3)_3Sb(OC_2H_5)_2+HXCH_2COOH \rightarrow (CH_3)_3Sb(XCH_2COO)+2\ C_2H_5OH$$

These two compounds were prepared in a manner similar to the above procedure, by using $(CH_3)_3Sb(OC_2H_5)_2$[1]. Recrystallization of $(CH_3)_3Sb(OCH_2COO)$ from methanol gave two crystal forms different in appearance; (I) needle-like and (II) cubic. These two forms exhibited different X-ray powder patterns and IR spectra, as shown in Fig. 1 and Table 3, respectively. However, the IR spectra of (I) and (II) in

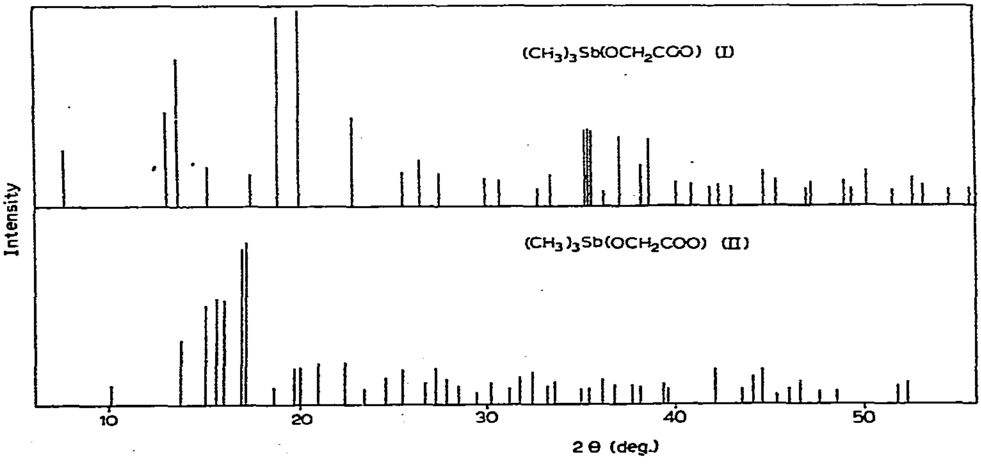


Fig. 1. X-ray powder patterns of $(CH_3)_3Sb(OCH_2COO)$, (I) and (II).

TABLE 1

PROPERTIES OF $R_3Sb(XCH_2COO)$

Compounds R	X	M.p. (°C)	%C found (calcd.)	%H found (calcd.)	Mol.wt.[a] found/concn.[b] (calcd.)
C_6H_5	S	141–142 decompn.	54.21 (54.20)	3.97 (3.87)	438/0.79 (443)
C_6H_5	O	179–180	56.21 (56.24)	4.17 (4.01)	413/0.83 (427)
cyclo-C_6H_{11}	S	159–162 decompn.	52.04 (52.07)	7.79 (7.65)	466/1.17 (461)
cyclo-C_6H_{11}	O	205–206 decompn.	53.65 (53.95)	8.09 (7.92)	443/1.14 (445)
CH_3	S	126–129 decompn.	23.19 (23.37)	4.36 (4.32)	291/0.77 (257)
CH_3	O (I)	224–225 decompn.	24.42 (24.93)	4.72 (4.60)	
CH_3	O (II)	218–220 decompn.	24.37 (24.93)	4.68 (4.60)	(241)

[a] At 25° in $CHCl_3$. [b] % [w(sample)/w(solvent)]. [c] See Fig. 2.

solution were found to be identical.

All the new compounds thus obtained are listed in Table 1.

Physical measurements

The X-ray powder patterns were measured using a Geiger-flex made by Rigaku–Denki Co. Ltd. The IR spectra were measured using a Hitachi EPI-2G or 225 spectrophotometer, both equipped with gratings. The PMR spectra were measured using a Japan Electron Optics JNM-3H-60 spectrometer operating at 60 MHz. Tetramethylsilane was used as an internal standard. Molecular weights were determined at 25° or 37° in $CHCl_3$ using a Mechrolab Model 302 or Hitachi Perkin–Elmer 115 vapor pressure osmometer.

Relevant IR frequencies of all the compounds studied are listed in Tables 2 and 3. With $(CH_3)_3Sb(OCH_2COO)$ in $CHCl_3$ solution, the intensities of the COO bands and the molecular weight are dependent on the concentration, as shown in Fig. 2 and Fig. 3. The results of PMR measurements of this compound at various temperatures are shown in Fig. 4.

TABLE 2

STRETCHING FREQUENCIES OF COO GROUP IN $R_3Sb(XCH_2COO)$ (in cm^{-1})

R=C_6H_5, X=S		R=C_6H_5, X=O		R=cyclo-C_6H_{11}, X=S		R=cyclo-C_6H_{11}, X=O		Assignment
Solid[a]	Solution[b]	Solid[a]	Solution[b]	Solid[a]	Solution[b]	Solid[a]	Solution[b]	
1658 s	1652 s	1585 s	1675 s	1588 s	1632 s	1580 s	1657 s	C=O str.
1300 s	1307 s	1385 s	1330 s	1368 s	1329 s	1386 s	1340 s	C–O str.

