

## THE INFRARED AND FAR INFRARED SPECTRA OF TRIALKYLTIN FORMATES: PRESENCE OF A LINEAR POLYMER IN THE SOLID STATE AND IN SOLUTION

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Although many of the observed properties of the organometallic compounds of the fourth group elements are similar, there are still some properties that are characteristic of one element. One of the most characteristic properties observed is the metal-oxygen bonding of carboxylate compounds of these elements. In the case of acetoxysilanes<sup>1</sup>, the characteristic absorptions of the acetoxy group in the infrared spectra are similar to those of organic esters and it has been assumed that the metal-oxygen bonding is covalent. Trimethyltin<sup>1</sup> and trimethyllead<sup>2</sup> carboxylate in the solid state, however, show the characteristic bands of the carboxyl group analogous to those of the carboxylate anion. As a tentative interpretation of these spectra it was at first assumed that a planar trimethyltin or trimethyllead cation and the carboxylate anion were present in the solid state. Further investigations in the far infrared region showed that trimethyltin formate and dimethyltin diformate have a characteristic absorption at near  $300\text{ cm}^{-1}$ . It is reasonable to assign this band to a weak coordination of the oxygen atom with the tin atom<sup>3</sup>. Thus it is understandable that these compounds sublime easily at their melting points. With such a weak coordination it is likely that both the symmetry and the characteristic frequencies of the carboxylate anion are maintained. X-ray analysis also clearly shows that in trialkyltin carboxylates the tin atom and the carboxylate group are arranged alternately along the direction of the needle axis with an identity period of 10.3 to 10.8 Å<sup>4</sup>. Hence we believe that in the crystalline state trialkyltin carboxylates consist of a planar SnC<sub>3</sub> skeleton bridged by carboxylate groups, thus forming a linear chain, as was suggested by Beattie *et al.*<sup>5</sup>

In order to make clear the difference between the weak coordination in the acetates and the formates and to obtain information about the configuration of these compounds, the infrared and far infrared spectra of triethyltin and tri-*n*-propyltin formate in the solid state and in solution were examined in the region of  $2\ \mu$  to  $35\ \mu$ . It was found that these formates not only show the characteristic absorptions similar to the other trialkyltin acetates, but also polymerize in solution<sup>6</sup>, while trialkyltin acetates are exclusively monomeric in solution<sup>3,9</sup>.

## EXPERIMENTAL

*Materials*

*Triethyltin formate.* A mixture of triethyltin hydroxide (18 g) and formic acid (4 g) was dissolved in ether and the solution washed several times with water saturated

with sodium formate, then dried with anhydrous sodium sulfate. The ether was distilled off and the white solid (15.5 g) obtained was sublimed *in vacuo*; m.p. 57–8° (reported<sup>7</sup> m.p. 50–60°). (Found: C, 33.62; H, 6.39; Sn, 47.34.  $C_7H_{16}O_2Sn$  calcd.: C, 33.51; H, 6.43; Sn, 47.31 %.)

*Tri-n-propyltin formate.* This compound was obtained from bis(tri-*n*-propyltin) oxide (26 g) and formic acid (6 g) by a procedure similar to that for triethyltin formate. The very viscous liquid (26 g) obtained, was distilled several times under reduced pressure; b.p. 105°–106°/3;  $n_D^{20}$  1.5039. (Found: C, 41.10; H, 7.45; Sn, 40.55.  $C_{10}H_{22}O_2Sn$  calcd.: C, 41.10; H, 7.57; Sn, 40.51 %.)

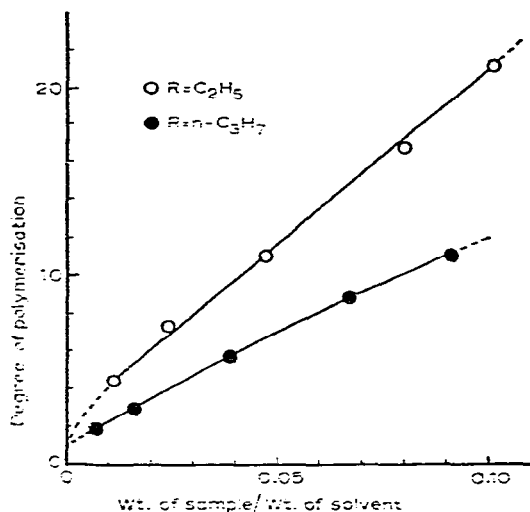


Fig. 1. Molecular weight of  $R_3SnOOCH$  ( $R = C_2H_5$  and  $n-C_3H_7$ ) in cyclohexane.

