

Studies on alkoxy complexes of alkyltin (IV) in non-aqueous solvents

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Abstract. Visual, conducto- and potentiometric titrations of mono-, di- and tri-alkyltin (IV) chlorides with alkali metal alkoxides have been carried out in anhydrous non-aqueous solvents. Evidence for the formation of a number of species of the type $M[(R'Sn)_2(OR)_n]$, $R'_nSn(OR)_{4-n}$ and $[(R'Sn)_2(OR)_3]Cl_3$ (where $M=Na$ or K ; $R'=Me, Et$ or Bu ; $R=Me, Et$ or Pr^i ; $n=1, 2$ or 3) has been obtained. Di- and tri-alkyltin (IV) moieties appear to have a negligible tendency to form double alkoxides with alkali metals.

Keywords. Alkyltin (IV) species; alkoxy complexes; non-aqueous solvents.

1. Introduction

The existence of a number of alkoxy complexes of aluminium (III), gallium (III), tin(IV), zirconium(IV), hafnium(IV), niobium(V) and tantalum(V) in non-aqueous solvents has been established (Mehrotra and Agrawal 1967; Mehrotra *et al* 1968; Mehrotra and Mehrotra 1972; Jain *et al* 1976a; Jain *et al* 1976b; Mehrotra *et al* 1978) using visual, conducto- and potentiometric titrimetric techniques. However, no attempt has been made till now to investigate the formation of alkoxy complexes of alkyltin(IV). It was, therefore, considered worthwhile to investigate the possibility of formation of alkoxy complexes of alkyltin(IV). For this purpose, titrations of alkyltin(IV) chlorides with alkali metal alkoxides have been carried out in non-aqueous solvents using visual indicators as well as by conductometric and potentiometric end points.

2. Experimental

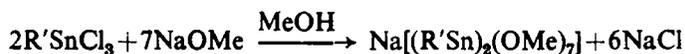
All titrations were carried out in a dry box under anhydrous condition.

Alkyltin chlorides (M and T Chemicals) were purified by distillation or sublimation. Potassium chloride (AR), freshly cut sodium (BDH) and potassium (Riedel) metals were used. Dimethyltin diisopropoxide was prepared by the reaction of Me_2SnCl_2 with $NaOPr^i$ in 1:2 molar ratio. It was purified by sublimation at 130-135°C/6 mm. Methanol, ethanol, isopropanol, benzene and acetonitrile (BDH) were dried by standard methods. All indicators were used in the solid form. Conductivity bridge (RLC Tesla) and pH-meter (Radiometer) were used (Jain *et al* 1976).

3. Results and discussion

3.1. Studies on alkoxy complexes of monoalkyltin(IV)

3.1.1. *Visual indicator studies:* Titrations of monoalkyltin chlorides with sodium methoxide in methanol using an alkaline range indicator (e.g., thymolphthalein, phenolphthalein or m-cresol purple) reveal the formation of double methoxide of the type $\text{Na}[(\text{R}'\text{Sn})_2(\text{OMe})_7]$. A similar type of species, $\text{Na}[\text{Sn}_2(\text{OMe})_9]$, has been reported earlier (Jain *et al* 1976). The data presented in table 1 indicate that the species formed $\text{Na}[(\text{R}'\text{Sn})_2(\text{OMe})_7]$, during the course of these reactions depict a weak tendency of dissociation resulting in the end point being observed at ~ 3.4 moles in place of 3.5 moles of sodium methoxide:

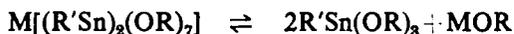


(where $\text{R}' = \text{Et}$ or Bu).

Table 1. Titrations of alkyltin (IV) chlorides with alkali metal alkoxides.

