PREPARATION AND SPECTROSCOPIC STUDIES OF DIALKYLTIN HYDROXIDE NITRATE, TRIMETHYLTIN NITRATE AND ITS MONOHYDRATE

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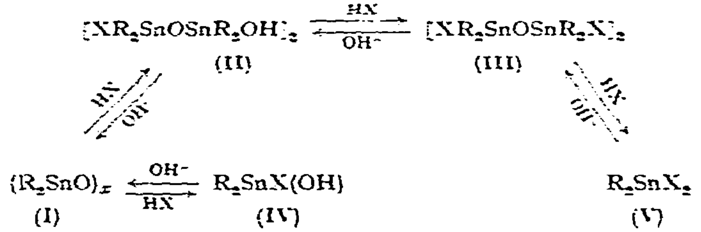
Recently several studies of the structures of alkyltin salts have been reported; evidence has been obtained from infrared spectra[1–6] and X-ray diffraction measurements[7,8]. Most of these salts are found to have an interesting configuration containing penta-coordinated tin. We have been studying the structures of alkyltin nitrates. During the course of our study, one of the present authors reported[3] in a short communication that there was infrared evidence of the existence of penta-coordinate trimethyltin nitrate (m.p. 142°), although there was some uncertainty as to the configuration of the trimethyltin group. Later Clark *et al.*[5] reported that trimethyltin nitrate (m.p. 127–128°) contains a pyramidal trimethyltin group which appeared to be coordinated by an unidentate NO_3 group. This paper describes a further study of the careful preparation of alkyltin nitrates, and their configurations as indicated by their infrared spectra are discussed.

We have obtained trimethyltin nitrate in two forms, the hygroscopic anhydrous compound (m.p. 140°), and a stable monohydrate (m.p. 98–99°). We have also isolated a stable, novel type of compound having peculiar properties, a dialkyltin hydroxide nitrate. It has been known[9] that there are at least two types of stable compounds, (II) and (III), that can be obtained in the interconversions of polymeric dialkyltin oxide (I) and dialkyltin dichloride (V).



However, the reaction of dialkyltin oxide with nitric acid gives a new type of compound, a dialkyltin hydroxide nitrate, which corresponds to formula (IV) and which is not analogous to either (II) or (III). The crystalline dialkyltin hydroxide nitrates are extremely stable* and are not easily condensed to give distannoxanes (III). In order to investigate the configuration of these compounds we have compared their be-

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* Their stability was studied by an infrared spectral technique. See ref. 9, p. 82, l. 32–34.

haviour and their infrared spectra with those of trimethyltin nitrate and hydroxide[10], and we have concluded that the configuration of a dialkyltin hydroxide nitrate is quite unique and is possibly one of those structures shown in Fig. 2.

Concerning the structure of anhydrous trimethyltin nitrate, careful experiments, in which contamination by moisture was avoided, have led to the conclusion that the planar trimethyltin groups are bridged by NO_3 groups, as shown in Fig. 3. With trimethyltin nitrate monohydrate, the configurations shown in Fig. 4 can be suggested as probable.

EXPERIMENTAL

Materials

Dialkyltin hydroxide nitrate. Dimethyltin oxide (4.0 g, 0.024 mole) or diethyltin oxide (4.6 g, 0.024 mole) was dissolved in 10 ml of a 2.5 molar nitric acid solution (0.025 mole) and the solution was evaporated to 0.5 ml on a hot plate. The solid product was recrystallized from dilute nitric acid or aqueous methanol. The crystalline dialkyltin hydroxide nitrate is soluble in water or methanol. Dimethyltin hydroxide nitrate: m.p. > 250°. (Found: C, 10.79; H, 3.04; Sn, 52.11. $C_2H_7NO_4Sn$ calcd.: C, 10.55; H, 3.10; Sn, 52.11 %.) Diethyltin hydroxide nitrate: m.p. 214° (decomp.). (Found: C, 18.49; H, 4.32; Sn, 46.20. $C_4H_{11}NO_4Sn$ calcd.: C, 18.79; H, 4.33; Sn, 46.40 %.). The deuterium-substituted dimethyltin hydroxide nitrate, $(CH_3)_2Sn(NO_3)(OD)$, was prepared by the repeated recrystallization of dimethyltin hydroxide nitrate from heavy water, and was characterized by its infrared spectrum.