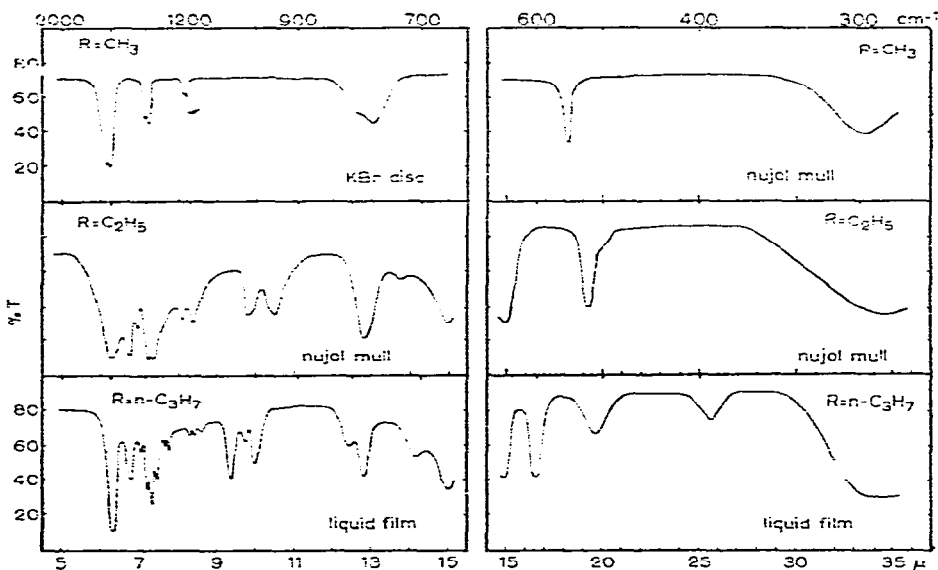


Fig. 2. Infrared spectra of  $R_3SnOOCH$ .

*Molecular weight determinations*

Molecular weights were determined cryoscopically in cyclohexane. The results are shown in Fig. 1.

*Infrared and far infrared spectra*

The infrared absorption spectra were recorded using a Perkin-Elmer Model 221 spectrophotometer and the far infrared spectra were measured by the instrument in the Department of Chemistry of Tokyo University with kind permission of Prof. T. SHIMANOUCHI. In the whole region from  $2 \mu$  to  $35 \mu$ , the spectra were examined in nujol mull or by means of liquid films. The spectra of the solutions were obtained in cyclohexane of various concentrations for the rock salt region and in *n*-heptane for the other regions. The spectra are shown in Fig. 2 and Fig. 3.

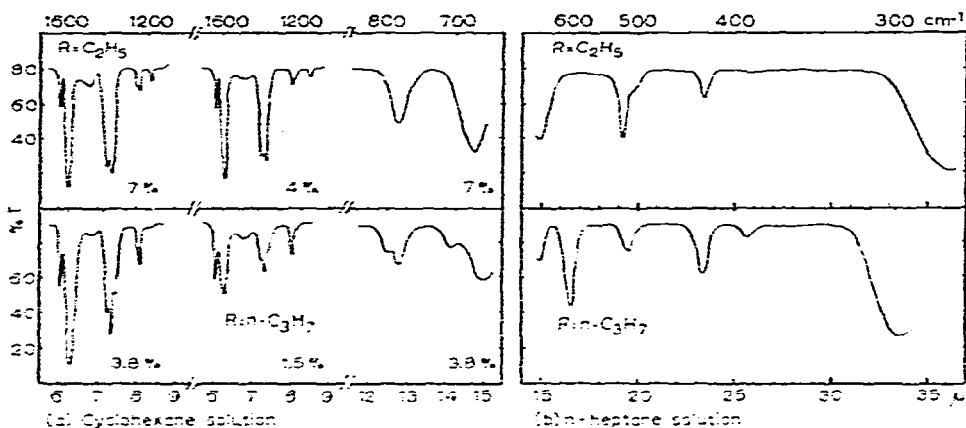


Fig. 3. Infrared spectra of  $R_3SnOOCH$  in solution.

## RESULTS AND DISCUSSIONS

The characteristic absorptions due to the formoxy group in triethyltin and tri-*n*-propyltin formate are similar to those of trimethyltin formate or the formate anion, as shown in Table I.