Alkyltin chloride in 25 ml solvent		Indicator used			MOR			Molar ratio MOR alkyltin chloride	Species detected and Remarks, if any
Alkyltin chloride (g)	Solvent		M	R	Nor-mality	Req. (ml)	Calc. (ml)		
EtSnCl_3 (0.2633)	MeOH	Thymolphthalein	Na	Me	0.8813	4.00	4.12	3.40	$\text{Na}[(\text{EtSn})_2(\text{OMe})_7]$
BuSnCl_3 (0.5727)	MeOH	„	Na	Me	0.8813	7.90	8.07	3.43	$\text{Na}[(\text{BuSn})_2(\text{OMe})_7]$
BuSnCl_3 (0.5413)	MeOH	Phenolphthalein	Na	Me	1.0048	6.50	6.68	3.41	-do-
BuSnCl_3 (0.2688)	MeOH	m-cresol purple	Na	Me	0.7838	4.15	4.26	3.41	-do-
EtSnCl_3 (0.2704)	EtOH	Thymolphthalein	Na	Et	0.7889	4.35	4.71	3.22	$\text{Na}[(\text{EtSn})_2(\text{OEt})_7] \rightleftharpoons \text{NaOEt} + 2\text{EtSn}(\text{OEt})_3$
EtSnCl_3 (0.3892)	Benzene	„	Na	Et	0.8034	6.30	6.68	3.30	-do-
BuSnCl_3 (0.1207)	EtOH	„	Na	Et	0.7889	1.75	1.90	3.22	$\text{Na}[(\text{BuSn})_2(\text{OEt})_7] \rightleftharpoons \text{NaOEt} + 2\text{BuSn}(\text{OEt})_3$
BuSnCl_3 (0.2914)	Pr^iOH	Thymolphthalein	K	Pr^i	0.9668	3.45	3.74	3.23	$\text{K}[(\text{BuSn})_2(\text{OPr}^i)_7] \rightleftharpoons \text{KOPr}^i + 2\text{BuSn}(\text{OPr}^i)_3$
Me_2SnCl_2 (0.2763)	MeOH	„	Na	Me	0.8813	3.00	2.86	2.10	$\text{Me}_2\text{Sn}(\text{OMe})_2$
Bu_2SnCl_2 (0.1999)	MeOH	„	Na	Me	1.0048	1.25	1.31	2.06	$\text{Bu}_2\text{Sn}(\text{OMe})_2$
Me_2SnCl_2 (0.3796)	EtOH	„	Na	Et	0.8034	4.30	4.30	2.00	$\text{Me}_2\text{Sn}(\text{OEt})_2$
Me_2SnCl_2 (0.8567)	MeOH	„	Na	Me	1.0048	4.40	4.28	1.03	$\text{Me}_2\text{Sn}(\text{OMe})_2$

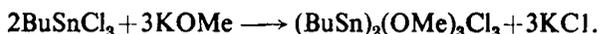
However, when these monoalkyltin chlorides were titrated with alkali ethoxide or isopropoxide in the parent alcohol or in an inert solvent like benzene, the neutralisation point occurs even earlier (table 1) than that obtained in the case of methoxide. This shows that double ethoxide or isopropoxide of monoalkyltin(IV) with alkali metals have even a greater tendency of dissociation than the corresponding methoxy derivatives:



(where R' = Et or Bu; R = Et or Pr'; M = Na or K).

3.1.2. Conductance studies

(a) *Titration of BuSnCl₃ with KOMe in methanol*: An increase in conductance up to $m \sim 1.5$ (m = molar ratio of KOMe:BuSnCl₃) was observed on addition of potassium methoxide to butyltin trichloride in methanol (figure 1, curve I):



This increase in conductance may be due to the presence of the following equilibria in the solution:

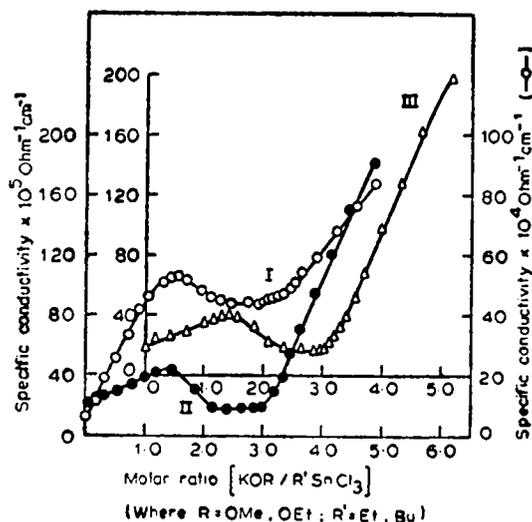
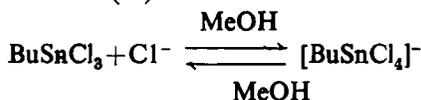
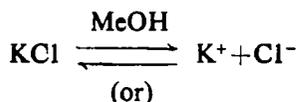
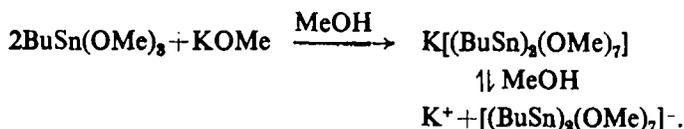


Figure 1. Titration of R'SnCl₃ with KOR in ROH. I: —○— KOMe M/0.87 vs 20 ml of BuSnCl₃ M/14.19. II: —●— KOEt M/1.05 vs 20 ml of EtSnCl₃, M/13.96. III: —△— KOEt M/0.84 vs 20 ml of BuSnCl₃ M/14.50.

