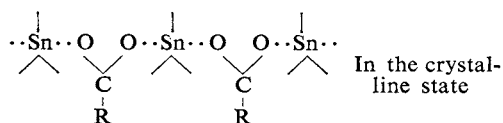


*Presence of a Low Polymer of Triethyltin  
Formate in Solution*

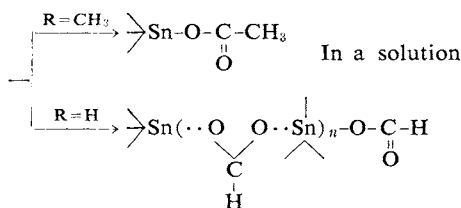
By Rokuro OKAWARA and  
Mitsuaki OHARA

(Received March 5, 1963)

It has been reported<sup>1)</sup> that the structure of a trialkyltin acetate in the crystalline state involves planar  $C_3Sn$  groups and  $CO_2$  groups with  $C_{2v}$  symmetry alternately arranged in one direction by the coordination of each oxygen atom of a  $CO_2$  group to tin. However, these compounds are *monomeric* in a cyclohexane solution or in the vapor phase, and the infrared spectra of the solutions show *only* the presence of terminal acetate groups with reduced symmetry, as is shown below:



1) R. Okawara et al., International Symposium on Molecular Structure and Spectroscopy, Tokyo, September, 1962. A complete report will be published in *J. Chem. Soc.*



Now we wish to report the existence of an intermediate type of structure (shown above) for polymeric triethyltin formate in a solution, in which type both bridging and terminal formoxy groups are present in the molecule. Triethyltin formate was prepared from triethyltin hydroxide and formic acid and purified by sublimation (m. p., 57~58°C). Cryoscopic molecular weight determinations show that polymeric triethyltin formate exists in the solution and that the degree of polymerization varies linearly with the concentration. For example, the degree of polymerization in cyclohexane is 4.5, 7.3, 11.0, 16.7 and 21.1 at concentrations of 1.08, 2.38, 4.52, 7.43 and 9.77, (g. of sample/g. of solution)  $\times 100$  respectively. In the infrared spectra of this compound in Nujol mull or in a KBr disk, the bands

associated with the stretching vibrations of the  $\text{CO}_2$  group appear at 1590 and 1360  $\text{cm}^{-1}$ , showing the presence of formoxy groups in  $\text{C}_{2v}$  symmetry; on the other hand, in a cyclohexane solution additional new bands due to formoxy group with reduced symmetry appear at 1667 and 1242  $\text{cm}^{-1}$ , and the intensity of these bands increases as the concentration decreases. These facts may be explained reasonably by assuming that a formoxy group having  $\text{C}_{2v}$  symmetry bridges two tin atoms, but in a reduced symmetry exists as a terminal group. In the crystalline state triethyltin formate is arranged, just like trialkyltin acetate, in a linear chain with an identity period of 10.86 Å along the needle axis<sup>2)</sup>, but in a solution this linear chain is cleaved at a coordination bond to give a low polymeric species with a terminal formoxy group with reduced symmetry.

*Department of Applied Chemistry  
Osaka University  
Miyakojima-ku, Osaka*

2) N. Kasai, T. Omae and R. Okawara, Symposium on Organometallic Compounds held by The Chemical Society of Japan, Tokyo, October, 1962.