REACTIONS OF ORGANOTIN COMPOUNDS

IV. COMPLEX FORMATION AND SOLVATION OF TRIMETHYLTIN DERIVATIVES

H. C. CLARK, R. J. O'BRIEN AND A. L. PICKARD
Department of Chemistry, University of British Columbia, Vancouver S, B.C. (Canada)
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INTRODUCTION

The importance of five-coordinate stereochemistry for triorganotin derivatives has been recognized in recent years. Compounds of the type R_3SnX (where X = carboxylate[1], perchlorate[2,3], fluoroborate[4,5], hexafluoroarsenate or -antimonate[5]) are typical, as well as complexes such as chloro(trimethyl)pyridinetin(IV)[6,7], $(CH_3)_3SnCl(C_5H_5N)$, and $[(CH_3)_3Sn(NH_3)_2]^+$ (ref. 2). The mode of interaction between a triorganotin group and an anion such as ClO_4^- is not yet understood, nor are the conditions known under which five-coordination for tin is the preferred geometry. This information may possibly be gained by studying the breakdown of the polymeric structure[2] of a compound such as trimethyltin perchlorate in the presence of donor compounds such as nitrogen bases or various solvents. It has been shown[8] that the five-coordinate, polymeric structures of trialkyltin carboxylates are completely destroyed in very dilute carbon tetrachloride solutions, but are re-formed as concentration increases. The interaction between triorganotin groups and carboxylate ions therefore appears weak, but further studies are required. Moreover it is of interest to determine, where possible, the changes in the stereochemistry about tin, as the polymeric structure is broken down. The planarity of the triorganotin group may be retained, or else, as in the triorganotin carboxylates in carbon tetrachloride solutions, the geometry may change to tetrahedral.

We have therefore examined spectroscopically the behaviour of trimethyltin perchlorate in methanol solutions and have also studied the complexes formed by trimethyltin derivatives with ammonia and pyridine. We have also re-examined the preparation and structure of trimethyltin nitrate, since it has previously been suggested[2,3] to have a tetrahedral structure, which would be unique among triorganotin derivatives of oxy acids.

EXPERIMENTAL

Except where otherwise stated, compounds were prepared and handled in a nitrogen atmosphere in a dry box. All solvents were of spectroscopic grade, or were carefully purified and dried by standard methods.

The preparations of trimethyltin perchlorate and trimethyltin nitrate under strictly anhydrous conditions have been previously described[2]. We have now found that the nitrate can be obtained from aqueous solution. A solution of silver nitrate, in slight excess, was shaken with an aqueous ethanolic solution of trimethyltin bromide. The filtered solution, on evaporation, gave a white solid which was sublimed *in vacuo* to give the white, crystalline anhydrous nitrate, identified analytically and spectroscopically by comparison with a standard sample prepared under anhydrous conditions[2]. On exposure to moist air, there were marked changes spectroscopically and analytically, although not in appearance, and the product appeared to be the monohydrate, $(CH_3)_3SnNO_3 \cdot H_2O$, m.p. 147°. (Found: C, 15.20; H, 4.68; $C_3H_{11}NO_4Sn$ calcd.: C, 14.76; H, 4.55 %.) It is interesting that removal of water *in vacuo* from the aqueous preparation, gave the anhydrous nitrate directly; the hydrated form could not be obtained by this process.

Infra-red spectra were obtained of samples of trimethyltin perchlorate that had been exposed on potassium bromide plates to methanol vapor for about one minute in a dry box. This was sufficient to change the powdered sample to a liquid. A series of spectra were also obtained for solutions of trimethyltin perchlorate in methanol, prepared under anhydrous conditions and in which the ratio of perchlorate to methanol (weight/weight) was 4.4:1.0, 1.9:1.0, 1.4:1.0, and 0.8:1.0. These spectra were taken using a 0.025 mm spacer between potassium bromide plates, against a reference of pure methanol.

