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Action of Pyridine upon Organotin Compounds of the R_2SnO–SnR'_2X_2 Mixed Type

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In a previous paper, the author[1)] reported various new organotin complexes of the mixed type R_2SnO–SnR'_2X_2. The position of halogens have not been determined and the problem whether these complexes are monomeric or polymeric in the solid state remains to be solved. The present investigation was performed in order to obtain further information regarding the chemical structure.

Experimental

$(Me_2SnO)_2$–$SnMe_2Cl_2$, by adding pyridine in water, gave Me_2SnO and pyridine hydrochloride. The same products were obtained from Me_2SnO–$SnMe_2Cl_2$ in aqueous and alcoholic solutions. Et_2SnO–$SnMe_2Cl_2$ gave a mixture of Et_2SnO, Me_2SnO and pyridine hydrochloride.

However, Me_2SnO–$SnMe_2Cl_2$,[3)] Et_2SnO–$SnMe_2Cl_2$[1)] and n-Bu_2SnO–$SnMe_2Cl_2$,[1)] in benzene or petroleum ether, gave the pyridine complex. This compound was identical with Me_2SnCl_2–$2NC_5H_5$ obtained from Me_2SnCl_2 and pyridine in benzene, which was confirmed by comparison of both infrared spectra shown in Fig. 1 and the melting point (163°C).[4,5,6b)] Et_2SnO–$SnEt_2Cl_2$ reacted with pyridine giving mainly Et_2SnCl_2–$2NC_5H_5$ (1.0 g of the sample gave 0.55 g of crystals, mp 135°C), which was identical with that obtained from Et_2SnCl_2 and two moles of pyridine. This was confirmed by infrared spectrum shown in Fig. 2 and the melting point (135°C).[5)] In the case of n-Bu_2SnO–Sn n-Pr_2Cl_2, n-Pr_2SnCl_2–$2NC_5H_5$ (mp 114°C)[5)] was obtained, on the contrary $H(Et_2SnO)_3OH$–$SnEt_2Cl_2$ was not reacted with pyridine.

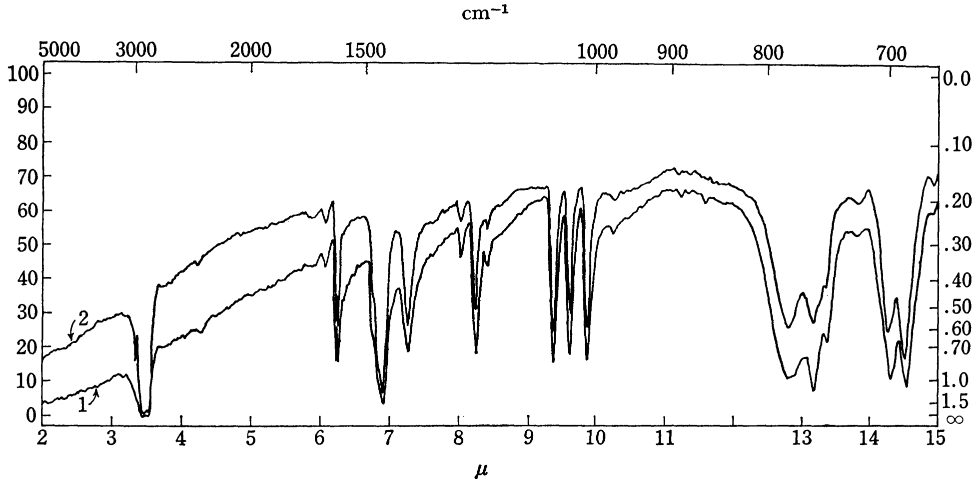

Fig. 1. Infrared spectra of Me_2SnCl_2–$2NC_5H_5$.
1. Obtained from Me_2SnCl_2 and pyridine
2. Obtained from Et_2SnO–$SnMe_2Cl_2$ and pyridine

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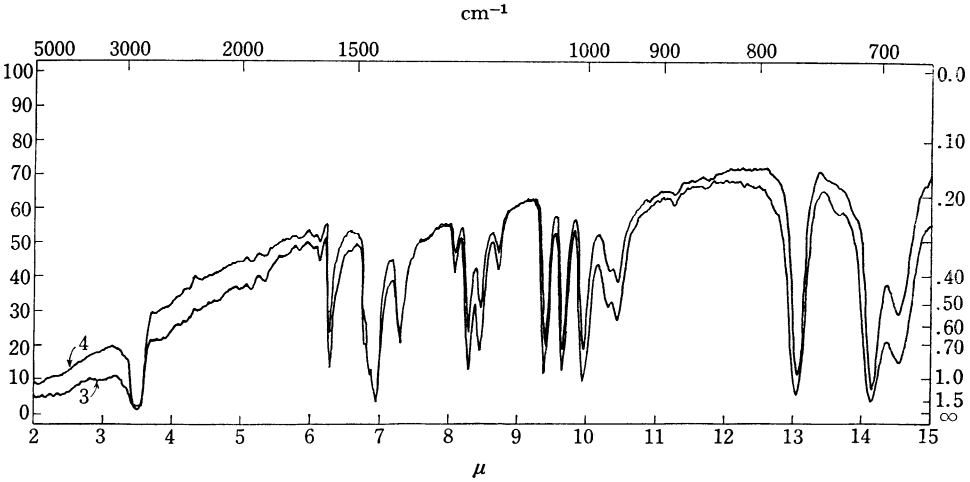

