Organotin Compounds of the $R_2SnO{\cdot}SnR'_2X_2$ and $H(R_2SnO)_3OH{\cdot}SnR'_2X_2$ Mixed Types

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The characteristic nature of R_3SnX, *i. e.,* its property of combining with one or two R_3SnOH and forming $R_3SnOH{\cdot}SnR_3X$ or $(R_3SnOH)_2{\cdot}SnR_3X$,[1,2] was found first; for it 5 or 6 coordination bond linkings were first introduced to organotin chemistry by the present author.[3-6] Then this conception is extended to the formation of many complexes of the type $R_2SnO{\cdot}SnR_2X_2$[*1] (I) and $H(R_2SnO)_3OH{\cdot}SnR_2X_2$(II) types and, further, to the mixed-type compound:[7] $R_2SnO{\cdot}SnR'_2X_2$ (III) and $H(R_2SnO)_3OH{\cdot}SnR'_2X_2$ (IV), and also $(Me_2SnO)_2{\cdot}SnMe_2Cl_2$ (V), in which the (Sn-O)$_2$ ring is present.[3,5] Recently, Rochow *et al.*[8] proposed a dimeric conception for I; then Okawara[9-11] proposed one for the compound of the I type where $X{=}OSiMe_3$ and the II type. The existence of III and IV, therefore, is very important in checking whether or not I, II, and V can be formulated by the dimeric hypothesis. The present investigation was carried out again with some new compounds of the R_2SnO and R'_2SnX_3 types, and of $3R_2SnO$ and R'_2SnX_2 compounds in the R°OH (R°=alkyl) solvent.

Experimental

Preparations. 1) n-$Pr_2SnO{\cdot}SnEt_2Br_2$[7] prepared by fusion. Both Et_2SnO and n-Pr_2SnBr_2, as well as n-Pr_2SnO and Et_2SnBr_2, in an exact mole ratio of 1 : 1, were fused at 110°C under exactly the same conditions; a melting point of 102—103°C was thus obtained for the former (A) and one of 104—105°C when crystallized from n-butyl alcohol, but the latter (B) gave a melting point of 83—84°C, which, upon its crystallization from the alcohol, was elevated to (87→93→97) 101°C. These two substances, A and B, are the same; *i. e.,* they gave the same amount of n-Pr_2Sn upon reduction with the Na-equivalent to Br_2 in liquid ammonia.[12] The process will be described later.

Other compounds of a similar type, 2) $Et_2SnO{\cdot}SnMe_2Cl_2$, 3) n-$Bu_2SnO{\cdot}Sn$$n$-$Pr_2Cl_2$, and 4) n-$Bu_2SnO{\cdot}SnMe_2Cl_2$, were also prepared.

The results of the analysis of the halogen contents, and the melting points or decomposition points are gives in Table 1. It is interesting to note here that n-$Bu_2SnO{\cdot}SnMe_2Cl_2$ (or this composition) could not be obtained by the action of n-Bu_2SnCl_2 on Me_2SnO as the case of n-Bu_2SnCl_2 on Et_2SnO.

Molecular Weight. The molecular weight of this mixed-type compound was not determined, but those of $Et_2SnO{\cdot}SnEt_2Br_2$ with higher concentrations in freezing benzene were obtained as 763, 900, and 947 at 5.000, 4.000, and 3.240 (by weight %) respectively. As has been shown above, the molecular weight decreases with the concentration or increases with the dilution (just as with n-$Bu_2SnO{\cdot}Sn$$n$-$Bu_2Br_2$,[13] Et_2SnI_2,[14] $SnCl_4$[14] and tetraalkyl ammonium halides[14]). Therefore, the compound may associate little or not at all at a point of saturation where a crystal sppears. On the other hand, $Me_2SnO{\cdot}SnMe_2(OAc)_2$[7] (which gives the 460 cm^{-1} band) indicates the reversing tendency (as do tetraalkyl ammonium nitrates[14]). Furthermore, the molecular weight of $H(Et_2SnO)_3OH{\cdot}SnEt_2(OAc)_2$[8] increases rapidly with the lapse of time, tripling in weight. Indeed, none of the halogen compounds in question except n-$Bu_2SnO{\cdot}Sn$$n$-$Pr_2Cl_2$ (Table 2) show the ring (Sn-O)$_n$ band[15] in the infrared spectrum. Therefore, there remains some uncertainty in determining whether they are in a monomer form or in a dimer on the base of these data only.[*1]