Ammonia adducts

(*i*) When dry ammonia was passed into a benzene solution of trimethyltin bromide under rigorously anhydrous conditions, the di-ammoniate[9] was precipitated as a white crystalline solid. (Found: N, 10.20. $C_3H_{15}BrN_2Sn$ calcd.: N, 10.01 %.) The same product was also obtained[9] by the passage of dry ammonia over solid trimethyltin bromide. The di-ammoniate did not change in composition over 4 days, and could be slowly sublimed *in vacuo* at 25°. When heated at 100° under atmospheric pressure ammonia was lost and the mono-ammoniate sublimed. (Found: C, 13.79; H, 4.62; N, 5.41. $C_3H_{12}BrNSn$ calcd.: C, 13.80; H, 4.68; N, 5.37 %.) The mono- and di-ammoniates could also be distinguished by their very different and reproducible X-ray diffraction powder photographs.

(*ii*) Trimethyltin chloride was allowed to react with ammonia under anhydrous conditions, removal of excess ammonia left the di-ammoniate. (Found: N, 13.30. $C_3H_{15}ClN_2Sn$ calcd.: N, 13.01 %.) When ammonia was passed into a benzene solution of trimethyltin chloride, without precautions being taken to exclude moisture, the mono-ammoniate was precipitated. (Found: C, 16.54; H, 5.76; N, 6.97. $C_3H_{12}ClNSn$ calcd.: C, 16.67; H, 5.55; N, 6.50 %.)

Pyridine adducts

(*i*) Dry pyridine was condensed on to anhydrous trimethyltin perchlorate, and the excess pyridine was removed *in vacuo* at 50° over 4 hours to give trimethyldi(pyridine)tin perchlorate (Found: C, 37.14; H, 4.98; N, 7.07; ClO_4, 23.65. $C_{13}H_{19}ClN_2O_4Sn$ calcd.: C, 37.05; H, 4.52; N, 6.66; ClO_4 ,23.62 %.) An attempt to prepare a mono-pyridine adduct of trimethyltin perchlorate by allowing equimolar quantities to react *in vacuo* gave a solid whose infra-red spectrum was inconclusive since it could be interpreted in terms of either a mixture of the free perchlorate and the dipyridine adduct, or of a 1:1 adduct.

(*ii*) When pyridine was added to a petroleum ether solution of trimethyltin chloride, precipitation of a white solid occurred; cooling to 0° gave additional product. (Found: C, 34.56; H, 4.57. $C_8H_{14}ClNSn$ calcd.: C, 34.51; H, 5.01 %.)

(*iii*) Trimethyltin bromide was allowed to react with pyridine as in (*ii*) to give the mono-pyridine adduct. (Found: C, 29.65; H, 4.26. $C_8H_{14}BrNSn$ calcd.: C, 29.90; H, 4.35 %.)

Samples for infra-red spectroscopic examination were prepared as either nujol or halocarbon oil mulls. Infra-red spectra were obtained in the 650–4000 cm^{-1} region using Perkin-Elmer model 21 double beam spectrophotometers, and in the 400–700 cm^{-1} region using a Perkin-Elmer model 137 spectrophotometer.

DISCUSSION

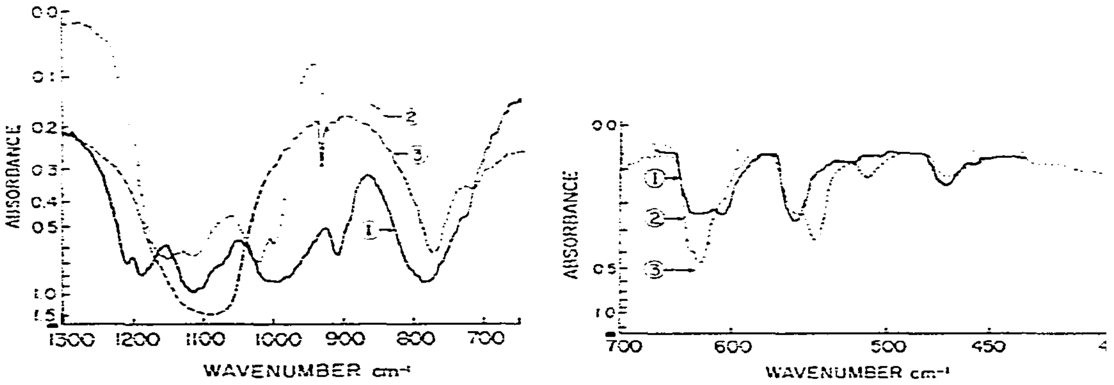
From spectroscopic evidence, it was concluded previously[2] that trimethyltin nitrate contained a monodentate ONO_2 nitrato group and a non-planar $(CH_3)_3Sn$ group. This conclusion was largely based on the similarity of the infra-red spectrum of trimethyltin nitrate to that of $(CO)_5MnNO_3$ which definitely contains a nitrato group, and on the presence in the spectrum of $(CH_3)_3SnNO_3$ of a weak band at 520 cm^{-1}, assigned to the Sn–C symmetric stretching vibration. When the nitrate is prepared from aqueous solution, or hydrolyzed in moist air, it is isolated as a hydrate, although the analytical results do not conclusively establish it as the mono-hydrate. This shows infra-red absorption bands at 1390 cm^{-1} (ν_3 NO_3^-), 823 cm^{-1} (ν_2 NO_3^-), and 728 cm^{-1} (ν_4 NO_3^-) which are very characteristic of the free NO_3^- ion. Bands associated with the trimethyltin group are found at 777 cm^{-1} (CH_3 rocking), 540 (Sn–C asymmetric stretch) and 510 cm^{-1} (Sn–C symmetric stretch). It is significant that the latter two bands are very different from those observed for the anhydrous compound, particularly in that their relative intensities are approximately of the order 2:1, whereas the ratio for the anhydrous compound is approximately 6:1. The shifts to lower frequencies, from 557 to 540 cm^{-1}, and from 520 to 510 cm^{-1}, are also significant.

