Conclusion

Capped trimetal clusters are readily reduced to the corresponding radical anions, but the subsequent electrochemical, kinetic and chemical behavior of the anions depends on the metal composition. Despite the complex electron-transfer processes in some cases this work shows that considerable information on the electronic structure of metal clusters can be obtained from studies of their electron-transfer properties coupled with other spectroscopic data. Further papers will extend this concept to clusters of higher nuclearity.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. H.V. also thanks the Deutsche Forschungsgeminschaft for support of research at Freiburg and Otago. We are also grateful for assistance from the University of Otago for the visits to Dunedin of H.V. and A.M.B.

Registry No. $MeCCo_3(CO)_9$, 13682-04-7; $PhCCo_3(CO)_9$, 13682-03-6; $MeGeCo_3(CO)_9$, 70686-34-9; $PhGeCo_3(CO)_9$, 29998-27-4; $MeCCo_2Cr(CO)_8Cp$, 68185-41-1; $PhCCo_2Cr(CO)_8Cp$, 68185-44-4; $MeCCo_2Mo(CO)_8Cp$, 68185-42-2; $PhCCo_2Mo(CO)_8Cp$, 68185-45-5; $MeCCo_2W(CO)_8Cp$, 68185-43-3; $PhCCo_2W(CO)_8Cp$, 68185-46-6; $MeGeCo_2Mo(CO)_8Cp$, 78793-63-2; $PhGeCo_2Mo(CO)_8Cp$, 78793-62-1; $MePCo_2Fe(CO)_9$, 87160-19-8; $PhPCo_2Fe(CO)_9$, 69569-55-7; $BuPCo_2Fe(CO)_9$, 88131-01-5; $Et_2NPCo_2Fe(CO)_9$, 88131-02-6; $MePCoFeMo(CO)_8Cp$, 87526-93-0; $PhPCoFeMo(CO)_8Cp$, 69569-57-9; t-$BuPCoFeMo(CO)_8Cp$, 87526-94-1; t-$BuPCoFeNi(CO)_6Cp$, 87527-00-2; $PhPCo(CO)_9$, 57143-38-1; $[MeCCo_3(CO)_9]^-$, 61024-79-1; $[PhCCo_3(CO)_9]$, 61024-80-4; $[MeGeCo_3(CO)_9]^-$, 88131-03-7; $[PhGeCo_3(CO)_9]^-$, 88131-04-8; $[MeCCo_2Mo(CO)_8Cp]^-$, 88131-05-9; $[PhCCo_2Mo(CO)_8Cp]^-$, 88131-06-0; $[PhCCo_2W(CO)_8Cp]^-$, 88131-07-1; $[MeGeCo_2Mo(CO)_8Cp]^-$, 88131-08-2; $[PhGeCo_2Mo(CO)_8Cp]^-$, 88131-09-3; $[MePCo_2Fe(CO)_9]^-$, 88131-10-6; $[PhPCo_2Fe(CO)_9]^-$, 71393-16-3; $[PhPCo_3(CO)_9]$, 88156-65-4; $[SCo_2Fe(CO)_9]^-$, 77845-72-8; $[PhCCo_2Cr(CO)_8Cp]^-$, 88131-11-7; $[PhPCoFeMo(CO)_8Cp]^-$, 88131-12-8; $[MePCoFeMo(CO)_8Cp]^-$, 88131-13-9; $[t$-$BuPCoFeNi(CO)_6Cp]^-$, 88156-66-5.

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^{119}Sn NMR Spectroscopic Studies of Organotin Phosphates as Catalysts for the Polymerization of Epoxides

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Various organotin phosphates and pyrophosphates were prepared as model compounds for organotin phosphate catalysts effective for polymerization of epoxides. Pyrolysis of the butyltin compounds thus obtained was conducted with the pure compounds or in the presence of dibutyl phosphate (DBP). ^{119}Sn NMR spectra allowed the characterization of these compounds. It was found that phosphato ligands are easily condensed to give P–O–P linkages and that DBP cleaves Sn–C bonds. Quite interestingly, however, the last butyl group attached to the tin resisted cleavage, and thus monobutyltin compounds resulted as final products in all cases. When an excess of DBP was present, condensation of this compound with pyrophosphato ligands took place. Condensates prepared from di- or tributyltin chlorides and oxides with tributyl phosphate under various reaction conditions also were characterized on the basis of ^{119}Sn NMR spectra. In every case, it was found that the final products are analogous to those derived from model compounds. Polymerization studies of epichlorohydrin by various organotin phosphates and pyrophosphates as model compounds led to the conclusion that the monobutyltin pyrophosphate **11** is associated with an actual active species. On the basis of these results, the nature of organotin phosphate catalysts is discussed.

Introduction

It has been found that condensates obtained by treating organotin halides or oxides with trialkyl phosphates at about 250 °C are highly active catalysts that afford high molecular weight polymers from epoxides.[2] That organotin derivatives show such a high catalytic activity seems quite surprising since the most commonly used catalysts are derived from more acidic metals such as aluminum[3] and zinc.[4] In addition, organotin phosphate catalysts have a practical advantage over organoaluminum and -zinc catalysts in that they can be handled in air. Another feature of organotin catalysts is that they afford polymers of high crystallinity, indicating that the polymerization proceeds highly stereospecifically. Therefore, it appeared to us of great interest to investigate the nature of these catalysts. Since they are presumed to be pyrolysis products of organotin phosphates, preparation and pyrolysis of authentic organotin phosphates would provide useful information. Thus far, studies on organotin phosphates have been rather limited. Ridenour et al. have investigated some di- and triorganotin dialkyl phosphates.[5] More recently, Zuckerman and his co-workers have reported the preparation and characterization of di- and triorganotin diphenyl phosphates.[6]

At the outset of our studies on organotin phosphate catalysts, we prepared various organotin phosphates and pyrophosphates. The pyrolysis products of these compounds were investigated by means of ^{119}Sn NMR spectra in the hope of elucidating the species involved and also the reaction mechanism of pyrolysis.