TABLE I  
CHARACTERISTIC FREQUENCIES OF  $R_3SnOOCH$  (in  $cm^{-1}$ )

| $R_3SnOOCH^a$<br>solid state | $R = CH_3^b$         | $R = C_2H_5$ |                         | $R = n-C_3H_7$ |                         | Assignment                             |
|------------------------------|----------------------|--------------|-------------------------|----------------|-------------------------|--|
|                              | nujol<br>KBr disc    | nujol        | cyclohexane<br>solution | liquid film    | cyclohexane<br>solution |  |
| 772                          | 790<br>or<br>770     | 778          | 778                     | 779            | 777                     | COO deform.                            |
| 1073<br>1366                 | —<br>1363            | —<br>1366    | —<br>1242<br>1359       | —<br>1362      | —<br>1245<br>1359       | CH out of plane bend.<br>COO sym. str. |
| 1377<br>1567                 | 1378<br>1590<br>1610 | —<br>1592    | —<br>1585<br>1658       | —<br>1587      | —<br>1587<br>1661       | CH in plane bend.<br>COO asym. str.    |

Whereas trimethyltin formate is insoluble in organic solvents, triethyltin and tri-*n*-propyltin formate are soluble in these solvents but not in water, and the spectra of the solution in the rock salt region showed additional new bands at 1660  $\text{cm}^{-1}$  and 1245  $\text{cm}^{-1}$ . The relative intensity of these absorptions with respect to those at 1585  $\text{cm}^{-1}$  and 1366  $\text{cm}^{-1}$  due to the  $-\text{OCO}-$  group having  $C_{2v}$  symmetry increases as the concentration decreases; this is shown in Fig. 3 (a) and Table 2.

TABLE 2  
RELATIVE INTENSITY OF THE ABSORPTIONS AT 1661  $\text{cm}^{-1}$  AND 1587  $\text{cm}^{-1}$  OF  
(*n*- $\text{C}_3\text{H}_7$ )<sub>3</sub>SnOOCH IN CYCLOHEXANE SOLUTION

| Conc.* | Log(I <sub>1661</sub> /I) |                       | Ratio |          |
|--------|---------------------------|-----------------------|-------|----------|
|        | 1661 $\text{cm}^{-1}$     | 1587 $\text{cm}^{-1}$ | found | calcd.** |
| 1.5    | 0.261                     | 0.310                 | 1.2   | 1.9      |
| 3.3    | 0.269                     | 1.123                 | 4.2   | 4.7      |

\* (weight of sample/weight of solvent)  $\times$  100.

\*\* Calculated from degree of polymerization: (number of bridging groups/number of terminal groups).

The new bands of triethyltin and tri-*n*-propyltin formate in solution are considered to be associated with the formoxy group having reduced symmetry of the  $-\text{OCO}-$  group, of which form is similar to that of organic esters. It has been reported<sup>3</sup> that in the crystalline state the acetoxy group of trialkyltin acetates is in the  $C_{2v}$  symmetry class, and that in solution, in which these acetates are monomeric, this group is exclusively in reduced symmetry.

The results of the molecular weight determinations given in Fig. 1, show that these formates are likely to form a linear chain in solution and that the formoxy group which appears newly in solution may exist as a terminal group.

If each oxygen in the carboxyl group of these alkyltin compounds can be coordinated to a tin atom and the coordination is weak enough to keep the characteristic frequencies of the carboxylate anion, it is to be expected that the band due to coordination will appear in the far infrared region. It has been shown<sup>3</sup> that in the solid state this band was found in trimethyltin formate at 306  $\text{cm}^{-1}$  and in dimethyltin diformate at 301  $\text{cm}^{-1}$ , the band being broad. As shown in Table 3, a similar band was found in

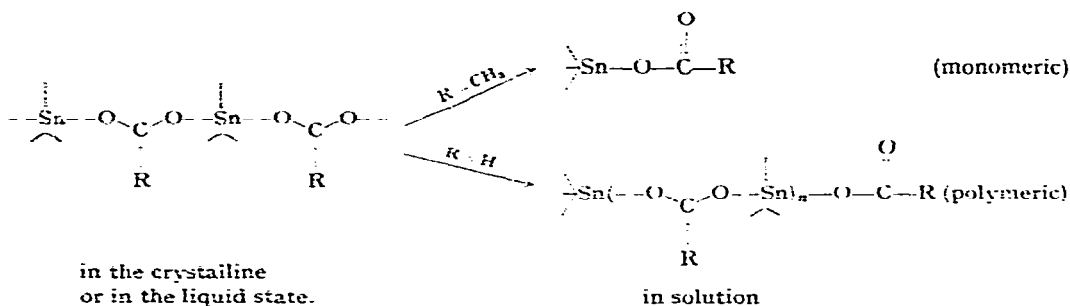
TABLE 3  
FREQUENCIES OF  $\text{R}_3\text{SnOOCH}$  IN THE REGION  $18\mu \sim 35\mu$  (in  $\text{cm}^{-1}$ )

