

Characterization of Triphenyltin Hydroxide and Bis-(triphenyltin) Oxide

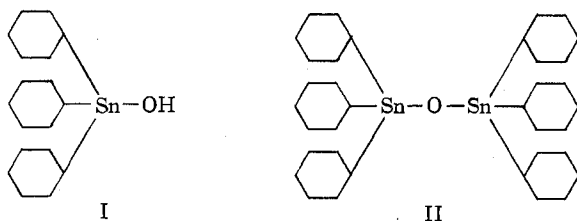
By B. KUSHLEFSKY, I. SIMMONS, AND A. ROSS

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Both triphenyltin hydroxide and bis-(triphenyltin) oxide have been prepared and identified. The compounds are interconvertible and are most easily distinguished and identified by their unique infrared spectra and by titration with Karl Fischer reagent.

Introduction

There have been many discrepancies in the published literature concerning triphenyltin hydroxide (I) and bis-(triphenyltin) oxide (II).¹⁻³



We have prepared both compounds by the methods described below and have succeeded in identifying and differentiating them.

Experimental

(A) **Preparation of Triphenyltin Hydroxide.**—An aqueous sodium hydroxide solution (180 g., 4.5 moles) in 600 ml. of water was added over a period of 10 min. to a filtered solution of triphenyltin chloride (1.16 kg., 3.0 moles) in 4 l. of acetone. A slight rise in temperature was observed and a voluminous white precipitate formed. After an additional 3 hr. of stirring, 3 l. of water was added and the solid phase was filtered off. The crude solid product was washed with boiling water until a negative silver nitrate test for chloride ion was obtained. After drying in air, the solid weighed 996.5 g. (90.6% yield; 2.72 moles); m.p. 115–122° dec. Recrystallization from 95% ethanol gave white crystals with an initial m.p. of 119°, decomposition occurring at 121°.

Anal. Calcd. for $C_{18}H_{16}OSn$: C, 58.90; H, 4.39; Sn, 32.36. Found: C, 58.69, 58.74; H, 4.52, 4.45; Sn, 32.37.

(B) **Preparation of Bis-(triphenyltin) Oxide.**—Triphenyltin hydroxide (73.4 g., 0.2 mole) in 200 cc. of anhydrous toluene was heated in a reflux apparatus equipped with a Dean-Stark type water trap. The solution became clear at the boiling point and water was collected in the trap. A gradually increasing turbidity was observed. When the calculated amount of water had been collected, and no more additional water came over (1 hr.), the solution was filtered hot. On cooling the filtrate again became turbid and a final filtration at ambient temperature gave a clear solution. After standing for 24 hr., the solution deposited 36.5 g. of white crystals of bis-(triphenyltin) oxide which were dried over P_2O_5 in a vacuum desiccator; m.p. 122–123.5°.

Anal. Calcd. for $C_{36}H_{30}OSn_2$: C, 60.37; H, 4.22; Sn, 33.15. Found: C, 60.22, 60.17; H, 4.40, 4.33; Sn, 33.10, 33.20.

(C) **Absorption Spectra.**—All the infrared spectra were run as Nujol and Fluorolube mulls in the fundamental region using a Beckman IR4 spectrophotometer with sodium chloride prisms. Water vapor and polystyrene were used for calibration.

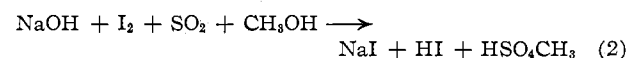
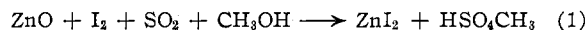
A Beckman DK2 spectrophotometer was used to study the near-infrared spectra of the bis oxide and hydroxide at concentrations of 0.005 to 0.01 *M* in Spectro Grade carbon tetrachloride, using special 1-cm, silica near-infrared cells between 2400 and 3400 $m\mu$.

Discussion

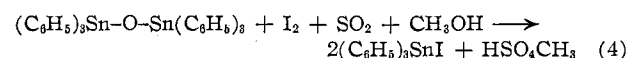
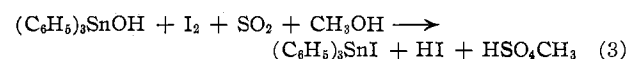
Although the elemental analyses for carbon, hydrogen, and tin agreed very well with the theoretical values for triphenyltin hydroxide and bis-(triphenyltin) oxide, it should be noted that the loss of a mole of water still leaves the calculated values for the two compounds very close to each other. Consequently, elementary analysis is not a good means of identification and is almost worthless for analyzing mixtures of both materials, which often are obtained.