Moreover, on the basis of these results, condensates prepared from di- or tributyltin chlorides and oxides were

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[1] (a) Okayama University of Science. (b) Osaka Soda Co., Ltd.

[2] Nakata, T. "Coordination Polymerization"; Price, C. C., Vandenberg, E. J., Eds.; Plenum Press: New York, 1983; p 55.

[3] Vandenberg, E. J. *J. Polym. Sci.* **1960**, *47*, 486.

[4] Furukawa, J.; Tsuruta, T.; Sakata, R.; Saegusa, T. *Makromol. Chem.* **1959**, *32*, 90.

[5] Ridenour, R. E.; Flagg, E. E. *J. Organomet. Chem.* **1969**, *16*, 393.

[6] Molloy, K. C.; Nasser, F. A. K.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 1711.

0276-7333/84/2303-0426\$01.50/0

Table I. Analytical Data and Melting Points of Organotin Phosphates

compd	% C found	% C calcd	% H found	% H calcd	mp, °C
$BuSn[OP(O)(OBu)_2]_3$ (1)	41.24	41.85	8.25	7.92	oil
$Bu_2Sn[OP(O)(OBu)_2]_2$ (3)	44.43	44.26	8.85	8.36	269-272
$Me_2Sn[OP(O)(OBu)_2]_2$ (5)	38.31	38.11	7.71	7.48	233-240
$Bu_3SnOP(O)(OBu)_2$ (6)	47.89	48.12	9.49	9.08	oil
$Bu_3SnOP(O)(OMe)_2$ (7)	40.64	40.51	8.28	8.01	oil
$Me_3SnOP(O)(OBu)_2$ (9)	35.10	35.45	7.48	7.32	oil
$Me_3SnOP(O)(OMe)_2$ (10)	20.78	20.80	5.29	5.25	137-142

characterized. Finally, polymerization of epichlorohydrin (ECH) was investigated by using a variety of the pyrolysates thus obtained in the hope that comparison of these results with those of ^{119}Sn NMR spectra should lead to clarification of the actual active species.

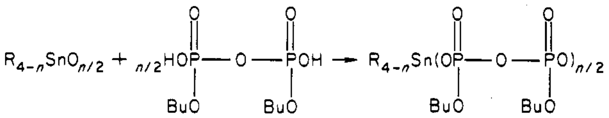
Experimental Section

Commercial organotin chlorides and oxides (products of Nitto Kasei Co. Ltd.) were used as received. Reagent grade dibutyl phosphate (DBP) and tributyl phosphate (TBP) were purified by distillation. Dimethyl phosphate was distilled from a commercially available mixture with monomethyl phosphate. The preparation of *P,P'*-dibutyl pyrophosphate (DBPP) was described in the literature.[7] ECH (product of Osaka Soda Co., Ltd.) was distilled and stored over molecular sieves (4A) as a hexane solution (30 wt/vol %). All solvents were purified by standard methods.

^{1}H NMR spectra were measured with a Hitachi R-24B spectrometer operating at 60 MHz at 35 °C. The measurements of ^{119}Sn FT NMR spectra were run by using a JEOL FX-100 spectrometer operating at 37.08 MHz at 22 °C with complete proton noise decoupling. Field frequency control was made with an external D_2O lock. The chemical shifts ($\delta(^{119}Sn)$) were determined relative to external Me_4Sn, negative signs indicating upfield shifts from the reference. The molecular weight measurements were carried out with a Hitachi Model 115 vapor pressure osmometer in chloroform at 35 °C. The GLC analyses were carried out on a Hitachi 163 gas chromatography equipped with a FID detector using 3 mm × 1 m column packed with Porapak-R.

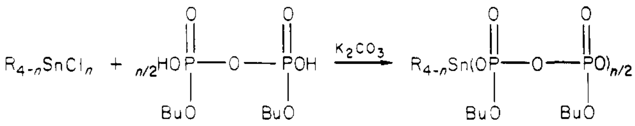
Preparation of Organotin Phosphates and Pyrophosphates. Two methods were developed; one employed organotin oxides (eq 1 and 2) and the other employed organotin chlorides (eq 3 and 4).