| R   | $\text{CH}_3^a$<br>nujol | R = $\text{C}_2\text{H}_5$ |                            | R = <i>n</i> - $\text{C}_3\text{H}_7$ |                            | Assignment  |
|-----|--------------------------|----------------------------|----------------------------|---------------------------------------|----------------------------|---|
|     |                          | nujol                      | <i>n</i> -heptane solution | liquid film                           | <i>n</i> -heptane solution |   |
| 552 | 520<br>488sh             | 525                        | 430                        | 513                                   | 514                        | Sn—C str.   |
|     |                          |                            |                            | 391                                   | 429                        | new band in soln.<br>inner vibration of <i>n</i> - $\text{C}_3\text{H}_7$<br>group* |
|     |                          |                            |                            |                                       | 390                        |   |
| 306 | 283                      | 283                        | 294                        | 299                                   | 299                        | coordination band   |

\* The band at 391  $\text{cm}^{-1}$  is common to tri-*n*-propyltin compounds.

triethyltin and tri-*n*-propyltin formate at  $283\text{ cm}^{-1}$  and  $294\text{ cm}^{-1}$ , respectively; on the other hand, trialkyltin acetates show no similar absorption in this region, but the similar band is likely to exist in the lower region. Assuming that this band is due to the coordination bond vibration, the difference between the coordination of the oxygen atom to the tin atom in the formates and the acetates could explain the behavior of both compounds in solution. In the far infrared spectra in *n*-heptane solution a new band occurred at  $430\text{ cm}^{-1}$  in triethyltin formate and at  $429\text{ cm}^{-1}$  in tri-*n*-propyltin formate, as shown in Table 3; this band can be assumed to be due to the terminal formoxy group. As to the shape of the trialkyltin group, since we can find only one absorption which can be assigned to the Sn-C stretching vibration as shown in Table 3, the  $\text{SnC}_3$  skeleton of trimethyltin and triethyltin formate is assumed to be planar or nearly planar. The band at  $513$  or  $514\text{ cm}^{-1}$  in tri-*n*-propyltin formate is tentatively assigned to the Sn-C stretching vibration, as shown in Table 3, because tri-*n*-propyltin halide and di-*n*-propyltin dihalide, in which the tin atom is tetrahedrally bonded, show only one absorption at near  $510\text{ cm}^{-1}$ . Thus it is difficult to decide whether in tri-*n*-propyltin formate the  $\text{SnC}_3$  skeleton is planar or not. It is, however, likely that it is planar in analogy with trimethyltin and triethyltin formate.

In conclusion, the carboxyl group in trialkyltin carboxylates certainly bridges two tin atoms by coordination of the oxygen to the tin atom, which has a planar  $\text{SnC}_3$  skeleton, to form a linear chain in the crystalline state or in the liquid state. In solution, the bridging is broken at the coordination bond as shown in the following scheme.



In the case of acetates the linear chain, as shown above, is completely broken, but in formates the configuration is partially maintained and a species having both bridging and a terminal formoxy group appears. Two kinds of  $\text{SnC}_3$  skeleton, the terminal and the chain forming planar one would appear, as shown in the scheme. The terminal skeleton, however, may not be so distorted as that of the acetates because the band due to the symmetric Sn-C stretching is not observed in the spectra of triethyltin formate in solution.

#### SUMMARY

Triethyltin and tri-*n*-propyltin formate were found to exist as low polymers in organic solvents. In the infrared spectra of these compounds in the solid state, the formoxy group shows bands similar to those of the formate anion at near  $1590\text{ cm}^{-1}$ ,  $1360\text{ cm}^{-1}$  and  $770\text{ cm}^{-1}$ ; furthermore a band which is due to a weak coordination of the oxygen

atom with the tin atom is found near  $300\text{ cm}^{-1}$ . The absorption due to the Sn-C stretching vibration appears only at  $520\text{ cm}^{-1}$  in triethyltin formate. In the spectra of solutions, additional new bands due to the terminal formoxy group appear at near  $1660\text{ cm}^{-1}$ ,  $1245\text{ cm}^{-1}$  and  $430\text{ cm}^{-1}$ . From these facts it is concluded that in the solid state trialkyltin formate is a linear polymer in which the planar  $\text{SnC}_3$  group is bridged by the  $-\text{OCO}-$  unit, and that even in solution this structure is partially maintained.

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