Karl Fischer Titration.—Gilman and Miller,² while attempting to determine the water content of silanols and silanediols by titration with Karl Fischer reagent, discovered that, in addition to the reaction with the water, the reagent was reacting with the OH of the silanols as well. They extended this reaction quantitatively to triphenyltin hydroxide. We found that the reagent not only reacts quantitatively with triphenyltin hydroxide but also with bis-(triphenyltin) oxide. This method, therefore, served as an excellent means of identification and differentiation.

Mitchell and Smith⁴ proposed eq. 1 and 2 to illustrate the reaction of Karl Fischer reagent with inorganic oxides and hydroxides.



Reactions analogous to (1) and (2) can be postulated



The stoichiometry of these equations indicates that 1 mole of iodine is consumed for each atom of tin in the

(1) R. West, R. H. Baney, and D. L. Powell, *J. Am. Chem. Soc.*, **82**, 6269 (1960).

(2) H. Gilman and L. S. Miller, *ibid.*, **73**, 2367 (1951).

(3) O. Schmitz-Dumont, *Z. anorg. allgem. Chem.*, **248**, 289 (1941).

(4) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 248–252.

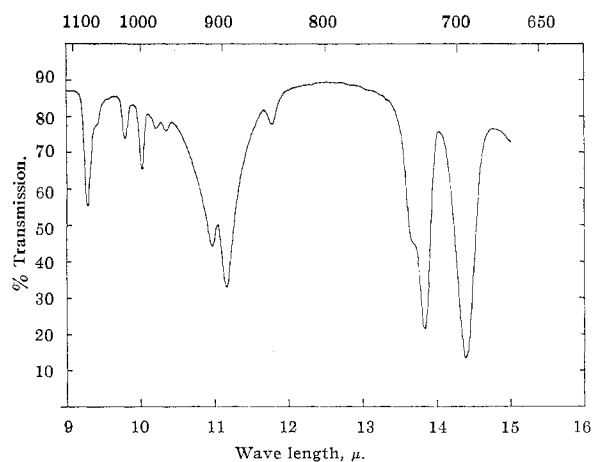


Fig. 1.—Infrared spectrum of triphenyltin hydroxide.

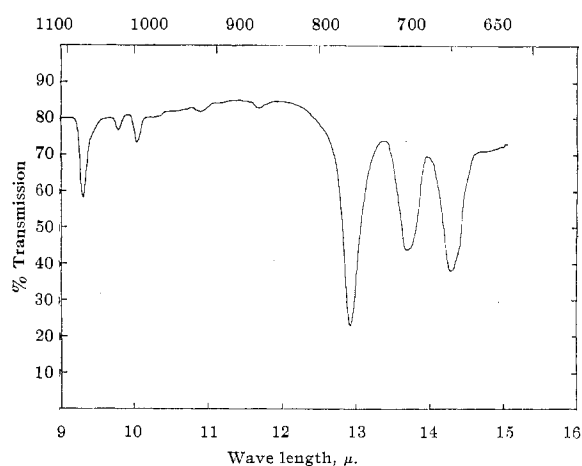


Fig. 2.—Infrared spectrum of bis-(triphenyltin) oxide.

case of the hydroxide, while in the case of bis-(triphenyltin) oxide each atom consumes 0.5 mole of iodine.

The results of titration with Karl Fischer reagent, given in Table I, confirm the postulated stoichiometry.

Compound	Calcd.	Found
Triphenyltin Hydroxide	1.000	0.984
Bis-(triphenyltin) Oxide	0.500	0.506

The large difference between these values makes this method one of the best for distinguishing between structures I and II. It also serves as a means of analyzing mixtures of the two.⁵

Infrared Spectra.—The middle-infrared spectra of triphenyltin hydroxide and bis-(triphenyltin) oxide are quite distinct and can easily be distinguished from one another by examination of the region below 1000 cm.⁻¹ (Fig. 1 and 2).

Triphenyltin hydroxide shows a strong doublet at 910 and 897 cm.⁻¹, which is completely absent in bis-(triphenyltin) oxide. We have observed similar band arrangements around 900 cm.⁻¹ in trimethyltin hydrox-

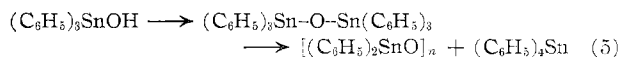
ide and tricyclohexyltin hydroxide. Although this is still under investigation the possibility exists that at least one of these bands may be an O-H deformation frequency. Bis-(triphenyltin) oxide shows a strong band at 774 cm.⁻¹, which is completely absent in the spectrum of triphenyltin hydroxide.