$$R_{4-n}SnO_{n/2} + n(BuO)_2P(O)OH \rightarrow R_{4-n}Sn[OP(O)(OBu)_2]_n \quad (1)$$



$$R_{4-n}SnO_{n/2} + {}_{n/2}HO\underset{BuO}{\overset{O}{\overset{\|}{P}}}\text{—}O\text{—}\underset{BuO}{\overset{O}{\overset{\|}{P}}}OH \rightarrow R_{4-n}Sn(O\underset{BuO}{\overset{O}{\overset{\|}{P}}}\text{—}O\text{—}\underset{BuO}{\overset{O}{\overset{\|}{P}}}O)_{n/2} \quad (2)$$

$$R_{4-n}SnCl_n + n(BuO)_2P(O)OH \xrightarrow{K_2CO_3} R_{4-n}Sn[OP(O)(OBu)_2]_n \quad (3)$$



$$R_{4-n}SnCl_n + {}_{n/2}HO\underset{BuO}{\overset{O}{\overset{\|}{P}}}\text{—}O\text{—}\underset{BuO}{\overset{O}{\overset{\|}{P}}}OH \xrightarrow{K_2CO_3} R_{4-n}Sn(O\underset{BuO}{\overset{O}{\overset{\|}{P}}}\text{—}O\text{—}\underset{BuO}{\overset{O}{\overset{\|}{P}}}O)_{n/2} \quad (4)$$

As a typical example of the former method, the procedure for dibutyltin bis(dibutyl phosphate) (**3**) will be described. A benzene suspension (200 mL) containing Bu_2SnO (2.49 g, 10 mmol) and DBP (4.20 g, 20 mmol) was heated at reflux to remove water azeotropically. Bu_2SnO disappeared gradually. After removal of water was complete (5 h), benzene was evaporated to leave a white precipitate that was purified by recrystallization from chloroform–hexane (4.59 g, 70%). The following description to prepare butyltin *sesqui*-(*P,P'*-dibutyl pyrophosphate) (**2**) is typical of the latter method. To an aqueous K_2CO_3 solution (4.14 g/50 mL of H_2O) containing DBPP (4.35 g, 15 mmol) was added $BuSnCl_3$ (2.82 g, 10 mmol) in 30 mL of dichloromethane with vigorous stirring. After the mixture had been stirred for 3 h at room temperature, the dichloromethane layer was separated, washed with water, dried ($MgSO_4$), and evaporated to give an oil (4.99 g, 82%). Either of these methods afforded the same products in 60–95% yields. As shown in Table I, satisfactory elemental analyses were obtained for the phosphates. As for the pyrophosphates, however, analytically pure samples were obtained in no cases due to the difficulty in purification; deviations in combustion analyses from calculated values usually amounted to ±1%. Nevertheless, since ^{1}H NMR spectra were completely consistent with the proposed structures (vide infra), the pyrophosphates obtained were, we believe, pure enough for the purpose of the present study.

Pyrolysis of Organotin Phosphates and Pyrophosphates. Pyrolysis was conducted by using a Kugelrohr distillation apparatus. Organotin compounds, together with varied amount of DBP, if necessary, were heated with gentle rotation at a required temperature. After 2 h, the reaction mixture was cooled to 80 °C and subjected to evaporation with an aspirator at this temperature to remove volatile materials. The products thus obtained that are viscous oils or sticky solids were used for NMR measurements.

Condensation of Butyltin Compounds with TBP. Into a glass reaction tube connected to a distillation apparatus and a gas holder were added organotin compounds and TBP in 1:2 molar ratio. The reaction tube was heated by using a cylindrical aluminum oven, at the center of which was carved a hole to accommodate the tube. When the temperature of the oven reached 200 °C, the reaction tube containing the reactants was inserted into the hole. Then, the oven was heated to the required temperature in 10 min, during which time gases were evolved vigorously. After the temperature of the oven had been fixed, the reaction mixture was heated for the required period. As the reaction proceeded, gas evolution ceased and a colorless liquid distilled. The viscosity of the reaction mixture increased gradually to leave an oil or, in some cases, a porous solid. The products were dissolved in dichloromethane and evaporated to afford samples for NMR measurements. The GLC analysis revealed that gases and distillates contained di-*n*-butyl ether and C_4 hydrocarbons as main components and *n*-butyl chloride also was detected when butyltin chlorides were employed.

Polymerization of ECH. The organotin catlayst (25 mg) in a 50-mL glass ampule was dried by heating at 160 °C under a flow of nitrogen for 30 min. After the ampule was cooled, 20 mL of a hexane solution of ECH (6 g) was injected into the ampule, which then was sealed. The ampule was shaken in a thermostated bath for the required period. The polymers, which generally were obtained as solid precipitates or slurries, were dissolved in hot benzene containing an antioxidant and washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and water. Evaporation and drying in vacuo of the benzene solution yielded pure polymers.

Results and Discussion

Characterization of Organotin Phosphates and Pyrophosphates. The ratio of alkoxy groups attached to phosphorus vs. alkyl groups attached to tin (*r* value) can be easily obtained from ^{1}H NMR spectra for the dimethyl phosphate derivatives **7** and **10**, since in these cases the signals attributable to both groups are fully separated,

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[7] Blackburn, G. M.; Cohen, J. S.; Todd, L. J. *J. Chem. Soc. C* **1966**, 239.