$(Me_2SnO)_2{\cdot}SnMe_2Cl_2$. The electric conductivity of this compound, formed between $(Me_2SnO)_2$ and Me_2SnCl_2, was measured. From the results (Table 3), the compound may be considered to be $[(Me_2SnO)_2{\cdot}SnMe_2]Cl_2$, since there are three ions and it gives an infrared 467 cm^{-1} ring band.[15] It is insoluble in organic solvent, Therefore, the molecular weight was not determined.

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2) T. Harada, This Bulletin, **14**, 472 (1939).

3) T. Harada, *Sci. Paps. I. P. C. R.,* **35**, 290 (1939).

4) *Ibid.,* **36**, 504 (1939).

5) *Ibid.,* **38**, 146 (1940).

6) *Ibid.,* **57**, 25 (1963).

[*1] To determine the location of the halogens and to determine whether the monomeric or dimeric structure is correct for the $Me_2SnO{\cdot}SnMe_2Cl_2$ and $Et_2SnO{\cdot}SnEt_2Br_2$-type compounds, some researchers (including the present author) of the Institute of Physical and Chemical Research are making X-ray analyses under the guidance of Professor Yoshihiko Saito of the Institute of Solid State Physics, The University of Tokyo.

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8) M. P. Brown, R. Okawara and E. G. Rochow, *Spectrochim. Acta,* **16**, 595 (1960).

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11) R. Okawara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.),* **86**, 543 (1965).

12) T. Harada, This Bulletin, **4**, 266 (1929).

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TABLE 1. PREPARED COMPOUNDS (IN THE REACTION RATIO: $1 \leq 1$)

Solvent	Reaction product	Found (Calcd)			Mp or dp °C	Yield %
		Halogen, %	C, %	H, %		
i-PrOH	$Et_2SnO \cdot SnMe_2Cl_2$	17.28(17.20)	17.21(17.46)	3.91(3.80)	191—192	
	$Me_2SnO \cdot SnEt_2Cl_2$*	17.09(17.20)	17.72(17.46)	3.82(3.80)	181—182	
	(By boiling in water these gave $H(Et_2SnO)_3OH \cdot SnEt_2Cl_2$ and insub. subs.)					
n-BuOH	$n\text{-}Pr_2SnO \cdot SnEt_2Br_2$	28.78(28.67)	21.65(21.53)	4.39(4.34)	104—105	
	$Et_2SnO \cdot Sn\,n\text{-}Pr_2Br_2$*	28.65(28.67)	21.73(21.53)	4.29(4.34)	101	
i-PrOH	$n\text{-}Bu_2SnO \cdot Sn\,n\text{-}Pr_2Cl_2$	13.50(13.52)	32.21(32.04)	6.04(6.15)	103	90
	$n\text{-}Pr_2SnO \cdot Sn\,n\text{-}Br_2Br_2$*	13.53(13.52)	(32.04)	(6.15)	102	84
i-PrOH then recrysz. by acetone	$n\text{-}Bu_2SnO \cdot SnMe_2Cl_2$	15.17(15.13)	25.66(25.61)	4.97(5.12)	95— 96	50
	(From this mother liquor $n\text{-}Bu_2SnO \cdot Sn\,n\text{-}Bu_2Cl_2$ (10%) was obtained.)					
i-PrOH	$Me_2SnO + n\text{-}Bu_2SnCl_2 \rightarrow$ dispropt. products ($n\text{-}Bu_2SnO \cdot Sn\,n\text{-}Bu_2Cl_2$ and other)					
n-BuOH then, 1 : 1	$H(Et_2SnO)_3OH \cdot SnMe_2I_2$		16.89(16.82)	3.92(3.83)	180—200	
(EtOH : H_2O)	$H(Et_2SnO)_3OH \cdot SnMe_2ClI_2$	8.79(8.69)	20.89(20.59)	5.08(4.69)	221—223	
Water	$(Me_2SnO)_2 \cdot SnMe_2Cl_2$	12.95(12.93)	13.09(13.11)	3.25(3.30)	—	
i-PrOH	$3n\text{-}Bu_2SnO + Me_2SnCl_2 \rightarrow \text{cryst.} \xrightarrow{EtOH/H_2O} H(n\text{-}Bu_2SnO)_3OH \cdot Sn\,n\text{-}Bu_2Cl_2$					
	Anal. for this	6.77(6.64)	36.02(35.97)	6.78(6.98)	120—125**	

