OCCURRENCE OF DIMERIC TRIMETHYLTIN HYDROXIDE

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Increasing interest is being focussed on the structure of trialkyltin salts in the solid state and in solution. In trialkyltin acetate[1], formate[2], or perchlorate[3] in the solid state, a tin atom is weakly coordinated with two oxygen atoms, so that a linear chain is formed in which the planar $(CH_3)_3Sn$ group is bridged by the -OCO-, or the -OClO- unit having C_{2v} symmetry. However, these weak bridges can sometimes be destroyed by a nonpolar solvent to give, in the case of the acetate in cyclohexane, monomeric trialkyltin acetate. In the case of the formate in cyclohexane[2], it was found that the molecule consists of a low polymeric trialkyltin formate with two kinds of formoxy groups, a bridging group having C_{2v} symmetry and a chain end group of reduced symmetry.

Here, we wish to report on the structure of another interesting compound, trimethyltin hydroxide. This compound can be sublimed without decomposition or condensation. It has a marked stability against condensation[4] compared with the other trialkyltin hydroxides[5], which readily give the hexaalkyldistannoxanes. It is very soluble in water and in alcohol, slightly soluble in benzene, carbon tetrachloride, and chloroform, and insoluble in most non-polar organic solvents. In order to obtain the information necessary to assign a configuration, we determined its molecular weight in solution and examined the infrared spectra of the solid and of the compound in solution.

On the basis of cryoscopic molecular weight determinations trimethyltin hydroxide has been reported[6] to be slightly polymerized in benzene. However, owing to the low solubility of the compound, cryoscopic measurements in benzene are not satisfactory. Furthermore, associated trimethyltin hydroxide is affected by the presence of water, and the hydroxide also reacts readily with atmospheric carbon dioxide, the insoluble carbonate being precipitated. Therefore, we made an ebulliometric determination, taking care to avoid contamination by water or carbon dioxide.

EXPERIMENTAL

Materials

Trimethyltin hydroxide was prepared by hydrolysing trimethyltin chloride, and purified by sublimation; m.p. 118°C. (Found: Sn, 65.50. $C_3H_{10}OSn$ calcd.: Sn, 65.65 %.) The solvents used for the molecular weight determinations were purified as follows. Carbon tetrachloride: guaranteed grade carbon tetrachloride was shaken with aqueous potassium hydroxide to remove traces of carbon disulfide, dried with calcium chloride and phosphorus pentoxide and then distilled; n_D^{20} 1.4603. Chloroform: guaranteed grade chloroform was dried and distilled; n_D^{20} 1.4456. Benzene: guaranteed reagent was dried with metallic sodium and distilled; n_D^{20} 1.5011.

Molecular weight determinations

The molecular weight was measured with the N. H. Ray type ebulliometer[7]. The results are given below. Found in CCl_4: mol. wt., 380, 360, 360, 370, 360, 360, 360, 360, at concentrations 0.088, 0.096, 0.145, 0.258, 0.296, 0.451, 0.683, and 0.759 % w(sample)/W(solvent) respectively; in $CHCl_3$: mol. wt., 410, 370 at concentrations 0.483 and 1.15 % w/W respectively; in C_6H_6: mol. wt., 410, 360, 400, 380, 400 at concentrations, 0.261, 0.347, 0.463, 0.618, and 0.824 % w/W respectively. Calcd. for $[(CH_3)_3SnOH]_2$, mol. wt., 361.6.

Infrared spectra

Infrared spectra were recorded in the 4000–270 cm^{-1} region on a Perkin-Elmer double beam Spectrometer Model 221 equipped with a grating, NaCl or KBr optics, and a Koken double beam Spectrometer Model DS-401 G equipped with a grating and CsBr optics. The spectra in the solid state were obtained as mulls in nujol or hexachlorobutadiene, using various polymer films to protect the plates. The solution spectra were in carbon tetrachloride. The spectra in solution in the region 1500–700 cm^{-1} could not be obtained, as carbon disulfide reacts with trimethyltin hydroxide[8] and another suitable solvent could not be found. The results are given in Fig. 1 and Table 1.

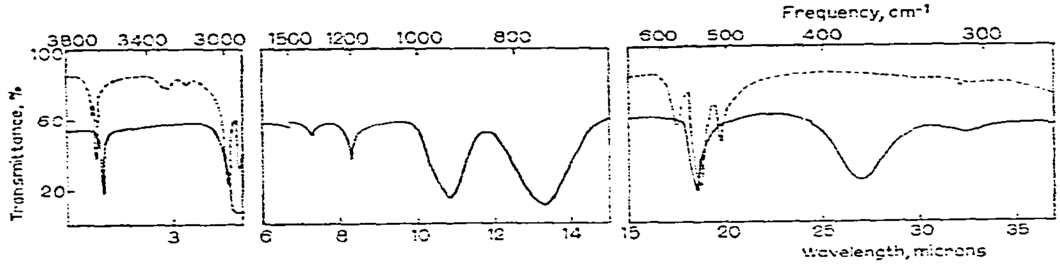


Fig. 1. Infrared spectra of trimethyltin hydroxide: —— nujol or hexachlorobutadiene mull; – – – carbon tetrachloride solution.