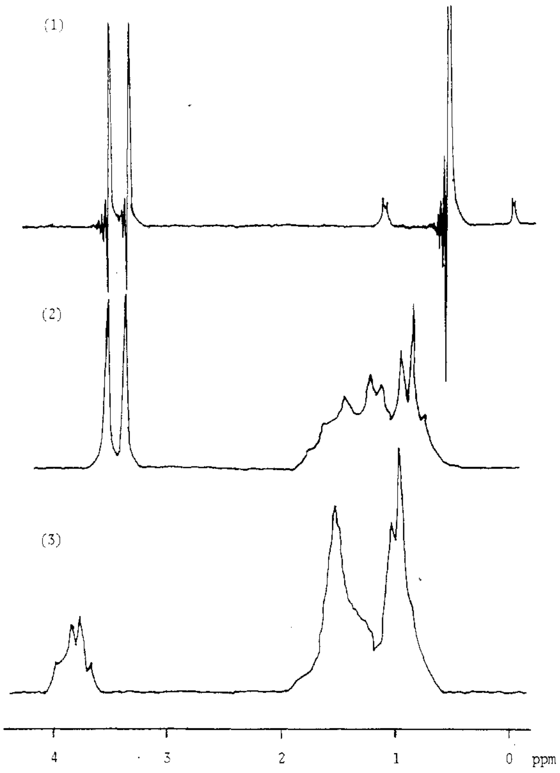


Figure 1. ^1H NMR spectra of organotin phosphates in $CHCl_3$: (1) $Me_3SnOP(O)(OMe)_2$; (2) $Bu_3SnOP(O)(OMe)_2$; (3) $Bu_2Sn[OP(O)(OBu)_2]_2$.

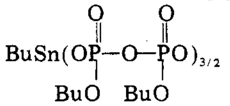
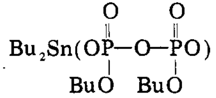
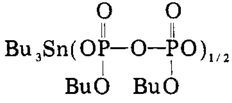
permitting measurement of an accurate integral ratio as shown in Figure 1. For the dibutyl phosphates and *P*,*P'*-dibutyl pyrophosphates, on the other hand, the overlap of signals derived from butoxy groups and alkyl groups attached to tin prevented a direct integration. The *r* values, however, were successfully calculated as follows. As shown in Figure 1, there appears a multiplet due to methylene protons α to oxygen in butoxy groups at 3.85 ppm, while the rest of protons in butoxy groups together with alkyl protons attached to tin give rise to broad signals at normal positions (0.70–1.70 ppm). Provided that the integral ratio of these signals is $a{:}b$, then the *r* values could be calculated as $a/2{:}(b - {}^7/_2a)/9$ for the butyltin derivatives and as $a/2{:}(b - {}^7/_2a)/3$ for the methyltin derivatives. In Table II are summarized the *r* values thus calculated along with the $\delta(^{119}Sn)$ values. Apparently, the *r* values are in complete agreement with the proposed structures.

The values of $\delta(^{119}Sn)$ of mono-, di-, and triorganotin derivatives except **8** fall in reasonable regions for seven-, six-, and five-coordinate alkyltin compounds, respectively,[8] the phosphato or pyrophosphato moieties acting as bidentate chelators.

As shown in Figure 2, molecular weight measurements indicate an unexpected contrast between the monobutyltin compound and other organotin compounds. Since the molecular weights of tri- and diorganotin derivatives are highly concentration dependent, these compounds are involved in equilibria between monomers and associated forms. In contrast, little association was observed for **1** irrespective of concentration, suggesting a discrete seven-coordinate configuration.

It should be noted that the $\delta(^{119}Sn)$ values of the phosphates, in general, lie at higher fields than those of corresponding alkyltin chelates reported thus far.[8] Accordingly, the phosphato ligands coordinate to tin more strongly than any other ligands usually employed such as acetylacetonato, oxinato, and tropolonate. On the other hand, the *P*,*P'*-dibutyl pyrophosphato ligand is much weaker than the phosphato ligands and comparable with oxinato in coordinating ability judging from $\delta(^{119}Sn)$ values. Therefore, the four-coordinate configuration can be suggested for tributyltin derivative **8**, as proposed for tributyltin oxinate.[9] Surprisingly, however, the monobutyltin derivative **2** gave rise to a $\delta(^{119}Sn)$ value analogous

Table II. The *r* Values and $\delta(^{119}Sn)$ of Organotin Phosphates and Pyrophosphates in $CHCl_3$

compd	*r*	$\delta(^{119}Sn)$
$BuSn[OP(O)(OBu)_2]_3$ (1)	6.0	−631, −679
 $BuSn(O\overset{O}{\underset{BuO}{P}}-O-\overset{O}{\underset{BuO}{P}}O)_{3/2}$ (2)	3.0	−632, −679
$Bu_2Sn[OP(O)(OBu)_2]_2$ (3)	2.0	−469
 $Bu_2Sn(O\overset{O}{\underset{BuO}{P}}-O-\overset{O}{\underset{BuO}{P}}O)$ (4)	1.0	−270
$Me_2Sn[OP(O)(OBu)_2]_2$ (5)	2.0	−425
$Bu_3SnOP(O)(OBu)_2$ (6)	0.67	−61
$Bu_3SnOP(O)(OMe)_2$ (7)	0.67	−55
 $Bu_3Sn(O\overset{O}{\underset{BuO}{P}}-O-\overset{O}{\underset{BuO}{P}}O)_{1/2}$ (8)	0.33	+94
$Me_3SnOP(O)(OBu)_2$ (9)	0.67	−39
$Me_3SnOP(O)(OMe)_2$ (10)	0.70	−32