* Does not represent the linking nor structure but represent the reactants of R'_2SnO and R_2SnX_2.

** Reported melting point 109—121°C.[10]

TABLE 2. IR BANDS FOUND IN THE REGION 350—800 cm⁻¹ (KBr)

1. $Me_2SnO \cdot SnMe_2(OAc)_2$: 435(vw), 460(s, shp), 620(w), 655(w), 685(w), 784(ms)
2. $H(Et_2SnO)_3OH \cdot SnMe_2I_2$: 360(ms, shld), 410(ms, shld), 434(s), 530(s), 570(s), 630(s), 687(s), 790(s)
3. $H(Et_2SnO)_3OH \cdot SnMe_2Cl_2$: 375(ms), 415(ms), 510(ms), 547(s), 584(s), 650(s), 695(s), 795(m)
4. $(Me_2SnO)_2 \cdot SnMe_2Cl_2$: 467(s), 520(s), 550(s), 576(s), 705(m), 780(s)
5. $Et_2SnO \cdot SnMe_2Cl_2$: 428(?, vw), 503(ms), 527(ms), 560(s), 605(s), 700(m), 800(s)
6. $n\text{-}Bu_2SnO \cdot SnMe_2Cl_2$: 400(?, vw), 425(?, vw), 530(s), 560(s), 610(s), 700(m), 800(ms)
7. $n\text{-}Bu_2SnO \cdot Sn\,n\text{-}Pr_2Cl_2$: 400(m), 420(m), 535(s), 600(s), 687(s), 780(w)
8. $(Me_3SnOH)_2 \cdot SnMe_3I$: 480(s), 520(ms), 553(s), 565(s), 780(s)
9. $(Me_3SnOH)_2 \cdot SnMe_3Cl$: 490(ms), 530(m), 557(ms), 570(?, m, shld), 784(m)

Compounds 1 and 4 prepared in water as solvent in which OH group does not enter in their molecules.

TABLE 3. CONDUCTANCE OF $(Me_2SnO)_2 \cdot SnMe_2Cl_2$ IN WATER AT 25°C (±0.01)

M=0.0001	0.0002	0.0005	0.0010	μ=221.28	208.41	197.45	193.22
C=0.0002	0.0004	0.0010	0.0020	Λ=110.64	104.21	96.78	96.61

M=mol. conc.
C=equiv. conc.
μ=mol. conduc.
Λ=equiv. conduc.

Reduction of $H(Et_2SnO)_3OH \cdot SnMe_2I_2$[6] in Liquid Ammonia. Compound (3.000 g) with the Na-equivalent to I_2 in liquid ammonia gave a 1/3 equivalent of (very roughly) Et_2Sn (0.35 g, free from the Me_2Sn group) upon being freed by 0.5 N HCl - aqueous alcohol (50/50 by volume). On the other hand, $n\text{-}Pr_2SnO \cdot SnEt_2Br_2$ (3.000 g) gave $n\text{-}Pr_2Sn$ (1.0 g, free from the Et_2Sn group), but not $(Cl\,n\text{-}Pr_2Sn)_2$ nor $(ClEt_2Sn)_2$; $Et_2SnO \cdot SnEt_2Br_2$ (6.000 g) gave Et_2Sn (1.8 g) upon a similar treatment. This may be explained as follows:

$$n\text{-}Pr_2SnO \cdot SnEt_2Br_2 \xrightarrow{2Na} n\text{-}Pr_2SnO \cdot SnEt_2$$

$$\longrightarrow n\text{-}Pr_2Sn \cdot OSnEt_2$$

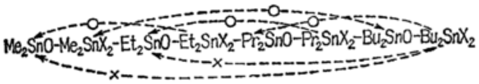
$$(\text{or} \longrightarrow n\text{-}Pr_2Sn + Et_2SnO)$$

$$\xrightarrow{2HCl} n\text{-}Pr_2Sn + Et_2SnCl_2.$$

For $H(Et_2SnO)_3OH \cdot SnMe_2I_2$, the same explanation can be given.

Discussion

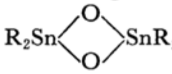
On Formation and Stability. The linking of $R_2SnO\cdot SnR'_2X_2$ where R (*e. g.*, R=*n*-Bu) is larger than R′ (*e. g.*, R′=Me) usually takes place along the model "streaming-down bridge" (*e. g.*, Me_2SnO—Bu_2SnX_2); it is somewhat difficult against the stream ⇢, and it is impossible or very difficult to jump over one or more bridges to the left, as shown below with the arrow (←-⚹--):



where the arrow --⊖-→ in dicates a possibility of linkings, of greater or lesser difficulty, whereas linking ←-⚹-- is impossible or very difficult. In comparison, R_2SnX_2 (R=*n*-Bu) is somewhat organic, whereas R'_2SnX_2 (R′=Me) is of an inorganic nature for solvents, causing the formation of disporportionate products when R_2SnX_2 is subjected to reaction on R'_2SnO. The *n*-$Bu_2SnO\cdot SnMe_2Cl_2$ compound clearly differes from the mixture of *n*-$Bu_2SnO\cdot$Sn*n*-Bu_2Cl_2 and $Me_2SnO\cdot SnMe_2Cl_2$ toward heat; it melts at 95—96°C (clearly or almost clearly) with a mild decomposition above the melting point; it gradually becomes very opaque, perhaps because of the formation of a mixture of the two chlorides, whereas the mixture (in an exact mole ratio of 1 : 1) melts partially at about 102°C, giving two layers (liquid of the former and solid of the latter), leaving the solid of the latter on the bottom of the capillary tube readily. A tendency more or less similar is seen in the case of $Et_2SnO\cdot Me_2Cl_2$. When the compound is heated at or near 140°C under a reduced pressure, it gives pure *n*-Bu_2SnCl_2 (as in the case of *n*-$Bu_2SnO\cdot$Sn*n*-Bu_2Cl_2). Therefore, the change may take as follows:

$$n\text{-}Bu_2SnO\cdot SnMe_2Cl_2 \xrightarrow[\text{heat}]{\text{Partially}} n\text{-}Bu_2SnCl_2 + OSnMe_2,$$

as in the case of the liquid ammonia method described above.