Addition of more potassium methoxide results in the decrease in conductance along with the formation of a precipitate which remains insoluble and a second inflexion was observed at $m \sim 3.0$. This decrease in conductance appears to be due to conversion of ionic species (I) into non-ionic species, i.e., $\text{BuSn}(\text{OMe})_3$:

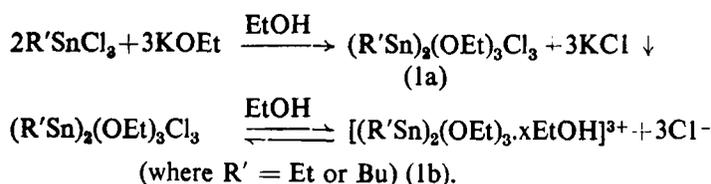


Further addition of KOME to the above titrand increases the conductivity and a third inflexion was observed at $m \sim 3.5$ which corresponded to the formation of double methoxide:



Beyond $m \sim 3.5$, the observed conductivity increases sharply and this increase corresponds roughly to the potassium methoxide added in excess. After completion of the titration, white particles of KCl were found to be present at the bottom of the cell.

(b) *Titrations of $\text{R}'\text{SnCl}_3$ with KOEt in ethanol (where $\text{R}' = \text{Et}, \text{Bu}$):* A white precipitate of KCl appears, when potassium ethoxide was added to ethyl (or butyl) tin trichloride in ethanol, which remains insoluble and consequently solution becomes milky. This results in the increase in conductance which continues up to addition of ~ 1.5 moles of KOEt (figure 1, curves II and III). This increase in conductance can be ascribed to the formation of (1a) which in turn may be in equilibrium as shown below:



Addition of more titrant decreases the conductivity which may be ascribed to the conversion of intermediate species (1a) or (1b) into the covalent simple ethoxide, i.e., $\text{R}'\text{Sn}(\text{OEt})_3$:



Further addition of KOEt increases the conductivity, but no definite point of inflexion corresponding to the formation of $\text{K}[(\text{R}'\text{Sn})_2(\text{OEt})_7]$ could be detected, which may be due to a higher dissociating tendency of the double ethoxide compared to the methoxide.

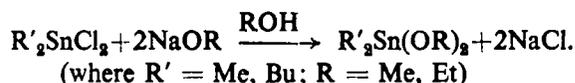
3.1.3. Potentiometric studies:

Titrations of EtSnCl_3 with KOME and KOPr^t : Titrations of ethyltin trichloride with potassium methoxide in methanol-acetonitrile medium and with isopropoxide in isoproponal-acetonitrile medium give final inflexions indicating the formation of the

species: $\text{EtSn}(\text{OMe})_3$ and $\text{EtSn}(\text{OPr}^t)_3$ respectively. Indications for the formation of some intermediate chloride alkoxides were obtained but no inflexion corresponding to the formation of the complex species $\text{K}[(\text{EtSn})_2(\text{OR})_7]$ could be observed.

3.2. Studies on alkoxy complexes of dialkyltin (IV) and trialkyltin (IV)

3.2.1. *Visual indicator studies:* Dialkyltin chlorides have been titrated with sodium alkoxides in the parent alcohols using thymolphthalein indicator. The neutralisation point in all these cases corresponds to the formation of dialkyltin dialkoxide only and no evidence could be obtained for the formation of double alkoxides in these systems:



The non-formation of double isopropoxide was confirmed by the titration of dimethyltin diisopropoxide with sodium isopropoxide in which thymolphthalein indicator showed a sharp colour change with the addition of the first drop of the NaOPr^t solution.

Tributyltin chloride with sodium methoxide in methanol has been titrated using thymolphthalein as indicator. The neutralisation point corresponded to the formation of $\text{Bu}_3\text{Sn}(\text{OMe})$ species:



3.2.2. Conductance studies:

(a) *Titration of Me_2SnCl_2 with KOMe in methanol:* An increase in conductance was observed up to the addition of ~ 1.0 mole of KOMe to Me_2SnCl_2 in methanol (figure 2, curve I). This increase in conductance may be due to the formation of

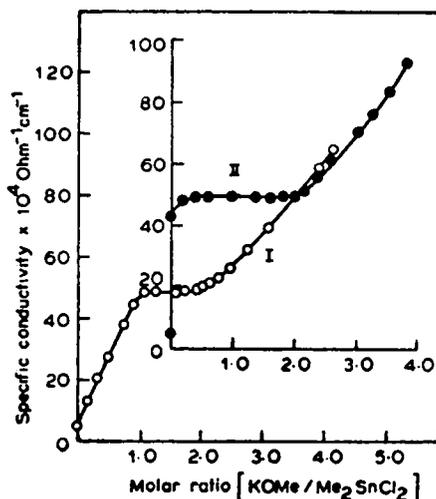
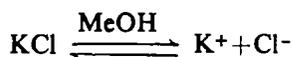
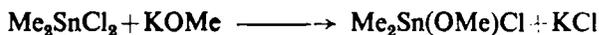


Figure 2. Titration of Me_2SnCl_2 with KOMe in MeOH . I. —○— KOMe M/0.955 vs 20 ml of Me_2SnCl_2 M/15.76. II. —●— KOMe M/0.71 vs 20 ml of Me_2SnCl_2 M/14.41 (+0.1515 gm KCl).