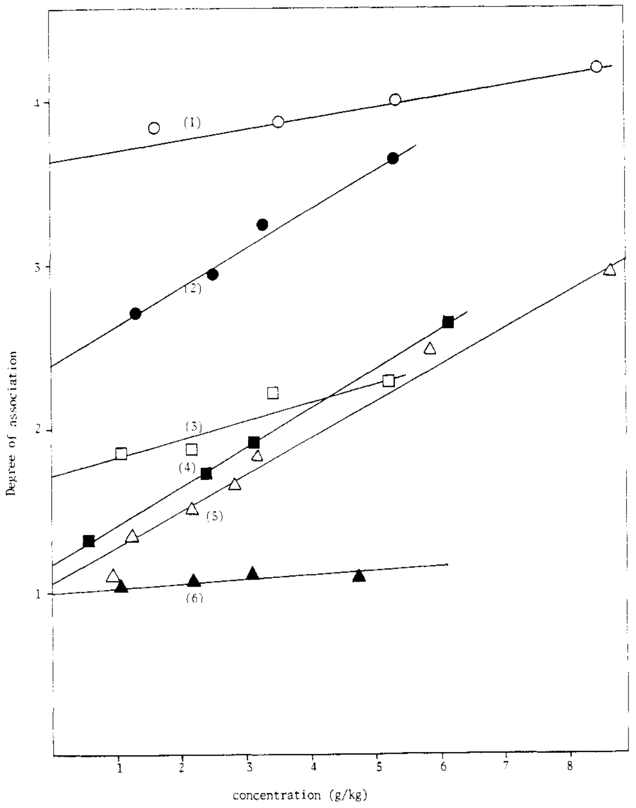


Figure 2. Degree of association of organotin phosphates vs. concentration: (1) $Me_3SnOP(O)(OMe)_2$; (2) $Me_2Sn[OP(O)(OBu)_2]_2$; (3) $Bu_2Sn[OP(O)(OBu)_2]_2$; (4) $Bu_3SnOP(O)(OBu)_2$; (5) $Bu_3SnOP(O)(OMe)_2$; (6) $BuSn[OP(O)(OBu)_2]_3$.

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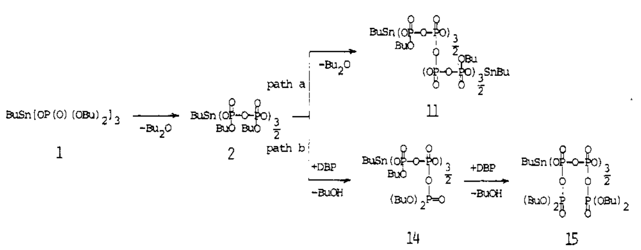
(8) (a) Otera, J. *J. Organomet. Chem.* **1981**, *221*, 57. (b) Otera, J.; Kusaba, A.; Hinoishi, T.; Kawasaki, Y. *Ibid.* **1982**, *228*, 223.

(9) Clark, H. C.; Jain, V. K.; McMahon, I. J. *J. Organomet. Chem.* **1983**, *243*, 299.

Scheme I



Scheme II

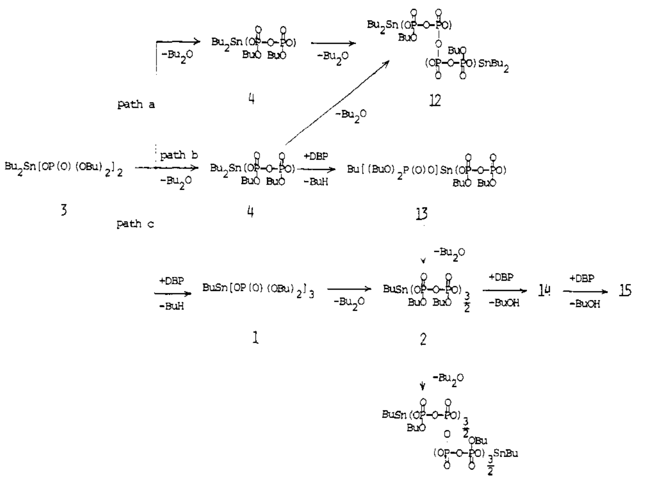
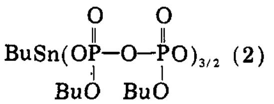
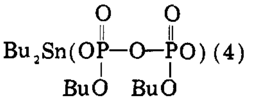
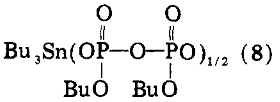
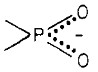


Table III. The r Values and $\delta(^{119}Sn)$ of Pyrolysates in $CHCl_3$

entry		DBP added[a]	r	$\delta(^{119}Sn)$
1	$BuSn[OP(O)(OBu)_2]_3$ (1)	0	3.9	-679
2		1	3.4	-672
3		2	4.7	-672
4		3	6.2	-665
5	 $BuSn(O\underset{BuO}{\overset{O}{\overset{\|}{P}}}-O-\underset{BuO}{\overset{O}{\overset{\|}{P}}}O)_{3/2}$ (2)	0	1.6	-679
6		1	3.7	-673
7		2	5.1	-673
8		3	6.1	-665
9	$Bu_2Sn[OP(O)(OBu)_2]_2$ (3)	0	1.6	-263, -469
10		1	2.0	-265, -679
11		2	3.6	-671
12		3	5.3	-673
13		4	6.3	-665
14	 $Bu_2Sn(O\underset{BuO}{\overset{O}{\overset{\|}{P}}}-O-\underset{BuO}{\overset{O}{\overset{\|}{P}}}O)$ (4)	0	0.7	-261
15		1	2.5	-679
16		2	3.6	-673
17		3	4.7	-673
18		4	6.6	-665
19	$Bu_3SnOP(O)(OBu)_2$ (6)	0	0.9	-259
20		1	1.2	-263, -679
21		2	1.6	-670
22		3	3.5	-670
23		4	5.4	-673
24		5	6.2	-665
25	 $Bu_3Sn(O\underset{BuO}{\overset{O}{\overset{\|}{P}}}-O-\underset{BuO}{\overset{O}{\overset{\|}{P}}}O)_{1/2}$ (8)	0	0.5	-263