On the Migration of X_2. The oxide having the  [15] skeleton is affected by two molecules of R'_2SnX_2, forming a new structural product, $R_2SnO\cdot SnR'_2X_2$ (which polymerizes[5] loosely in a solvent) at a moderate dilution. In the both X_2's are unstable and, hence, may migrate very mildly from the tin of the larger alkyltin to the tin of the smaller alkyltin; *e. g.*, $Me_2SnO\cdot SnEt_2Cl_2$, $Et_2SnO\cdot$Sn*n*-Pr_2Br_2, and *n*-$Pr_2SnO\cdot$Sn*n*-Bu_2Cl_2, as in the cases of the liquid ammonia treatments, give $Et_2SnO\cdot SnMe_2Cl_2$, *n*-$Pr_2SnO\cdot SnEt_2Br_2$, and *n*-$Bu_2SnO\cdot$Sn*n*-Pr_2Cl_2, respectively. Thus, the two reactions, that between R'_2SnO and R_2SnX_2 and that between R_2SnO and R'_2SnX_2, should give only one compound as the stable product. Therefore, the difference in the melting points of the two products (Table 1) prepared by the two different reactions is due to the degrees of purity. This is shown by X-ray diffraction patterns; *e. g.*, the product (mp 103°C) prepared by the action of *n*-Pr_2SnCl_2 on *n*-Bu_2SnO appeared to be pure, whereas the product (mp 102°C) prepared by the action of *n*-Bu_2SnCl_2 on *n*-Pr_2SnO appeared to be slightly impure. On the other hand, in the reaction between Me_2SnO and *n*-Bu_2SnCl_2 in a solvent, the *n*-Bu_2SnO formed in the migration of X_2 readily combines with the free *n*-Bu_2SnX_2 to form the most stable linking products (disproportionate products). The reaction between *n*-Bu_2SnO and Me_2SnX_2 proceeds fairly normalily, giving *n*-$Bu_2SnO\cdot SnMe_2X_2$. In a very dilute solution, this mixed-type compound, the oxide, and the halogens are freely move, giving a mixture of the most stable compounds. The stability in question, therefore, depends completely on the energy level between R'_2Sn– and –SnR_2 in the linkings.

Mode of Formation. For the formation mechanism of the compounds of the II type, Davies *et al.*[13] Proposed the following hydrolytic mechanism:

$$R_2SnX_2 \rightarrow R_2SnXOH \rightarrow$$
$$XR_2Sn\text{-}O\text{-}SnR_2X \rightarrow XR_2Sn\text{-}O\text{-}SnR_2OH$$

the latter two dimerise readily in non poler solvents. On the other hand, the present author[5,6] has proposed the following mechanism:

$$R_2SnO \xrightarrow[\substack{2R^\circ OH\\ \text{(alcohol)}}]{2HX} R_2SnX_2 \xrightarrow{R_2SnO}$$

$$R_2SnO\cdot SnR_2X_2 \xrightarrow{2R_2SnO} R^\circ(R_2SnO)_3OR^\circ\cdot SnR_2X_2.$$

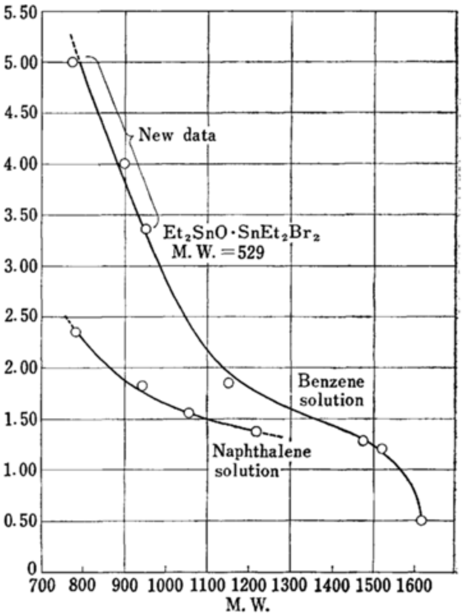
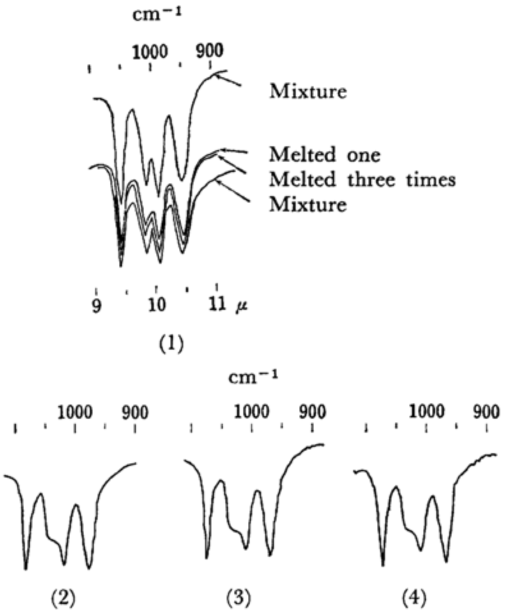