Brown, Okawara, and Rochow⁶ stated that the Sn-O-Sn link probably vibrates in the region 580 to 650 cm.⁻¹. However, Vyshenskii and Rudnevskii⁷ examined the spectrum of bis-(triethyltin) oxide and assigned the frequency of an intense absorption band at 778 cm.⁻¹ to the unsymmetrical stretching vibration of Sn-O-Sn. We examined the infrared spectrum of bis-(tributyltin) oxide and found an extremely intense band at 775 cm.⁻¹. Furthermore, bis-(triisobutyltin) oxide and the mixed bis-(di-*n*-propyl-*n*-octyltin) oxide showed bands at 772 and 781 cm.⁻¹, respectively. It is only in the dimeric state, such as exists in the bis oxides, that the band at 774 cm.⁻¹ appears, and it is reasonable to assign this frequency to Sn-O-Sn in bis-(triphenyltin) oxide. In addition, if the triphenyltin hydroxide were in reality a hydrated form of bis-(triphenyltin) oxide, the linkage would not vanish as it does.

The OH region of the triphenyltin hydroxide showed no typical OH stretching bands. Baney⁸ has attributed this to lower band intensity coupled with low concentration of OH because of the mass of the tin atom.

West and Baney⁹ reported that a band at 3647 cm.⁻¹ in triphenyltin hydroxide was the free OH stretching frequency. We further examined bis-(triphenyltin) oxide and triphenyltin hydroxide in the near-infrared region and found that *both* compounds showed a band at 3646 cm.⁻¹. West, Baney, and Powell¹ further reported that samples of triphenyltin hydroxide prepared by them in different ways showed not only the OH band at 3647 cm.⁻¹ but also a water band at 3681 cm.⁻¹.

These results led us to try exhaustive drying of bis-(triphenyltin) oxide in an Abderhalden drying pistol using P₂O₅ as the desiccant, 24-hr. drying periods, and the temperatures: ambient, 50, 80, and 100°. The band at 3646 cm.⁻¹ was not affected in any way but in the spectrum obtained from material dried at 100° other bands appeared, indicating the possibility of changes according to eq. 5.



Interconvertibility.—The sample of bis-(triphenyltin) oxide, the analysis of which is given in the Experimental section, was converted to triphenyltin hydroxide by boiling with 90% ethanol. The infrared spectrum which had originally shown the strong band at 774 cm.⁻¹ changed to that typical of the hydroxide with the doublet at 910 and 897 cm.⁻¹. This conversion was further confirmed by Karl Fischer titration, the moles

(6) M. P. Brown, R. Okawara, and E. G. Rochow, *Spectrochim. Acta*, **16**, 595 (1960).

(7) N. N. Vyshenskii and N. K. Rudnevskii, *Optics and Spectroscopy*, **10**, 412 (1961).

(8) R. H. Baney, "Acid and Base Properties of Some Group IV Organohydroxy Compounds," Ph.D. Thesis, University of Wisconsin, Jan., 1960.

(9) R. West and R. H. Baney, *J. Phys. Chem.*, **64**, 822 (1960).

(5) B. Kushlefsky and A. Ross, *Anal. Chem.*, **34**, 1666 (1962).

of iodine per tin atom changing from 0.506 to 0.992.

All the evidence we have presented indicates distinct bis oxide and hydroxide structures, which leads us to

suppose that the band at 3646 cm.^{-1} cannot be explained simply as an OH stretching frequency; this work is being continued.

CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY,
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Crystalline Methylsilsesquioxanes

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The sublimates obtained by the base-catalyzed pyrolysis of methyl silicone gels have been fractionated and the major components characterized. These were found to be crystalline silsesquioxanes $(\text{CH}_3\text{SiO}_{1.5})_x$, where $x = 8, 10,$ and 12 . In addition, small amounts of incompletely condensed crystalline nonamers $(\text{CH}_3)_6\text{Si}_9\text{O}_{13}(\text{OR})$ and numerous non-crystalline minor components were detected. The octasilsesquioxane obtained ("methyl- T_8 ") was identical with the octamethylpentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane which has been reported previously. Infrared and n.m.r. spectra indicated that the nonamers were 15-alkoxy-pentacyclo-[9.7.1.1^{3,9}.1^{5,15}.1^{7,13}]-nonasiloxanes, the decamer was a hexacyclo-[9.9.1.1^{3,9}.1^{5,15}.1^{7,13}.1^{13,19}]-decasiloxane, and the dodecamer was probably a heptacyclo-[13.9.1.1^{3,13}.1^{5,11}.1^{7,21}.1^{9,19}.1^{17,23}]-dodecasiloxane. The known methyl- T_8 , T_8 , T_{10} , and T_{12} compounds thus appear to constitute a homologous series of prismatic cage-like polycyclics, which can be regarded as the cyclic analogs of the linear double chain polymers found in the phenylsilsesquioxane series. The relative molar concentrations of methyl- T_8 , T_8 , T_{10} , T_{12} , and T_{14} in equilibrated solutions were in the ratio 0:1:2:1:0, indicating that the decamer is the most stable member of the series.