[a] Molar equiv/organotin compounds.

to that of the corresponding dibutyl phosphate 1, indicative of a seven-coordinate structure. The results of this NMR spectrum along with the molecular weight measurement for 1 strongly suggest that there exists enhanced affinity of a monobutyltin moiety for a



chelate. As a result, no equilibration between intra- and intermolecular chelation is involved and an unusual configurational stability of the seven-coordinate species seems to obtain.

Pyrolysis of Organotin Phosphates and Pyrophosphates. Since the most common organotin phosphate catalysts are obtained from butyltin chlorides or oxides and TBP, butyltin phosphates were selected as model compounds. Although catalysts are usually prepared at about 250 °C, the present pyrolysis was conducted at lower temperatures (170–190 °C) in order to detect the intermediate species.

The values of r and $\delta(^{119}Sn)$[10] of the pyrolysis product are given in Table III. When pyrolysis was carried out with the pure compounds, a marked contrast was found between mono- or dibutyltin derivatives 1 or 3 and the tributyltin compound 6. Pyrolysis of the former two compounds resulted in a decrease of the r values (entries 1 and 9), which can be explained by the condensation of butoxy groups to yield the pyrophosphato structure (path a in Schemes I and II). In accord with this, ^{119}Sn NMR spectrum of the pyrolysate of 3 exhibited a new signal at −263 ppm in addition to that of unreacted 3 (−469 ppm). It should be noted that $\delta(^{119}Sn)$ of the new signal appeared close to but not consistent with that of 4. This is ascribed to the concomitant condensation of butoxy groups of the resulting pyrophosphate 4 to afford 12. To confirm this postulate, 4 was separately subjected to pyrolysis, which resulted in a decrease of the r value and induced a new signal at −261 ppm in the product (entry 14).[11] Analogously, it is reasonably assumed that the monobutyltin compound 1 afforded pyrophosphate 11 (entry 1) as shown in Scheme I. The results of entry 5 give supporting evidence for this postulate.

On pyrolysis of 6, the r value was increased and $\delta(^{119}Sn)$ appeared at the region of the dibutyltin pyrophosphate (entry 19). The path a in Scheme III provides a reasonable explanation for these NMR spectral data. Initial formation of 8 as an unisolable intermediate was supported by the separate pyrolysis of 8, which gave consistent NMR results (entry 25). Furthermore, it is in agreement with this mechanism that the formation of Bu_4Sn was observed in the distillate of this reaction.

Next, pyrolysis in the presence of DBP was investigated. As the amount of DBP added to 1 was increased, the r values of the pyrolysates were increased (entries 2–4). This is rationalized by assuming the condensation of DBP with pyrophosphato moieties of resulting 2 to afford 14 (Scheme I). In line with this, a large amount of n-butyl alcohol was detected by GLC analysis of the volatile components of the pyrolysis. The signal around −670 to −673 ppm is therefore attributable to 14. Employment of 3 molar equiv of DBP resulted in the formation of a new species (−665 ppm) whose r value is 6.2. This is in accord with 15 which

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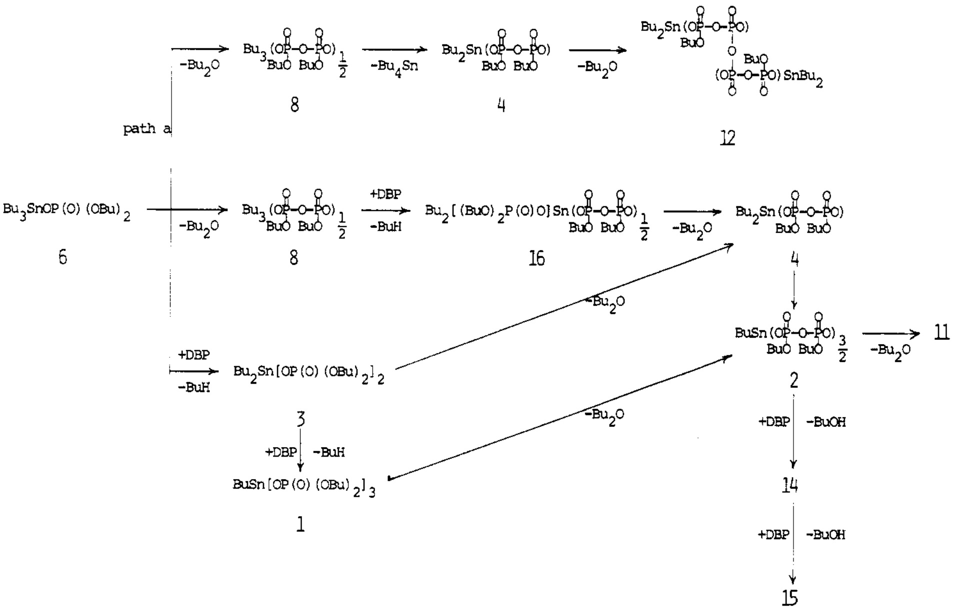
[10] ^{119}Sn NMR spectra of pyrolysates exhibited broad signals since these compounds, as expected, consist of not a single species but various associates and condensates. Therefore, the $\delta(^{119}Sn)$ values should be considered to correspond to a major species involved or to represent the statistical average of those derived from the species involved.