Fig. 1



(1)

(2) (3) (4)

Fig. 2. Infrared spectral bands (Nujol).
(1) Mixture of exact mole ratio (1 : 1) of $Et_2SnO \cdot SnEt_2Br_2$ and n-$Pr_2SnO \cdot Sn$$n$-$Pr_2Br_2$ in powdered states. (2) Crystal obtained from n-Pr_2O and $Et_2 \cdot SnBr_2$ ($1 < 1$) mixture in alcohol, recrystallized. (3) Crystal obtained from exact mole ratio (1 : 1) mixture (Fig. 1) in 99% alcohol. (4) Fused substance of exact mole ratio (1 : 1) mixture of n-Pr_2SnO and Et_2SnBr_2.

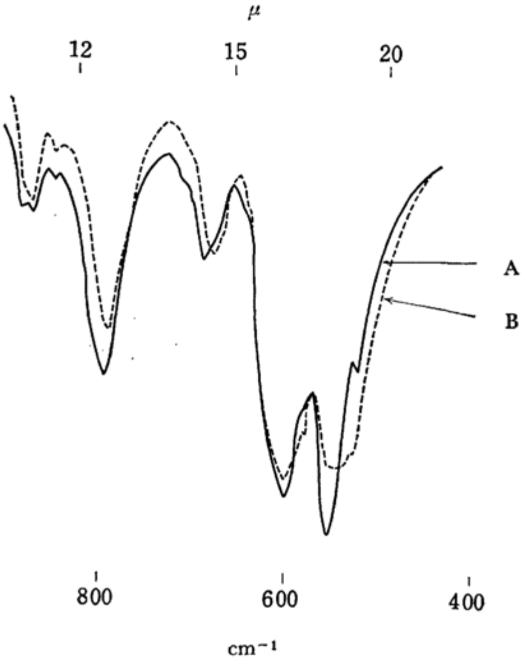


Fig. 3

A: n-$Bu_2SnO \cdot SnMe_2Cl_2$

B: Mixture of n-$Bu_2SnO \cdot Sn$$n$-$Bu_2Cl_2$ and $Me_2SnO \cdot SnMe_2Cl_2$ in exact mole ratio 1 : 1

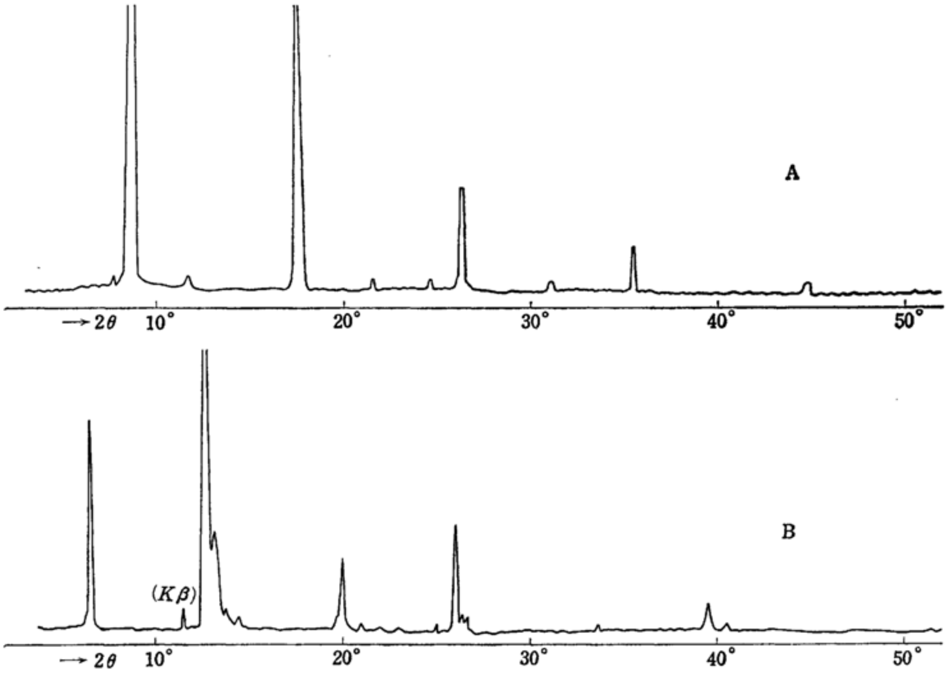
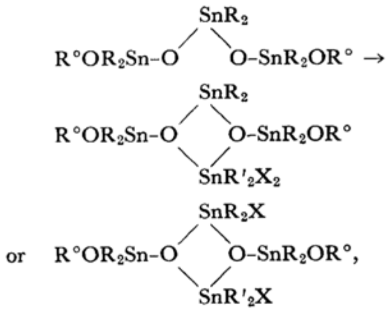