[a] Mulls in nujol or hexachlorobutadiene. [b] $CHCl_3$ solution.

TABLE 3

IR FREQUENCIES OF $(CH_3)_3Sb(OCH_2COO)$(in cm^{-1})

Solid[a]		Solution[b]	Assignment
(I)	(II)		
		1670 vw	C=O str.
1603 vs	1623 vs	1590 vs	
1433 m	1437 m	1445 m	CH_2 scissor.
1420 s	1408 s	1412 vs	C–O str.
1410 s		1333 vw	
1312 s	1307 s	1314 s	CH_2 wag.
1111 vs	1119 vs	1098 vs	C–O str.
		1073 w (sh)	
929 w	923 w	917 w	CH_2 rock.
865 s	848 vs	852 s	CH_3–(Sb) rock.
844 s		833 s	
723 m	717 m	724 m	CO_2 scissor.
587 m	579 vs	587 s	Sb–C str.
556 s		558 s	
549 s		548 (sh)	
526 (sh)	528 w		
512 s	488 vs	515 s	CO_2 rock.

[a] Mulls in nujol or hexachlorobutadiene. [b] 4.0% (w/w) in $CHCl_3$ or $CHBr_3$.

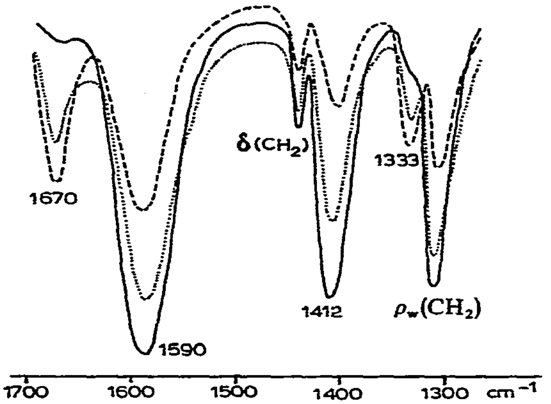


Fig. 2. The COO vibrational bands for $(CH_3)_3Sb(OCH_2COO)$ in $CHCl_3$ at concentrations; ——4.17, ······1.45 and - - - - 0.21% (w/w).

RESULTS AND DISCUSSION

$R_3Sb(XCH_2COO)$ (R=cyclo-C_6H_{11} or C_6H_5; X=S or O)

As listed in Table 2, the IR frequencies associated with the COO group in the $CHCl_3$ solutions of these four compounds are close to those of trimethylantimony diacetate, in which it has been suggested[2] that the COO groups are bound to the antimony atom by an ester-type linkage. This fact, together with the results of the molecular weight determinations shown in Table 1, indicates that these compounds

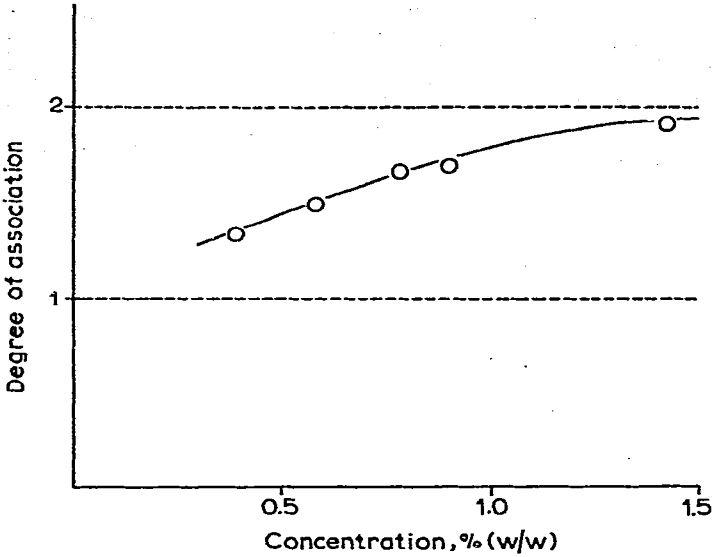


Fig. 3. Degree of association of $(CH_3)_3Sb(OCH_2COO)$ in $CHCl_3$ at 37°.