[11] The observed r value (0.7) is somewhat larger than the calculated one for 12 (0.5). This seems to be due to contamination by 4. The ^{119}Sn NMR signal due to 4, which should appear at −270 ppm, might be included in the relatively broad signal of 12.

Scheme III



was produced by further condensation of DBP with **14**. It is noteworthy that as the degree of condensation of DBP with the pyrophosphato moieties is increased, $\delta(^{119}Sn)$ of the condensates moves downfield. A slight change of the coordination mode is induced by introduction of bulky dibutyl phosphato groups, resulting in the weakening of coordination of pyrophosphato ligands.

When 1 molar equiv DBP was added to **3** (entry 10), the ^{119}Sn NMR spectrum of the product exhibited two signals at −265 and −679 ppm, respectively. As shown in Scheme II, the former can be assigned to **12**, while the latter to **11** which has been produced from monobutyltin compound **1** as described already. It is thus apparent that the butyl groups attached to tin were replaced by a dibutyl phosphato group. Two pathways (path b and c) are probable for the formation of **11**. According to path b, **3** is condensed to give **4**, a part of which is further condensed to give **12**. The rest of **4** is subjected to reaction with DBP, by which a butyl group is cleaved to afford an intermediate monobutyltin compound **13**. Condensation of the phosphato group of **13** gives **2** and finally **11**. Another route (path c) involves an initial attack of DBP on **3** to give **1**, which is converted into **2** and **11** by the stepwise condensation of butoxy groups. GLC analysis demonstrated formation of di-*n*-butyl ether as well as of *n*-butane at the initial stages of pyrolysis, a result which suggests that both reactions (paths b and c) take place in parallel. When the amount of added DBP was increased (entries 11–13), stepwise formation of **14** and **15** resulted as described for **1**.

Pyrolysis of the tributyltin compound **6** in the presence of DBP (entries 20–24) can be explained quite analogously as shown in Scheme III. It is reasonable that one more equivalent of DBP is required to give the same results with those of **3** since 2 molar equiv of DBP was consumed for cleavage of two of the butyl groups attached to tin.

That the pyrophosphates are formed as intermediates in all of these mechanisms is supported by pyrolysis of the isolated pyrophosphates which afforded completely consistent results.

In summary, pyrolysis of all butyltin phosphates is explained by analogous mechanisms. The initial reaction involves condensation of butoxy groups to give P–O–P linkages. In the pyrolysis of di- and tributyltin derivatives, cleavage of butyl groups by DBP may also occur to some extent. Although such a facile cleavage of butyl groups seems rather unexpected, it should be stressed that the last butyl group was never replaced. Accordingly, when an excess of DBP was employed, the same final product was obtained from any type of butyltin derivative.

Table IV. $\delta(^{119}Sn)$ Values of Condensates Prepared from Butyltin Compounds and TBP under Various Reaction Conditions in $CHCl_3$

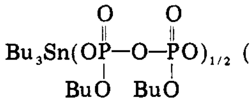
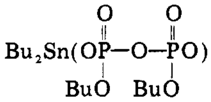
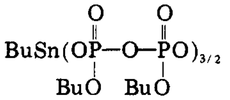
		reaction		
entry	butyltin compd	temp, °C	time,[a] min	$\delta(^{119}Sn)$
1	Bu_2SnCl_2	240	10	−265
2		240	30	−264
3		260	10	−263
4		260	15	−263, −676
5		260	20	−263, −676
6	Bu_3SnCl	250	0	−49
7		250	30	−57, −263
8		250	45	−263, −640, −679
9		250	60	−263, −676
10	Bu_2SnO	260	0	−58, −255
11		260	5	−56, −255
12		260	10	−263, −637, −673
13		260	15	−262, −633, −668

[a] Reaction time after the temperature of the oven was fixed at a required temperature (see Experimental Section).

Characterization of Condensates of Butyltin Compounds with TBP. Di- or tributyltin chlorides and oxides were treated with TBP under various reaction conditions. The $\delta(^{119}Sn)$ values of the condensates thus obtained are summarized in Table IV. It is apparent that the reaction proceeds quite analogously to those of the model compounds to afford monobutyltin species as final products.

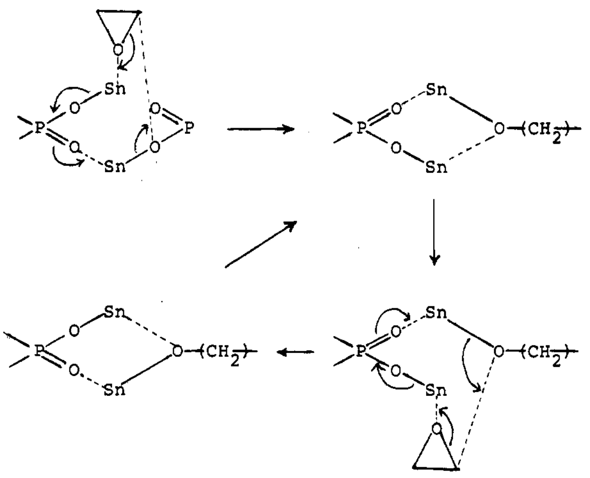
Polymerization of ECH. Polymerization of ECH by pyrolysates of various types of organotin phosphates and pyrophosphates was conducted in hexane at 50 °C for 3 h. In the cases where polymer yields had been low under these conditions, polymerization was separately run for a prolonged period at 21 °C. The results are summarized in Table V. None of tri- and dibutyltin compounds showed catalytic activity without pyrolysis (entries 1, 4, 11, and 12), whereas monobutyltin compounds gave low yields of high polymers even without thermal hysteresis (entries 8 and 15). Throughout these results, the most