Fig. 4. X-Ray diffraction pattern.

A: n-$Bu_2SnO \cdot MeSnCl_2$ B: $Me_2SnO \cdot Me_2SnCl_2$ - n-$Bu_2SnO \cdot n$-Bu_2SnCl_2 mixture

If we accepted the former mechanism and applied it to mixed type compounds, it should give (XR_2Sn-O-SnR'_2OH). In fact, however, no such compound was formed. However, the latter mechanism accounts for the formation of mixed-type compounds, which can be represented as follows:

$3R_2SnO + R'_2SnX_2 + 2R°OH \rightarrow$



which gives the free OH band[11] in the case of $R°=H$, $R'=R$.

This $>SnR_2X$ linking is possible, but improbable judging from the results of the Na-liquid ammonia treatment and from the formation of R_2SnS and SnR_2X_2 (but not XR_2Sn–S–SnR_2X) upon H_2S treatment; it may differ from the structure of $(Me_3SiOMe_2Sn)_2O$[16] pointed out by Poller *et al.*[17] Very recently Davies *et al.*[18] have prepared several mixed-type compounds, $R_2SnO\cdot SnR'_2Cl_2$, $R_2SnO\cdot SnR'_3Cl$, $R_2SnO\cdot SnCl_4$, *etc.* They reported that the degree of association of these compounds is slight.

On Infrared Spectral Bands. In the region of 800—4000 cm⁻¹, bands of n-$Bu_2SnO\cdot SnMe_2Cl_2$ and a mixture*[2] (in an exact mole ratio of 1 : 1) of the two compounds n-$Bu_2SnO\cdot Sn$$n$-$Bu_2Cl_2$ and $Me_2SnO\cdot SnMe_2Cl_2$ are the same, but in the 400—800 cm⁻¹ region the first compound gives bands at 530, 558, 608, 643, 698, and 780, while the mixture gives a broad band (530—570) and others at 607, 683 and 780. In the case of n-$Pr_2SnO\cdot SnEt_2Br_2$, shoulder bands (Nujol) appear at 995 and 1020, but in the case of a mixture (exact mole ratio of 1 : 1) of n-$Pr_2SnO\cdot Sn$$n$-$Pr_2Br_2$ and $Et_2SnO\cdot SnEt_2Br_2$, there are sharp individual bands at 995 and 1020 cm⁻¹. These are listed in Table 2 and illustrated in Fig. 2. For n-$Pr_2SnO\cdot SnEt_2Br_2$, see Fig. 3.

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[16] Wm. J. Considine, G. A. Baum and R. G. Jones, *J. Organometal Chem.*, **3**, 308 (1965).

[17] R. C. Poller and J. A. Spillmann, *ibid.*, **7**, 259 (1967).

[18] A. G. Davies and P. G. Harrison, *ibid.*, **7**, 13 (1967).

*[2] X-Ray diffraction analysis shows these two substances to be quite different from each other. (Fig. 4A and B) The same is true in the case of n-$Bu_2SnO\cdot Sn$$n$-$Pr_2Cl_2$ (mp 103°C).