Trimethyltin nitrate and its monohydrate. Trimethyltin hydroxide (2.7 g, 0.015 mole) was dissolved in 6 ml of a 2.5 molar nitric acid solution (0.015 mole) and the solution was evaporated to 1 ml under reduced pressure at room temperature. The crystallization of the solid product from acetone gave crystalline trimethyltin nitrate monohydrate, which is soluble in water, methanol or acetone, m.p. 98–99°. (Found: C, 14.90; H, 4.59; Sn, 48.58. $C_3H_{11}NO_4Sn$ calcd.: C, 14.78; H, 4.59; Sn, 48.68 %.) Sublimation of the monohydrate under vacuum gives anhydrous trimethyltin nitrate, m.p. 140° (decomp. in a sealed tube). (Found: C, 15.98; H, 4.36; Sn, 52.50. $C_3H_9NO_3Sn$ calcd.: C, 15.96; H, 4.02; Sn, 52.56 %.) The anhydrous trimethyltin nitrate is fairly hygroscopic* and on standing a few days in air it absorbs one mole of water to give the monohydrate. This change was followed by observing the decrease in melting point which accompanies the increase in weight of the sample, and also by noting the increase in the intensities of the bands associated with OH stretching and the bending vibrations of the hydrated water molecule. The deuterium-substituted compound was prepared and characterized as in the case of dimethyltin hydroide nitrate.

Infrared spectra

The infrared spectra were taken as mulls in nujol or hexachlorobutadiene, protecting the plates with polyethylene or polytetrafluoroethylene, on a Hitachi EPI-421G spectrophotometer equipped with gratings and a Perkin-Elmer 221 spectrophotometer

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* The melting point of trimethyltin nitrate has been reported[5] as 127–128° with the description that this compound is unaffected by exposure to moist air. The material used for the investigation of the structure of trimethyltin nitrate in this reference could be a mixture of the anhydrate and its monohydrate.

equipped with CsBr optics. Spectra are shown in Fig. 1. The positions and the assignments of the absorption bands are listed in Table 1. The solution spectra of the compounds were not measured because of their insolubility in non-polar solvents.