Table V. Polymerization of ECH by Various Butyltin Phosphate Catalysts

		conditns for pyrolysis			polymer yield, %	
entry	butyltin compound	DBP added[a]	temp, °C	δ(^{119}Sn)	A[b]	B[c]
1	$Bu_3SnOP(O)(OBu)_2$ (6)	[d]		−61	0	
2		2	190	−670	0	4 (6 h)
3		4	190	−665	0	
4	$Bu_2Sn[OP(O)(OBu)_2]_2$ (3)	[d]		−469	0	
5		0	180	−263, −460	3	36 (15 day)
6		1	180	−265, −679	70	
7		4	180	−665	3	58 (15 day)
8	$BuSn[OP(O)(OBu)_2]_3$ (1)	[d]		−631, −679	2	5 (17 h)
9		0	170	−679	60	
10		3	170	−667	3	74 (15 day)
11	 $\mathrm{Bu_3Sn(O\underset{BuO}{\overset{O}{P}}-O-\underset{BuO}{\overset{O}{P}}O)_{1/2}}$ (8)	[d]		+94	0	
12	 $\mathrm{Bu_2Sn(O\underset{BuO}{\overset{O}{P}}-O-\underset{BuO}{\overset{O}{P}}O)}$ (4)	[d]		−270	0	0 (22 h)
13		0	190	−261	0	10 (22 h)
14		1	190	−679	57	
15	 $\mathrm{BuSn(O\underset{BuO}{\overset{O}{P}}-O-\underset{BuO}{\overset{O}{P}}O)_{3/2}}$ (2)	[d]		−632, −679	8	
16		0	170	−679	23	
17		1	170	−673	2	

[a] Molar ratio/butyltin compound. [b] Polymerization conditions: 50 °C, 3 h. [c] Polymerization conditions: 21 °C; reaction time is indicated in parentheses. [d] A raw compound was employed without pyrolysis.

Scheme IV



characteristic feature is that the catalytic activity depends dramatically on the pyrolysis conditions. The pyrolysates involving 11 (−679 ppm) as a main species gave rise to the maximum activity (entries 6, 9, 14, and 16), though others afforded only slight yields. It should be noted that the catalysts prepared from butyltin chlorides or oxides and TBP give similar results (65% yield at 50 °C for 3 h). As already described in the former section, these catalysts also involve 11 as one of the main components. Accordingly, the pyrophosphates 11 can be reasonably associated with an actual active species.

For the polymerization of epoxides by organozinc and -aluminum catalysts, polymetallic aggregates are known to be the active species.[3,4] As for organotin phosphate catalysts, a polymetallic mechanism as shown in Scheme IV has been suggested by Nakata.[2] This mechanism requires proximate location of tin atoms. Organotin phosphates or pyrophosphates are, in general, associated to some extent, thus satisfying this requirement. However, condensation of bulky DBP with a pyrophosphato moiety to afford 14 and 15 would result in a weakening of the association, which is unfavorable for aggregation of tin atoms. On the other hand, tin atoms are closely situated in compounds 12 and 11, in which pyrophosphato moieties are linked through condensation of butoxy groups. It seems more important that formation of the P–O–P linkages provides a rigid reaction field on which a stereoregular propagation proceeds. Despite the existence of similar P–O–P linkages, 12 is much less active than 11. Although the reason for this difference is not clear, two explanations may be put forth. First, the Lewis acidity of tin in the monobutyltin compound 11 is greater than that in the dibutyltin compound 12. That this effect is not negligible is suggested by a slight activity exerted by 1 and 2 without pyrolysis. Next, the pyrophosphato network is more rigid in 11 than 12 because three pyrophosphato ligands coordinate to tin in 11 giving rise to a seven-coordinate tin, while two pyrophosphato ligands coordinate to tin in 12. This may be consistent with unusual configurational stability of a seven-coordinate monobutyltin moiety as suggested for 1 and 2. Since formation of the rigid reaction field appropriate for coordination of monomers as well as a stereoregular propagation is of prime importance, there seems to be formed a unique reaction field in 11.

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Registry No. 1, 88158-33-2; 2, 88158-34-3; 3, 85128-65-0; 4, 88179-94-6; 5, 88158-35-4; 6, 29105-78-0; 7, 28089-28-3; 8, 88158-36-5; 9, 88158-37-6; 10, 88158-38-7; Bu_2SnCl_2, 683-18-1; Bu_3SnCl, 1461-22-9; Bu_2SnO, 818-08-6; $BuSnCl_3$, 1118-46-3; ECH, 106-89-8; DBP, 107-66-4; TBP, 126-73-8; DBPP, 69537-43-5; dimethyl phosphate, 813-78-5.