n-Butyltin Trioxinate in Solution. A Hepta-coordinated Organotin Compound

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It has been reported[1] that phenyltin tritropolonate is monomeric in methylene chloride and this suggests a hepta-coordinated structure. n-Butyltin trioxinate, $BuSnOx_3$, is also expected to be an example of a novel hepta-coordinated tin compound in addition to the previously reported penta-,[2] hexa-[2] and octa-[3] coordinated ones. To verify this the UV spectra of the tin compound were measured under various conditions together with the NMR, the IR spectra and the molecular weight.

Experimental

$BuSnOx_3$ was obtained in the following two ways. During our course of studies, Foldesi *et al.* reported[4] similar findings. i) $BuSnO_{3/2}$ (2.0 g, 0.01 mol) and oxine (4.5 g, 0.031 mol) were heated for 4 hr in benzene, removing water azeotropically. The yellow precipitates were recrystallized from 1 : 1 ligroin-benzene mixture and dried at 140°C under reduced pressure, mp 229—231°C. (Reported[4] mp 223°C.)

Found: C, 60.81; H, 4.45; N, 7.08; Sn, 19.80%. Calcd for $C_{31}H_{27}N_3O_3Sn$: C, 61.21; H, 4.45; N, 6.91; Sn, 19.51%.

ii) $BuSnCl_3$ and OxNa in methanol[2] gave yellow crystals of $BuSnOx_3$, mp 229—231°C. $BuSnOx_3$ is a stable yellow compound showing a constant melting point and showing no OH stretching band in the solid state, after remaining in air for several months.

UV, IR and NMR spectra were obtained as described elsewhere.[2]

Results and Discussion

The molecular weight was determined by a vapor pressure osmometer (Mechrolab Model 302). The compound is nearly monomeric in about 3.5 wt% solution in benzene.[*1] The molecular weight decreases on dilution to apparently one half of the monomer value. This tendency is more enhanced in anhydrous polar solvents, as shown in Fig. 1. Cryoscopic measurements were made in benzene under rigorously dry conditions but the results hardly changed. On the other

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[1] E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 5132 (1964).

[2] K. Kawakami and R. Okawara, *J. Organometal. Chem.*, **6**, 249 (1966); and references therein.

[3] K. Ramaiah and D. F. Martin, *Chem. Comm.*, 130 (1965); E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **87**, 4706 (1965).

[4] I. Foldesi and G. Stramer, *Acta Chim. Acad. Sci. Hung.*, **45**, 313 (1965); *Chem. Abstr.*, **64**, 3591 (1966).

[*1] Measurements could not be made in more concentrated solutions because of the poor solubility. Benzene was refluxed over phosphorus pentoxide for a whole day and distilled directly into the flask containing $BuSnOx_3$ to prepare solutions. The whole assembly was dried by heating under reduced pressure before hand. These procedures were carried out to obtain as rigorously dry conditions as possible.

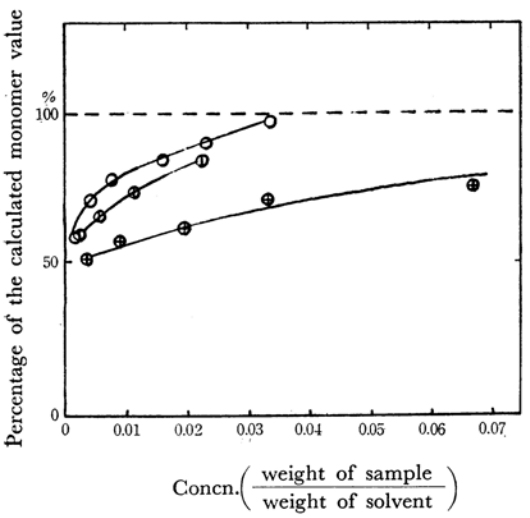

Fig. 1. Molecular weight of $BuSnOx_3$.
○ benzene; ⦶ chloroform; ⊕ dimethylformamide

hand conductivity measurements showed that $BuSnOx_3$ is a non-electrolyte in 1×10^{-3} M solution in dimethylformamide and does not have the structure, $(BuSnOx_2)^+Ox^-$. From these results it is reasonable to consider that the monomeric $BuSnOx_3$ might be hydrolyzed in dilute solutions unavoidably contaminated by water.[*2]

$$BuSnOx_3 + H_2O \rightleftharpoons BuSnOx_2(OH) + OxH \quad (1)$$

In fact, the IR spectra of $BuSnOx_3$ in 2.0 wt% benzene and chloroform solutions show two OH stretching bands at about 3650 and 3420 cm^{-1}. Since the latter is independently shown to be associated with free oxine, the former may be assigned to the hydroxy group attached directly to the tin atom.5)