Introduction

The methylsilsesquioxanes are polycyclic polysiloxanes which may be regarded as total condensation products of methylsilanetriol, $\text{CH}_3\text{Si}(\text{OH})_3$. This series of compounds is known to contain several distinct crystalline species in addition to the expected resins and gels. Reported examples of crystalline methylsilsesquioxanes include the hexamer, methyl- T_6 $(\text{CH}_3\text{SiO}_{1.5})_6$ ²; the octamer, methyl- T_8 ²⁻⁵; a "dodecamer"⁵; and four unidentified species from the pyrolysis of methyl-T gel.⁵

The present investigation was undertaken in order to characterize the unidentified crystalline members of the series, and to determine the structural and stability relations among the group as a whole. It was hoped that this might shed some light upon the structural nature of the network polymers found when trifunctional monomers such as $\text{CH}_3\text{Si}(\text{OH})_3$ undergo polycondensation.

Results and Discussion

Following the general procedure of Barry, *et al.*,⁵ base-containing methyl silicone gels were prepared by hydrolyzing methyltriethoxysilane with KOH-water-methanol mixtures, and then pyrolyzed at $325\text{--}400^\circ$ *in vacuo*

to yield sublimates containing methylsilsesquioxanes. The relative proportions of the sublimate components varied somewhat with the conditions used for preparing the gels. It also was noted that some of the "gels" were largely methyl- T_8 even before pyrolysis. However, the higher silsesquioxanes appeared to be formed by rearrangement of the gel rather than T_8 ; heating methyl- T_8 with alkali under the reaction conditions yielded no other volatile products.

The sublimates were partially separated by crystallization, and then analyzed by g.l.c. (gas-liquid chromatography). They were found to contain 66-91% methyl- T_8 ; 2-9% methyl- T_{10} ; 1-17% methyl- T_{12} ; 1-9% methyl- $\text{T}_9(\text{OR})$, where R = methyl or ethyl; and 3-11% of an oil which contained about 30 minor components. No methyl- T_6 could be detected, either by g.l.c. or by infrared spectroscopy.

The methyl- T_8 obtained was identical with that reported by various other investigators.²⁻⁵ The methyl- T_{10} appeared to be the same as the "Compound B" obtained by Barry, *et al.*,⁵ and reported as a "dodecamer" on the basis of borderline molecular weight determinations. The methyl- T_{12} is probably the same as their unidentified "Compound C" or "D." The methyl- $\text{T}_9(\text{OC}_2\text{H}_5)$ appeared to be their "Compound F." No species corresponding to "Compound E" was obtained. However, it is not certain that the unidentified compounds C, D, and E could not all have been methyl- T_{12} ; polymorphism and mixed crystal formation are both quite prevalent among the silsesquioxanes.

The presence of methyl- $\text{T}_9(\text{OCH}_3)$ and methyl- $\text{T}_9(\text{OC}_2\text{H}_5)$ in the product indicated that exchange with methanol occurred during the hydrolysis, and also

(1) (a) Rensselaer Polytechnic Institute, NASA Interdisciplinary Materials Research Center, Troy, New York; (b) This work is part of a thesis submitted by L. H. Vogt, Jr., to the Graduate School of Rensselaer Polytechnic Institute, Troy, N. Y., January, 1961, in partial fulfillment of the requirements for the degree of Master of Science.

(2) M. M. Sprung and F. O. Guenther, *J. Am. Chem. Soc.*, **77**, 3990 (1955).

(3) M. M. Sprung and F. O. Guenther, *ibid.*, **77**, 6045 (1955).

(4) D. W. Scott, *ibid.*, **68**, 356 (1946).

(5) A. J. Barry, W. H. Daudt, J. E. Domicone, and J. W. Gilkey, *ibid.*, **77**, 4248 (1955).