The only reasonable conclusion is that the hydrated form contains a non-planar $(CH_3)_3Sn$ group, possibly as the tetrahedral mono-hydrated cation, $(CH_3)_3Sn^+ \cdot H_2O$. It is interesting, also, that these changes are readily reversible, the anhydrous nitrate being easily recovered by vacuum sublimation of the hydrated form.

Further, these significant spectroscopic changes strongly suggest that the geometry about the tin atom has changed on hydration, so that the anhydrous nitrate probably cannot contain a tetrahedral tin atom. The geometry of the anhydrous trimethyltin nitrate is therefore not known with certainty, and a revision of our previous conclusion[2] is required. We are inclined to consider that the solid nitrate possibly contains planar $(CH_3)_3Sn$ groups linked by NO_3 groups of C_{2v} symmetry. Our previous assignment of the 520 cm^{-1} band to the Sn–C symmetric stretching mode must therefore be incorrect, and we suggest that it is in fact an Sn–O vibration. Such vibrations associated with the Sn–O bond have been reported over the wide range 400–700 cm^{-1} and in trimethyltin hydroxide a band at 518 cm^{-1} has been assigned[10] to an Sn–O vibration

It should be noted that the above results emphasize the difficulties encountered, particularly for metal nitrates, in trying to deduce a structure purely on the basis of infra-red spectroscopic data. This is also true for a recent study[13] of dimethyltin dinitrate. Although Addison *et al.* conclude that the dinitrate is a simple monomer with two monodentate nitrato groups, the infra-red evidence does not lead unambiguously to this structure in preference to one in which *non-linear* dimethyltin groups are *bridged* by nitrate groups in a polymeric chain. Our own infra-red studies of trimethyltin nitrate certainly do not establish the structure conclusively, and an X-ray structure determination is necessary, but our present conclusions are at least supported by the results of our further studies of trimethyltin perchlorate.

Trimethyltin perchlorate has been shown[2] to consist of planar trimethyltin groups linked by ClO_4 groups of C_{2v} symmetry. It was of interest to determine the manner in which this structure behaved when the compound was dissolved in a solvent of moderately strong solvating ability, in this case methanol. Over the concentration range studied, only one spectrum different from that of the anhydrous compound was observed. The single characteristic spectrum was obtained on exposure of the perchlorate to methanol vapor and for solutions in which the *molar* ratio of perchlorate to methanol varied from approximately 1:1.8 to 1:10, and is spectrum (2) of Fig. 1. Allowing for maxima at 1114 and 1027 cm^{-1} due to methanol, three peaks occur in the 900–1200 cm^{-1} range. These can be assigned to ν_4 (ClO* asymmetric bend) at 1150, to ν_1 (ClO_3 symmetric stretch) at 995, and to ν_2 (Cl–O* symmetric stretch) at 910 cm^{-1}, and are in good agreement with similar assignments[11] for the perchlorate group in thus showing the ClO_4 group to be a monodentate ligand of C_{3v} symmetry. Moreover, there are no changes in bands associated with the $(CH_3)_3Sn$ group, only the Sn–C asymmetric stretching vibration at 553 cm^{-1} being observed in the 400–650 cm^{-1} region. The $(CH_3)_3Sn$ group thus retains its planarity. Therefore on absorption of methanol, the polymeric structure of trimethyltin perchlorate is destroyed, the ClO_4 groups becomes monodentate rather than bridging, the $(CH_3)_3Sn$ group remains planar, and presumably the fifth coordination site about the tin atom is occupied by a solvating methanol molecule.