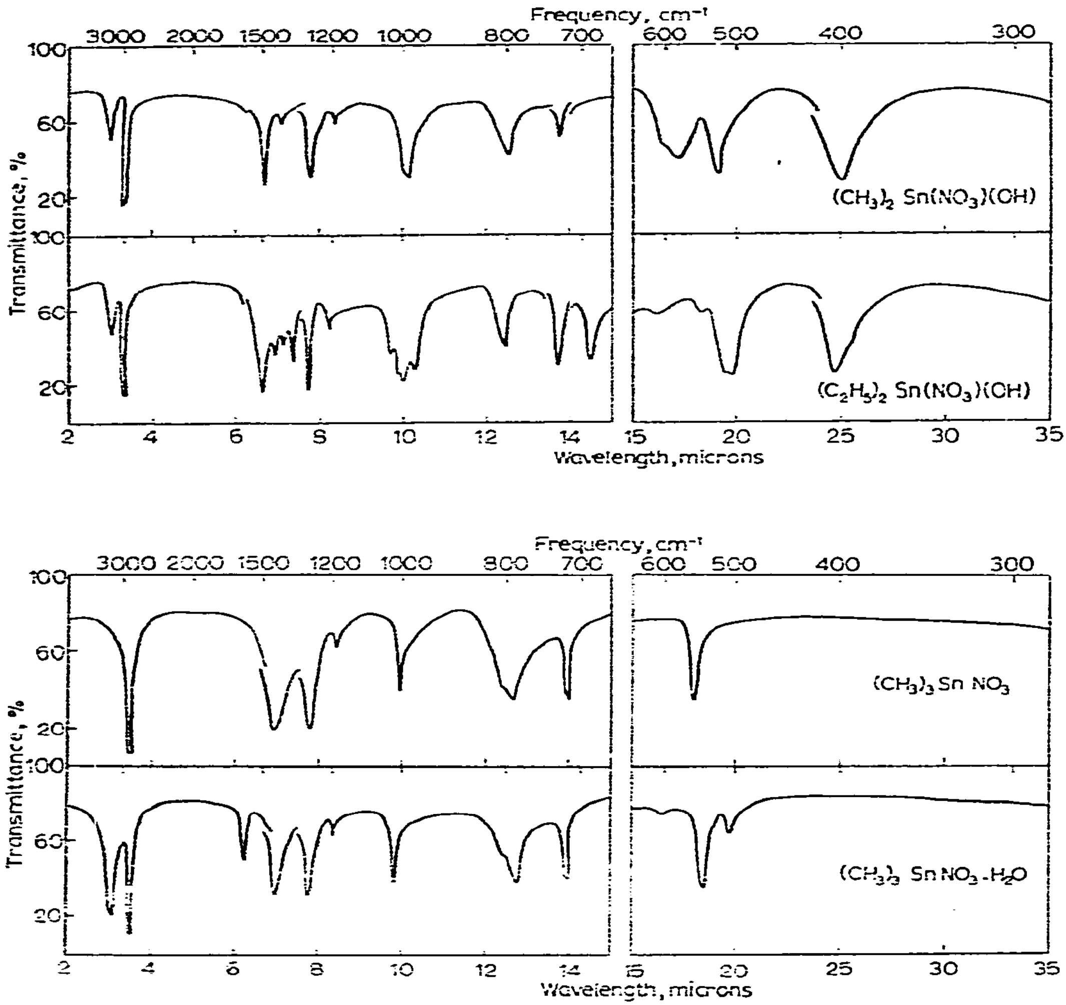


Fig. 1. Infrared spectra of dialkyltin hydroxide nitrates, trimethyltin nitrate and its monohydrate in nujol or hexachlorobutadiene mulls.

DISCUSSION

Structure of dimethyltin hydroxide nitrate

In the absence of molecular weight data (as a consequence of the insolubility of this compound in non-polar solvents), the proposal of a structural formula, compatible with the empirical formula, $C_2H_7NO_4Sn$, must be based on a comparison of the peculiar properties of this compound with the facts obtained for the distannoxanes[9] and trimethyltin hydroxide[10]. Three possible structures, $(CH_3)_2Sn(NO_3)(OH)$ (VI), or distannoxane formulas, $(NO_3)(CH_3)_2SnOSn(CH_3)_2(NO_3) \cdot H_2O$ (VII), and $(NO_3)(CH_3)_2SnOSn(CH_3)_2(OH) \cdot HNO_3$ (VIII), can possibly be taken into account. However, the infrared spectrum of this compound lacks the band associated with the deformation of a coordinated or a free water molecule; the OH bending vibration band is observed at 1000 cm^{-1}, which shifts to 756 cm^{-1} in the deuterium-substituted compound. For this reason, formula (VII) does not seem to be suitable. Furthermore, the presence of only one kind of NO_3 group, indicated by the infrared spectrum, shows that formula (VIII) is inadequate. In conclusion, this compound is probably best represented as $(CH_3)_2Sn(NO_3)(OH)$ (VI), within the limits of these three possible formulas. This formulation is therefore assumed in our following interpretation of the infrared spectra (Fig. 1).