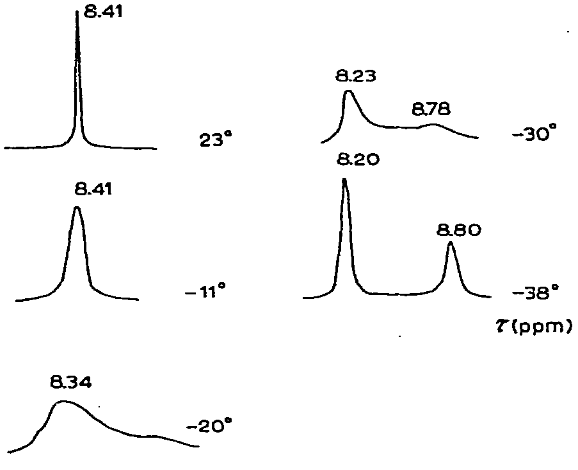
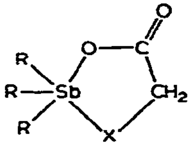


Fig. 4. The PMR spectra of the methyl protons of $(CH_3)_3Sb(OCH_2COO)$ 2.0% (w/w) in $CHCl_3$ at various temperatures.

may have the structure (A) shown below, in which the configuration around the Sb atom is thought to be analogous to that of trimethylantimony *o*-phenylenedioxide[3], with a non-planar C_3Sb group.



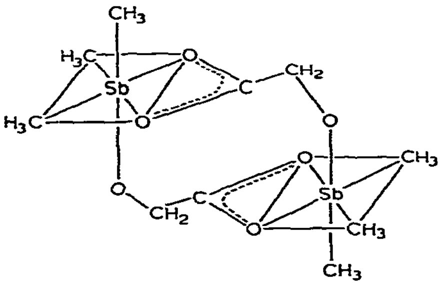
($R = cyclo\text{-}C_6H_{11}$ or C_6H_5; $X = S$ or O)

(A)

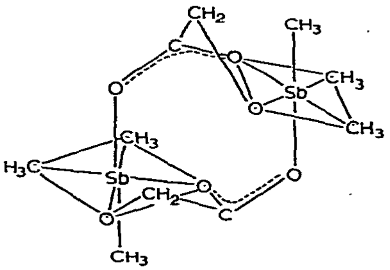
In the solid state, the IR spectrum of $(C_6H_5)_3Sb(SCH_2COO)$ is similar to that in solution. On the other hand, in the solid spectra of the other three compounds, the C=O bands appear at lower frequency and the C–O bands appear at higher frequency than those in solution. This may indicate that in the solid state the C=O groups in these compounds coordinate to the antimony atoms. By analogy with trimethylantimony glycolate (which is discussed later), these three compounds in the solid state are thought to have an associated structure with hexa-coordinated antimony atoms.

$(CH_3)_3Sb(OCH_2COO)$

At room temperature the molecular weight and the intensities of the IR bands associated with the COO group of this compound in chloroform solution are dependent on the concentration. At lower concentrations, the average molecular weight of this glycolate is between that of the monomer and dimer as shown in Fig. 3, and there are two kinds of COO groups as indicated in Table 3 and Fig. 2. As the concentration increases, the relative intensity of the band at 1670 to the band at 1590 cm^{-1} (or 1333 to 1412 cm^{-1}) decreases, and at the highest concentration* shown in Fig. 2, there is practically only one kind of COO group. These facts suggest that at higher concentrations, a dimeric structure with either chelating or bridging COO groups, (B) or (C)**, becomes predominant, and at lower concentrations two species, either (A) and (B) or (A) and (C), exist in solution.



(B)



(C)

The PMR spectrum of trimethylantimony glycolate at 23° in chloroform shows two sharp singlets at τ 8.41 and 5.81 ppm due to the methyl and methylene protons, respectively, and these chemical shifts change only by 3 Hz when the concentration is varied from 0.5 to 4.0% (w/w). Analogous results were observed in dichloromethane. These observations can be interpreted by assuming that the chemical shifts of the monomeric and dimeric species are nearly the same and a fast exchange exists between the two species.

As shown in Fig. 4, the peak due to the methyl protons becomes broad at lower temperatures and at −38° splits into two peaks*** at τ 8.20 and 8.80 ppm with

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* Almost saturated at 25°.

** A dimeric structure, in which three methyl groups are coplanar, was eliminated because of a sterically overcrowded model.

*** Trimethylantimony *o*-phenylenedioxide showed[3] a sharp singlet at τ 8.60 ppm even at −70°.

relative intensities of 2/1. This intensity ratio is independent of concentration over the range 0.6 to 4.0% (w/w). However, the peak due to the methylene protons of the glycolate group shows no appreciable change from 23° down to −40°. Moreover, the IR spectrum between ca. −15° and −20° at concentration 2.0% (w/w) shows only the set of COO stretching vibrations (1585 and 1410 cm^{-1}) attributed to the dimeric species. From these findings, it can be concluded that at lower temperatures the dimeric species, (B) or (C), is predominant over the wide concentration range studied.

Both dimeric structures, in which there are two methyl groups *trans* to carboxyl oxygens and one methyl group *trans* to a hydroxyl oxygen, are consistent with a 2/1 intensity ratio of methyl protons at −38°. However, the two methyl groups *trans* to carboxyl oxygen might become magnetically nonequivalent in structure (C), since this structure has no plane of symmetry bisecting the C–Sb–C angle.

In the solid state, the IR spectrum of (I) is very similar to that in solution at a high concentration. The structure of (I) in the solid may be assumed to be a repetition of the dimeric moieties with hexa-coordinated antimony atoms.

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