Fig. 2. Infrared spectra of Et_2SnCl_2–$2NC_5H_5$.
3. Obtained from Et_2SnCl_2 and pyridine
4. Obtained from Et_2SnO–$SnEt_2Cl_2$ and pyridine

Results and Discussion

From the results it is concluded that the complex $R'_2SnX_2\cdot 2NC_5H_5$ is formed according to the following reaction.

$$R_2SnO\cdot SnR'_2X_2+2NC_5H_5=R'_2SnX_2\cdot 2NC_5H_5+R_2SnO.$$

This reaction is very important for the investigation of the positions of halogens. The erroneous structure for Et_2SnO–$SnEt_2Cl_2$ in question is a linear structure, $ClEt_2Sn$–O–$SnEt_2Cl$, proposed by Pfeiffer and Brach,[6a] or a dimeric form, proposed by Brown, Okawara and Rochow,[3] and by Okawara and Wada.[7] The former structure should take up two moles of pyridine to form $ClEt_2\underset{\underset{NC_5H_5}{|}}{Sn}\cdots O\cdots \underset{\underset{NC_5H_5}{|}}{Sn}Et_2Cl$, or should not take up any pyridine. The linking $Et_2SnO\cdot Cl_2Et_2SnEtCl_2\begin{smallmatrix}\diagup NC_5H_5\\ \diagdown NC_5H_5\end{smallmatrix}$, *i. e.* 7-coordinated tin, may also be considered, on referring to a typical 7-coordinated tin complex like Et_2SnCl_2–$3NH_3$.[5] However, this is unstable and decomposed into Et_2SnO and Et_2SnCl_2–$2NC_5H_5$. This decomposition can be verified by examining the residue after evaporation of the solvent.

When R_2SnO–SnR_2X_2 was treated by H_2S in acetone,[8] R_2SnS and R_2SnX_2 were formed, instead of the expected XR_2Sn–S–SnR_2X. R_2SnS was trimeric[9] in benzene and naphthalene. R_2Sn and R'_2SnO were formed, when R_2SnO–SnR'_2X_2 was treated with liquid ammonia-sodium.[1] The result for the mixed type compound does not contribute so much to the determination of the chemical structure, since it seems that the state of mobile halogens and the unbalanced bond energy exist between R_2Sn and R'_2Sn, when oxygen is located at the center. However, even in the case of $R=R'$ such as Et_2SnO–$SnEt_2Cl_2$, a similar result is also obtained, yielding Et_2SnCl_2–$2NC_5N_5$ (mp 135°C).

Regarding the question whether these mixed type complexes are monomeric or polymeric in the solid state, the complexes of the lower members of alkyls (R=Me and Et) do not show the infrared band around 400 cm^{-1} which is attributed to the ring $(Sn$–$O)_n$ skeletal mode.[10] Thus they may be in a monomeric form, which is in agreement with the molecular weight determination in benzene and naphthalene.[1]

Alleston *et al.*[11] found two kinds of tin by NMR spectrum in chloroform, but not in the solid state. In benzene Et_2SnO–$SnEt_2Br_2$ takes a monomeric or a polymeric form depending upon its concentration; a monomeric form in a higher concentration and a polymeric from in a lower concentration. On the contrary, Me_2SnO–$SnMe_2$-$(OAc)_2$[2] indicates the reverse tendency. This complex shows the ring $(Sn$–$O)_n$ band.[1]

Such an extraordinary result in molecular weight is not rare in electrolytic complex compounds.[1,12]

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Thus the question has not been settled only by means of molecular weight determination. If the formation of the compounds $R_2SnO\text{-}SnR'_2X_2$[1,13] and $R_2SnO\text{-}SnR_2X_2$ is considered as a result of the pyridine complex formation, the structure of the compound in question should take $Et_2SnO\cdot SnEt_2X_2$ linking (or less probably its polymer), rather than $XEt_2Sn\text{-}O\text{-}SnEt_2X$ (or its polymer). On the other hand, the compound $R^\circ(R_2SnO)_3\text{-}OR^\circ\text{-}SnR'_2X_2$ (R°=alkyl of solvent alcohol or H of water)[1] takes the form $R^\circ OR_2Sn\text{-}O\left\langle\begin{matrix}SnR_2\\SnR'_2X_2\end{matrix}\right\rangle O\text{-}SnR_2OR^\circ$ at first, and then gradually turns to a stable form $R^\circ OR_2Sn\text{-}O\left\langle\begin{matrix}SnR_2X\\SnR_2'X\end{matrix}\right\rangle O\text{-}SnR_2OR^\circ$ by the migration of one of the halogens, since this type compound does not yield the pyridine complex but indicates free OH stretching band[14] in the case (R°=H).

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