TABLE 1

INFRARED VIBRATIONAL FREQUENCIES OF ALKYLTIN NITRATE DERIVATIVES*

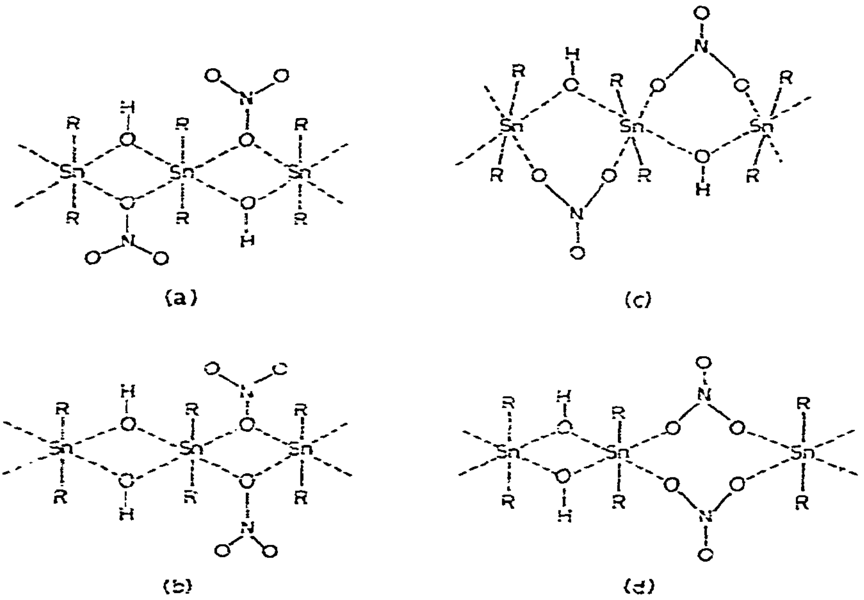
Positions of bands (in cm^{-1})

Dialkyltin hydroxide nitrate *$R_2Sn(NO_3)(OH)$*			*Trimethyltin nitrate and its monohydrate*		
$R = CH_3$	*$R = C_2H_5$*	*Assignment*	*$(CH_3)_3SnNO_3$*	*$(CH_3)_3SnNO_3 \cdot H_2O$*	*Assignment*
403 s	398 sh	Sn–O str.		510 m	Sn–C sym. str.
	413 s		552 s	540 s	Sn–C asym. str.
530 s	510 s	Sn–O str.		606 vw	(H_2O rock. or wag.)
	517 s	(Sn–C str.)	702 m	715 m	NO_3 def.
585 s	547 m	Sn–C str.	803 sh	812 sh	NO_3 def.
611 m	630 m	NO_3 def.	1021 s	1020 s	NO_3 str.
729 s	729 s	NO_3 def.	1300 s	1300 s	NO_3 str.
797 sh	803 m	NO_3 def.	1452 s	1455 s	NO_3 str.
994 s	994 s	NO_3 str.		1645 m	H_2O def.
1000 s	1006 s	Sn–OH def.		3280 m	O–H str.
1287 s	1290 s	NO_3 str.			
1506 s	1493 s	NO_3 str.			
3390 s	3344 s	O–H str.			

* Frequencies associated with the inner vibrations of methyl groups are 790 ± 10 s, 1201 m, 1408 m, 2915 m and 2985 m, and that of ethyl groups are 690 s, 964 w, 1026 w, 1195 w, 1370 m, 1408 m, 1470 m, 2920 m and 2950 m.

The dialkyltin hydroxide nitrates contain two functional groups, NO_3 and OH. In solid trimethyltin hydroxide[10], the oxygen atom of the OH group has been found to coordinate with the other tin atom, and in this compound the OH absorption band associated with the stretching vibration is observed at 3620 cm^{-1}. In dimethyl- and diethyltin hydroxide nitrate, however, the position of the OH band is found at 3390 and 3344 cm^{-1}, respectively. These absorption bands are sharp and lead us to expect that hydrogen bonding is absent. Therefore, it is considered that the decrease in the wave number of the OH band in a dialkyltin hydroxide nitrate is due to stronger coordination of the oxygen with tin than in the case of trimethyltin hydroxide. This conclusion is further supported by the position of the Sn–O stretching vibration. In the region of 600–300 cm^{-1}, only three absorption bands were observed in dimethyltin hydroxide nitrate, as given in Fig. 1 and Table 1. The strong band at 585 cm^{-1} is assigned to the Sn–C asymmetric stretching vibration, since in dimethyltin diformate[1] and dimethyl(2,2'-bipyridine)tin dichloride, in which tin is hexa-coordinated[12], the Sn–C asymmetric stretching band has been observed at 592 and 578 cm^{-1}, respectively. The band at 530 cm^{-1} could be assigned to the Sn–C symmetric stretching vibration; however, the symmetric stretching vibration usually does not give such a strong absorption, and so it is reasonable to assign this to Sn–O stretching or to an overlapping of Sn–O stretching and the Sn–C symmetric stretching absorption bands. The strong band at 403 cm^{-1} is assigned to an Sn–O stretching vibration, for no other vibration is expected in this region. Thus, the frequencies of the Sn–O stretching vibrations of this compound are higher than in solid trimethyltin hydroxide (370 cm^{-1}) and stronger coordination of oxygen with tin is indicated.