KCl, which is soluble in methanol (solubility of KCl in methanol was found to be 3.4 g/litre). The conductance was found to remain almost constant from $m \sim 1.0$ to $m \sim 2.0$ ($m = \text{molar ratio of KOME}:\text{Me}_2\text{SnCl}_2$). Thus two sharp inflexion points were observed which corresponded to the formation of chloride methoxide, $\text{Me}_2\text{Sn}(\text{OMe})\text{Cl}$ and simple methoxide, $\text{Me}_2\text{Sn}(\text{OMe})_2$:



Further addition of KOME increases the conductivity linearly and does not give any evidence for the formation of double methoxide.

In order to check whether the initial increase in conductances up to $m \sim 1.0$ is due to KCl alone or due to KCl as well as to the species, $\text{Me}_2\text{Sn}(\text{OMe})\text{Cl}$, formed in the reaction, excess of KCl was added in the beginning of the titration. Thus solution of Me_2SnCl_2 in methanol was made saturated with KCl and the titration was repeated with this solution. Conductivity was found to remain almost constant (figure 2, curve II) up to $m \sim 2.0$, which shows that increase in conductance up to $m \sim 1.0$ in the previous case was mainly due to KCl. Therefore, it appears that intermediate species, $\text{Me}_2\text{Sn}(\text{OMe})\text{Cl}$, does not contribute significantly to the conductance of the solution. Conductance curve beyond $m \sim 2.0$ is approximately similar to that observed in the earlier case.

(b) *Titration of Me_2SnCl_2 with KOR in ROH (where $R = \text{Et}$ and Pr^i):* Formation of a white precipitate of KCl appears on addition of potassium ethoxide (or isopropoxide) to dimethyltin dichloride solution in the parent alcohol, which remains insoluble and solution becomes milky. A sharp inflexion at $m \sim 2.0$ ($m = \text{molar}$

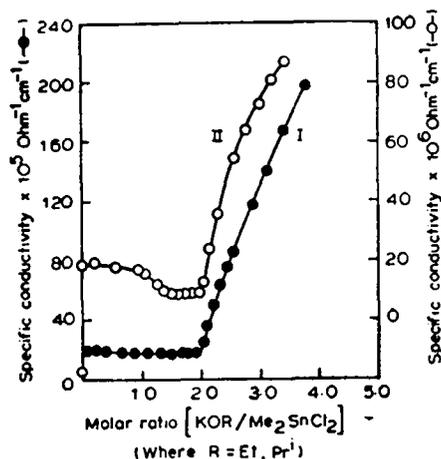
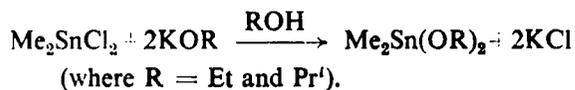


Figure 3. Titration of Me_2SnCl_2 with KOR in ROH. I: —●— KOEt M/0.909 vs 20 ml of Me_2SnCl_2 , M/13.73. II: —○— KOPrⁱ M/0.87 vs 20 ml of Me_2SnCl_2 , M/14.93.

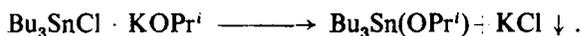
ratio of KOR: Me_2SnCl_2) was observed (figure 3, curves I and II), which corresponded to the formation of dimethyltin dialkoxide:



A sharp increase in conductance beyond $m \sim 2.0$ appears to be simply due to the addition of potassium alkoxide.

(c) *Titration of Bu_3SnCl with KOMe in methanol*: Continuous increase in conductance was observed on addition of potassium methoxide to tributyltin chloride solution in methanol and no definite point of inflexion could, however, be obtained. The increase in conductance may be mainly due to the formation of KCl, a major portion of which remains soluble.

(d) *Titration of Bu_3SnCl with KOPr^t in isopropanol*: Addition of potassium isopropoxide to tributyltin chloride in isopropanol gives a sharp inflexion at $m \sim 1.0$ (m = molar ratio of KOPr^t : Bu_3SnCl), which corresponds to the formation of the $\text{Bu}_3\text{Sn}(\text{OPr}^t)$ species:



The above titrations indicate that in contrast to the complex, $\text{K}[(\text{R}'\text{Sn})_2(\text{OR})_7]$ formed by the monoalkyltin moieties, the dialkyl- and trialkyltin species do not appear to form any complex species, which is understandable due to the lesser positive charge induced on tin in the latter two cases.

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