DISCUSSION

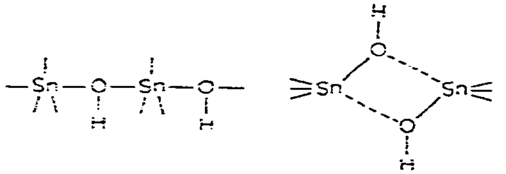
The strong absorption found at 920 cm^{-1} in the solid is assigned to the Sn–OH deformation vibration, for this band shifts to 651 cm^{-1} in the deuterium substituted compound, $(CH_3)_3SnOD$. Although Poller[9] erroneously assumed that the similar band which appeared at 855 cm^{-1} (in our experiment, 889 cm^{-1}) in triethyltin hydroxide is due to the Sn–O stretching vibration, Kriegsmann[10] has tentatively assigned this band to the Sn–OH deformation, and a weak band at 518 cm^{-1} to the Sn–O stretching vibration. However, in our spectra obtained with a sample carefully prepared to avoid contamination by carbonate, no other band was observed in the KBr region except one strong band at 540 cm^{-1} due to the Sn–C asymmetric stretching vibration; this shows that in this compound the trimethyltin group has the planar trigonal configuration as in the case of other trimethyltin salts[1,2,3,11]. In the far infrared spectra in the solid state, a strong absorption band was found at 370 cm^{-1}, which in $(CH_3)_3SnOD$

TABLE I

INFRARED VIBRATIONAL FREQUENCIES OF TRIMETHYLTIN HYDROXIDE $(CH_3)_3SnOH$

Nujol or hexachlorobutadiene mull.	*In carbon tetrachloride solution (ca 0.6%)*
316 w	
370 s	
	504 m
540 s	531 s
	571 m
765 s	↑
920 s	
	(not examined)
1195 m	↓
1405 w	
2915 m	2916 m
2985 m	2986 m
3620 m	3658 m

was not markedly shifted. This band is assumed to be associated with the weak Sn–O coordination bond, for a similar broad band was found in trimethyltin formate at 300 cm^{-1}, triethyltin formate at 283 cm^{-1}, and tributyltin acetate at below 270 cm^{-1}. This absorption found in tributyltin acetate in the solid state shifted to 298 cm^{-1} in *n*-heptane solution. If we assume that a similar shift could occur in the case of trimethyltin hydroxide, one of the three bands in the KBr region, presumably the band at 531 cm^{-1}, could be associated with this shift. Then the other two bands can be assigned to two Sn–C stretching vibrations. This leads to the conclusion that in solution the $(CH_3)_3Sn$ group should have a non-planar configuration. As shown in Table 1, a similar shift can be seen in the OH stretching vibration, which means that the O–H bond in the dimer, like the Sn–O bond, is stronger than that in the solid. Thus an associated dimer, as shown in the Fig. 2, could be assumed.



In the crystalline state

In C_6H_6, CCl_4 or $CHCl_3$ soln.

Fig. 2. Configurations of trimethyltin hydroxide in the crystalline state and in solution.

A similar weak coordination of the hydroxyl oxygen atom to the four-coordinated tin atom could be assumed in the dimeric tetraalkyl-1-halo-3-hydroxydistannoxane $(XR_2SnOSnR_2OH)_2$[12], which can easily be obtained from $(XR_2SnOSnR_2X)_2$[13], for the absorption due to the OH stretching vibration of these compounds in carbon tetrachloride solution was found at 3660 cm^{-1} and the hydroxyl group is very stable towards condensation.

SUMMARY

The infrared spectra of trimethyltin hydroxide are examined in the solid state and in solution. These spectra are discussed in terms of a weak coordination of the oxygen

atom with the tin atom. Ebulliometric molecular weight determinations of trimethyltin hydroxide in carbon tetrachloride, chloroform or benzene solution indicate a dimeric molecule $[(CH_3)_3SnOH]_2$. The Sn–O stretching vibration band in solid trimethyltin hydroxide is observed at 370 cm^{-1}, while in carbon tetrachloride solution it is found in the 500–580 cm^{-1} region. The O–H stretching vibration band which is observed at 3620 cm^{-1} in the solid shifts to 3658 cm^{-1} in solution. Only one Sn–C stretching vibration band is observed at 540 cm^{-1} in the solid state, while in solution an additional absorption associated with the Sn–C stretching vibration is observed. These facts suggest that in the solid state trimethyltin hydroxide is a linear polymer in which the planar $(CH_3)_3Sn$ group is bridged by the –O(H)– unit, whereas in solution it has a dimeric structure, in which two Sn–O groups form a four-membered ring.

REFERENCES

1 H. Sato and R. Okawara, *International Symposium on Molecular Structure and Spectroscopy*, Tokyo, Japan, Sept., (1962).
2 R. Okawara and M. Ohara, *Bull. Chem. Soc. Japan*, 36 (1963) 624; *J. Organometal. Chem.*, 1 (1964) 360.
3 R. Okawara, B. J. Hathaway and D. E. Webster, *Proc. Chem. Soc.*, (1963) 13.
4 T. Harada, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, 38 (1940) 115.
5 R. K. Ingham S. D. Rosenberg and G. Gilman, *Chem. Rev.*, 60 (1960) 491; R. West, R. H. Baney and D. L. Dowell, *J. Am. Chem. Soc.*, 82 (1960) 6269.
6 C. A. Kraus and R. H. Bullard, *J. Am. Chem. Soc.*, 51 (1929) 3605.
7 N. H. Ray, *Trans. Faraday Soc.*, 48 (1952) 809.
8 W. T. Reichle, *Inorg. Chem.*, 1 (1962) 650.
9 R. C. Poller, *J. Inorg. Nucl. Chem.*, 24 (1962) 593.
10 H. Kriegsmann, H. Hoffmann and S. Pischtschan, *Z. Anorg. Allgem. Chem.*, 315 (1962) 283.
11 R. Okawara, D. E. Webster and E. G. Rochow, *J. Am. Chem. Soc.*, 82 (1960) 3287.
12 R. Okawara and M. Wada, *J. Organometal. Chem.*, 1 (1963) 81.
13 R. Okawara, *Proc. Chem. Soc.*, (1961) 383.