The remarkable changes of the UV spectra of $BuSnOx_3$ in the presence of oxine and water are shown in Fig. 2. $BuSnOx_3$ in the 1×10^{-3} M solutions in anhydrous benzene shows an absorption maximum around 385 mμ with molecular extinction coefficients, $\varepsilon=6.19$ (2.5 times that of Me_3SnOx), 7.01 (2.8), 7.39 (3.0), 7.42 (3.0) and 7.42×10^3 (3.0) at concentrations, 0, $1/2\times10^{-3}$, 1×10^{-3}, 2×10^{-3} and 1×10^{-2} M of oxine, respectively and shows in benzene saturated with water a maximum at 383 mμ with $\varepsilon=5.42\times10^3$ (2.2), while oxine itself shows a maximum at 315 mμ with $\varepsilon=2.49\times10^3$. The increase of the ε value from 2.5 to 3 times that of trimethyltin oxinate with increasing concentrations of oxine shows that the presence of a sufficient amount of oxine shifts Eq. (1) to the left, so that all three oxinato-ligands of $BuSnOX_3$ may be chelated to form a hepta-coordinated tin atom.

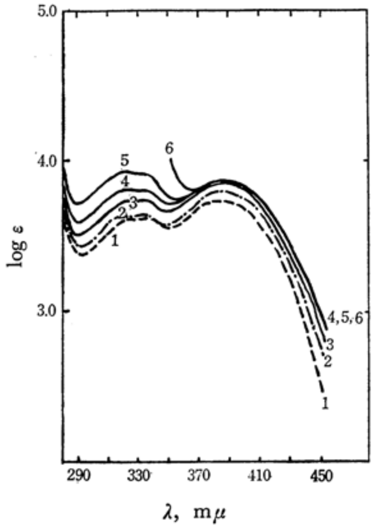

Fig. 2. UV spectra of $BuSnOx_3$ (1×10^{-3} M) in benzene containing various amounts of water (1) or oxine (3—6).
(1) in benzene saturated with water
(2) in anhydrous benzene
(3) $(1/2)\times10^{-3}$ M
(4) 1×10^{-3} M
(5) 2×10^{-3} M
(6) 1×10^{-2} M of oxine, respectively

The maximum at 383 mμ with $\varepsilon=5.42\times10^3$ in benzene saturated with water may be considered to be mainly associated with $BuSnOx_2(OH)$, since in 50% aqueous dioxane, $BuSnOx_3$ shows an absorption maximum at 370 mμ, $\varepsilon=5.02\times10^3$, nearly twice that of trimethyltin oxinate. These UV data suggest that $BuSnOx_3$ may be hydrolyzed to the hexa-coordinated $BuSnOx_2(OH)$, the two oxinato-ligands of which are not hydrolyzed even in the presence of a large amount of water.

The NMR spectrum of $BuSnOx_3$ was obtained in 3×10^{-1} M solution in anhydrous methylene chloride. It was found that signals from the α and the γ protons on the hetero ring of oxine were observed at 0.99 and 1.95 ppm, from an internal tetramethylsilane, respectively and that there appeared only one set of the resonance spectrum of the α and γ protons. On the other hand the spectrum of a mixture of $BuSnOx_3$ and oxine shows two sets of resonances (0.96 and 1.97; 1.23 and 1.84 ppm, the chemical shift of the latter set of resonance agree with that of oxine, 1.20

[*2] In 0.75 wt% solution in benzene, for example, 78% of the calculated monomer value was observed which shows that about 28% of $BuSnOx_3$ molecules are hydrolyzed. About 0.06 g of water in 1 *l* benzene is sufficient to hydrolyze 28% of $BuSnOx_3$ molecules at this concentration, while 0.44 g of water is soluble in benzene at 20°C. (Black *et al.*, *J. Chem. Phys.*, **16**, 437 (1948).)

5) R. Okawara and K. Yasuda, *J. Organometal. Chem.*, **1**, 356 (1964).

and 1.82 ppm) which are due to the presence of both compounds. These data suggest that the three oxinato-ligands of $BuSnOx_3$ are equivalent, since the rate of the ligand exchange can be considered to be slow at room temperature, if any.

In conclusion, *n*-butyltin trioxinate may have a hepta-coordinated tin atom without the influence of water but is easily hydrolyzed in dilute solution to hexa-coordinated *n*-butyltin dioxinate hydroxide which is stable to further hydrolysis.