In the infrared spectra of the dialkyltin hydroxide nitrates, six bands are found which are due to the vibrations of the NO_3 group. According to the selection rule, it can be concluded that the NO_3 group does not have a D_{3h} point group but a C_{2v} or a much lower point group. The degree of distortion of the NO_3 group, indicated by the shift of the NO_3 stretching vibration frequencies from those of an NO_3 anion of a D_{3h} point group, is larger in the dialkyltin hydroxide nitrates than in trimethyltin nitrate, as can be seen in Table 1. Thus it can be assumed that the coordination of oxygen in the NO_3 group with tin is stronger in this compound than in trimethyltin nitrate. Accordingly, we can tentatively give the following possible structures, shown in Fig. 2, in which the tin atom is hexa-coordinated. If we take into account the important fact that four-membered ring structures, formed alternatively by tin and oxygen atoms, have been found in distannoxanes[9] or in trimethyltin hydroxide[10] in solution, we can assign the simplest structure shown in (a), or others, for example (b). In structure (a), the dimethyltin groups are bridged by an oxygen atom of the NO_3


(a) (c)

(b) (d)

Fig. 2. Some possible configurations of dialkyltin hydroxide nitrate.

group as well as by that of the OH group. However, since the infrared spectra show that the NO_3 group has C_{2v} symmetry or lower, structures involving bridging by two oxygen atoms of each NO_3 group can also be considered, for example (c) or (d).

The differences in the physical properties of the dialkyltin hydroxide nitrates from those of trimethyltin nitrate or trimethyltin hydroxide support these strong coordinations. The dialkyltin compounds do not sublime, have high melting points, and are insoluble in non-polar organic solvents, while the trimethyltin nitrate and hydroxide sublime easily. The stability of the dialkyltin hydroxide nitrates against condensation to give distannoxanes is also readily understood in terms of this strong coordination[9].

Structure of trimethyltin nitrate and its monohydrate

The symmetry of the NO_3 group in trimethyltin nitrate has been reported[3,5] to be C_{2v} or lower. Our study of anhydrous trimethyltin nitrate leads to the same conclusion. In the KBr region only one absorption band is observed at 552 cm^{-1}, which can be assigned to the Sn–C degenerate stretching vibration band*. This fact suggests the structure given in Fig. 3 (a), in which the planar trimethyltin groups are bridged by two oxygen atoms of the NO_3 group. A Stuart model shows that bridging by a single oxygen atom of the NO_3 group, (b), is also possible.

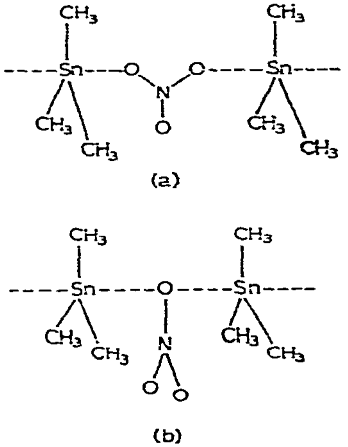


Fig. 3. Possible structures of anhydrous trimethyltin nitrate.

The positions of the bands associated with the NO_3 group in the anhydrate and in the monohydrate are almost identical, which shows that the configuration of the NO_3 group is similar in both compounds. However, two bands due to the Sn–C stretching vibration are observed in the monohydrate, as shown in Fig. 1. The positions of the bands associated with the water molecule are 3280, 1645, and 606 cm^{-1},

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[*] In refs. 3 and 5, two absorption bands due to the Sn–C stretching vibration have been reported; a strong band at 557 and a weak one at 520 cm^{-1}(ref. 5). This we assume may be attributed to contamination by moisture, which results in formation of the monohydrate as described above. The strength of the weak band at 520 cm^{-1} (510 cm^{-1}, in our experiments) increases with absorption of moisture.