Figs. 1 and 2. Spectroscopic observations for trimethyltin perchlorate. [Spectrum ① anhydrous perchlorate, spectrum ③ hydrolyzed perchlorate (ionic).]

Apparently even in the presence of excess methanol this structure is preserved, and we have no evidence that the free ClO_4^- ion is released at any stage (although this may well happen in very dilute solution), or that the trimethyltin group changes its planar geometry.

TABLE 1

INFRA-RED ASSIGNMENTS FOR THE MONO- AND DI-AMMONIATES OF TRIMETHYLTIN BROMIDE

$[Me_3Sn(NH_3)_2]^+Br^-$		$Me_3Sn(NH_3)Br$		*Assignment*
3270 cm^{-1}	(S)	3220 cm^{-1}	(S)	N–H str.
3150	(S)	3150	(S)	
3090	(S)	3090	(S)	
3000	(M)	3000	(M)	C–H str.
2900	(M)	2900	(M)	
1840	(W)	1820	(W)	?
1600	(M)	1600	(M)	N–H_3 asym. def.
1405	(M)	1400	(M)	C–H_3 asym. def.
1240	(Sh.)			
1200	(S)	1200	(S)	NH_3 or CH_3 sym. def.
1190	(S)	1185	(S)	
1175	(Sh.)	1175	(Sh.)	
793	(VS)	787	(VS)	CH_3 rocking
625	(M)	625	(M)	NH_3 rocking
645	(Sh.)	640	(Sh.)	?
544	(S)	541	(S)	Sn–C asym. str.
		503	(VW)	Sn–N str?

Quite different spectroscopic changes are observed upon hydrolysis of trimethyltin perchlorate, particularly in the 400–650 cm^{-1} region. Exposure of the perchlorate to moist air causes rapid changes in the 900–1200 cm^{-1} region; free ClO_4^- ions are produced as shown by the broad, strong peak at 1100 cm^{-1} and the weak, sharp maximum at 940 cm^{-1}. Fig. 2 shows the changes occurring in the 400–650 cm^{-1} region after progressively longer exposures to moist air. The change of the doublet at 625–606 cm^{-1} to virtually a single peak at 625 cm^{-1}, and the disappearance of the 468–450 cm^{-1} doublet are those expected for conversion of a bridging ClO_4 group of C_{2v} symmetry to a free ClO_4^- ion. Very marked changes occur in the 500–560 cm^{-1} region with the disappearance of the 553 cm^{-1} peak and its replacement by two peaks at 542 and 509 cm^{-1}. These changes must be due to conversion of the planar $(CH_3)_3Sn$ group to a pyramidal geometry on hydrolysis. The reverse changes have been observed[12] as complex formation occurs between trialkyltin chlorides and Lewis bases.

It is interesting that the hydrolysis products of trimethyltin nitrate and perchlorate contain pyramidal $(CH_3)_3Sn$ groups, since trimethyltin hydroxide, a possible hydrolysis product, has been shown[10] to contain planar $(CH_3)_3Sn$ groups and bridging OH groups. Possibly these hydrolyses products can be regarded as derived by protonation of the hydroxide, breaking the polymeric structure and yielding tetrahedral ionic products, $[(CH_3)_3SnOH_2]^+$ X^-, where $X^- = NO_3$ or ClO_4^-.