and these bands shift to 2457, 1080, and 417 cm^{-1}, respectively, in the deuterium-substituted compound, $(CH_3)_3SnNO_3 \cdot D_2O$. The weak band at 606 cm^{-1} can be assigned to a rocking or wagging vibration of the water molecule, which suggests that the water molecule coordinates weakly to the tin atom, lowering the symmetry of the trimethyltin group. Possible structures in accord with these facts are shown in Fig. 4 (a) and (b). The trimethyltin group and the central tin atoms are bridged by the NO_3 groups, as in the anhydrous compound.

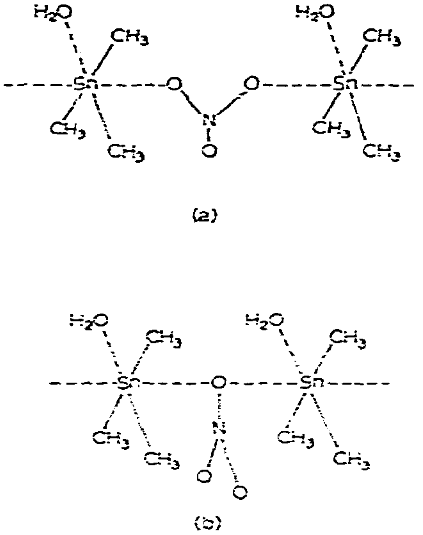

Fig. 4. Possible structures of trimethyltin nitrate monohydrate.

If we assume either one of the structures shown in Fig. 4, three infrared-active Sn–C stretching vibrations are expected. However, as shown in Fig. 1, only two of the observed bands can be assigned to Sn–C vibrations. It is often found in such cases that overlapping of two of the very close absorption bands occurs. An alternative structure, in which a pyramidal trimethyltin group is coordinated by NO_3 and H_2O, might give only two infrared-active Sn–C stretching vibrations. However, this should also result in a significant difference in the configuration of the NO_3 group as compared to that of anhydrous trimethyltin nitrate, and therefore this structure is considered to be inappropriate.

An absorption band which is due to the weak Sn–O coordination bond in other solid trimethyltin salts has been observed in 381, 370 and 306 cm^{-1} in bis(trimethyltin) carbonate[13], trimethyltin hydroxide[10], trimethyltin formate[11], respectively. In trimethyltin nitrate or in its monohydrate, however, no absorption band was observed in this region down to 300 cm^{-1}, and it is assumed that the coordination of oxygen of the NO_3 group with tin in these compounds is weaker than that in the carbonate, hydroxide or formate.

Trimethyltin nitrate in the solid state gives a band at 1021 cm^{-1} in its infrared spectrum; however, the Raman spectrum of its aqueous solution includes a band at 1050 cm^{-1}, which is due to the NO_3^- anion. Perhaps the trimethyltin group is hydrated in aqueous solution, and the structure of the whole molecule is different from that in the solid state, as was found in dimethyltin dichloride[14].

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SUMMARY

The reaction between a dialkyltin oxide (alkyl = CH_3 or C_2H_5) and dilute nitric acid gives a new type of compound, the dialkyltin hydroxide nitrates $R_2Sn(NO_3)(OH)$. These are stable, high-melting, crystalline substances, which are soluble in water and in methanol but insoluble in non-polar solvents. Their infrared spectra indicate that the oxygen atoms of the OH and NO_3 groups are coordinated strongly with the tin atoms.

The reaction of trimethyltin hydroxide with dilute nitric acid yields trimethyltin nitrate monohydrate (m.p. 98–99°), the sublimation of which gives anhydrous trimethyltin nitrate (m.p. 140°). The anhydrous compound is hygroscopic and reverts to the monohydrate upon the absorption of moisture. In anhydrous trimethyltin nitrate it is suggested that the planar trimethyltin groups are bridged by NO_3 units. The most probable structure of trimethyltin nitrate monohydrate is one in which the bridged structure of the anhydrous compound is retained but with the water molecule located in the plane of the trimethyltin group and weakly coordinated to the tin atom.

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