Nitrogen base complexes

Trimethyltin halides have long been known[9,13,14] to form mono- and di-adducts with nitrogen bases. The mono-adducts were considered[9] ionic with a tetrahedral cation, while the di-adducts were assigned[15] octahedral structures. However, chloro(trimethyl)pyridinetin(IV) has recently been shown[6,7] to have a trigonal bipyramidal geometry with a five-coordinate tin atom. Moreover, the di-ammonia adducts of trimethyltin perchlorate and trimethyltin nitrate contain[2] the five-coordinate cation $[(CH_3)_3Sn(NH_3)_2]^+$. The five-coordinate configuration may therefore be common to both the mono- and di-adducts formed with nitrogen bases.

In contrast to trimethyltin nitrate and perchlorate which form only di-ammoniates, trimethyltin bromide and chloride form unstable di-ammoniates which readily lose ammonia to give the mono-adducts. The infra-red absorption frequencies of the two ammonia adducts of the bromide are recorded in the table and the close similarity between them is obvious. The spectra of the two chloride adducts were virtually identical to those of the bromide compounds. Such similarity of the spectra requires a close relationship between the symmetry of di- and mono-ammoniates. Since the Sn–C symmetric stretching vibration is missing from all spectra the compounds must contain planar $(CH_3)_3Sn$ groups, so that the di-ammoniates can only be formulated as ionic $[(CH_3)_3Sn(NH_3)_2]^+ X^-$, and the mono-ammoniates as molecular $(CH_3)_3SnX \cdot NH_3$, where $X = Br$ or Cl. These conclusions are consistent with the earlier results obtained for the perchlorate and nitrate di-adducts, and with the known structure[6,7] of $(CH_3)_3SnCl(C_5H_5N)$.

The weak band observed at 503 cm^{-1} for the mono-ammoniate has been tentatively assigned as the Sn–X stretching vibration, in agreement with the similarly weak band observed[2] at 490 cm^{-1} for the di-ammoniate of trimethyltin perchlorate.

The infra-red spectrum of the pyridine adduct of trimethyltin chloride has been examined previously[6,16] and in the present study was observed just for comparison with that of the corresponding adduct of trimethyltin bromide. The earlier results were confirmed, and both spectra were found to consist of simply the spectrum of pyridine[17] superimposed on that of the planar trimethyltin group (*i.e.* the Sn–C symmetric stretching vibration was absent), although there were some slight shifts of pyridine frequencies (*e.g.* the 604 band shifted to 617 cm^{-1}). Similarly, the spectrum of the di-pyridine adduct of trimethyltin perchlorate was comparable to that of $[(CH_3)_3Sn(NH_3)_2]^+ClO_4^-$. The characteristic absorptions of the free ClO_4^- ion, observed at 1100 and 618 cm^{-1}, were superimposed on those of pyridine and a planar $(CH_3)_3Sn$ group. The compound must therefore be formulated as $[(CH_3)_3Sn(C_5H_5N)_2]^+$-$ClO_4^-$.

The very considerable tendency for tin in triorganotin derivatives to become five-coordinate is again clearly shown. For $(CH_3)_3SnX$ compounds where X is a simple atom or group capable of occupying one coordination site (*e.g.* X = halogen), the mono-adducts are the stable nitrogen-base adducts, and they all appear to be five-coordinate, monomeric, covalent compounds. The di-adducts are unstable and readily lose one mole of base to be converted to the stable five-coordinate mono-adducts. When X is a group not usually found in the coordination sphere of complexes (*e.g.* $X = ClO_4^-$), the di-adducts are the stable nitrogen-base adducts. [*e.g.* $(CH_3)_3Sn(NH_3)_2ClO_4$]. In such cases, the corresponding mono-adduct would contain either the tetrahedral $(CH_3)_3SnB^+$ cation, or alternatively the group X (*e.g.* ClO_4^-) would have to occupy one coordination position in a five-coordinate monomer. Clearly, the five-coordinate symmetrical ions $(CH_3)_3SnB_2^+$ are more stable. All available evidence thus indicates that the adducts of triorganotin derivatives attain five-coordinate structures in preference to alternative geometries based on four- or six-coordination.

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UMMARY

An alternative preparation from aqueous solution, and a revised structure, of rimethyltin nitrate are described, as well as the infra-red spectroscopic changes which ccompany the solvation by methanol of trimethyltin perchlorate. The importance of ve-coordination in both of these compounds is stressed, and is further illustrated by he five-coordinate structures which are possessed by both the mono- and di-adducts ormed by ammonia or pyridine with several trimethyltin derivatives.

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