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Rate Study on the Redistribution Reactions of Organotin Compounds

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The redistribution reactions between R_3SnMe ($R = Me$, Et, n–Pr, iso–Pr, and Bu) and Me_2SnCl_2 in methanol, have been investigated. The reactivity order is: $Me > Et > n{-}Pr > Bu > iso{-}Pr$. The second order observed rate constants and the activation parameters are reported. A reaction mechanism involving the electrophilic attack on the carbon centre of the methyl group by the Me_2Sn^{2+} species, assisted by the solvent, is proposed.

Introduction

Inspection of work in the literature[1-3] dealing with redistribution reactions of tetraalkylmetals of group IVb with metal tetrahalides, reveals that most of the investigators were interested in the synthetic use of these reactions rather than in elucidating the reaction mechanisms. In the field of organotin chemistry, one of the most thoroughly investigated exchange reaction is the redistribution of tetraalkyltin compounds with tin(IV) tetrahalides,[4,5] for which some quantitative work on equilibria involving the scrambling of substituents on tin has been done.[4,6]

Redistribution reactions in solution may be considered as organo-metal substitutions.[7] Mercury-alkyls redistributions have been the subject of extensive kinetic investigations under a variety of conditions,[8,9] but no rate studies have been done up to this time for organometallics of group IVb.[9]

In our previous paper[10] the equilibrium constant of the reaction,

$$Me_4Sn + Et_3SnCl \rightleftarrows Et_3SnMe + Me_3SnCl \qquad (1)$$

has been determined in methanol, and the reactions,

$$Me_6Sn_2 \xrightarrow{Me_3SnCl} Me_4Sn + 1/n[Me_2Sn]_n \qquad (2)$$

$$Me_6Sn_2 + Et_3SnCl \longrightarrow Et_3SnMe + Me_3SnCl + 1/n[Me_2Sn]_n \qquad (3)$$

also have been investigated in the same medium.

We wish to report here a kinetic study concerning «redistribution reactions» of the following kind:

$$R_3SnMe + Me_2SnCl_2 \xrightarrow{\text{methanol}} R_3SnCl + Me_3SnCl \qquad (4)$$

where R = Me, Et, n–Pr, n–Bu, and iso–Pr.

This work represents a preliminary effort to establish the mechanism by which these reactions occur.

Experimental Section

Materials. All the organotin compounds used have been prepared and purified by the methods reported previously.[11] Methanol (reagent grade from C. Erba, Milan) was purified by Lund and Bjerrum's method.[12] Standard solutions of tetraalkyltin (0.3 M) as well as of dimethyltin dichloride (10^{-2} M) were prepared by dissolving known amounts in methanol, previously degassed with dry nitrogen. All solutions were stored in the dark in order to avoid any decomposition. All other chemicals used were reagent grade.

Procedure. Stoichiometries of reaction (4) have been ascertained by analysis of the Me_3SnCl product by means of polarography.[13] Reactions go completely to the right, and the possible reaction of the Me_3SnCl with either the tetraalkyltin or the trialkylmethyltin, as described by equilibrium (1), seems to be negligible in view of the slow rates of the two reactions leading to this equilibrium.[10]

Reactions (4) where followed by measuring the absorbance A of the Me_2Sn–PAR complex[14] (PAR = 4-(2-pyridylazo)-2-resorcinol) (molar extinction coefficient $\varepsilon = 41{,}700$).

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Reactions were shown to be first order with respect to the examined substrates (R_3SnMe or $Et_{4-n}SnMe_n$, $n=1, 2, 3$, and 4), and apparently of first order for Me_2SnCl_2 in its concentration range $1-6\times10^{-4}\,M$. At higher concentrations of Me_2SnCl_2 a decrease in rate is observed (see Table I). As the reactions were followed under pseudo-first order conditions (excess of R_3SnMe or $Et_{4-n}SnMe_n$), second order rate constants, $k_{2(obs)}$, have been calculated from:

$$k_{2(obs)}=k_{1(obs)}/[R_3SnMe]$$

in which,

$$k_{1(obs)}=\frac{2.303}{t}\log\frac{A_0-A_\infty}{A_t-A_\infty}$$

First order fits were obtained for over 70% of the reactions.

Table I. Effect of varying Me_2SnCl_2 concentration for the reaction, $Me_4Sn+Me_2SnCl_2\rightarrow2Me_3SnCl$ at 30°C

$[Me_4Sn]\times10^2$	$[Me_2SnCl_2]\times10^4$	$k_{1(obs)}\times10^5$ (sec^{-1})	$k_{2(obs)}\times10^3$ ($l.mole^{-1}sec^{-1}$)
3.0	1.00	3.75	1.25
6.5	1.96	8.20	1.26
3.0	5.00	3.80	1.26
6.0	6.00	7.44	1.24
3.0	10.00	3.42	1.14
3.0	10.00	3.35	1.12

Table II. Rate constants $k_{2(obs)}$ and activation parameters for the reactions: $R_3SnMe+Me_2SnCl_2\rightarrow R_3SnCl+Me_3SnCl$

Substrate	$k_{2(obs)}\times10^4$ ($l.mole^{-1}\,sec^{-1}$) 25°	30°	35°	40°	ΔE^*_{obs} [a] (kcal/mole)	$-\Delta S^*_{obs}$ [b] (u.e.)
Me_3SnMe	8.1	12.4	20.0	—	16.6	17.0
Et_3SnMe	3.5	5.9	9.4	—	18.2	13.3
$n-Pr_3SnMe$	2.7	4.2	5.8	9.0	14.7	25.6
$n-Bu_3SnMe$	2.2	3.1	4.4	—	12.7	32.5
$iso-Pr_3SnMe$	1.3	2.0	2.9	—	14.8	26.8

[a] From Arrhenius plots of $\log k_{2(obs)}$ *vs.* 1/T. [b] Calculated at 30°C.

Table III. Rate constants $k_{2(obs)}$ for $Et_{4-n}SnMe_n$ substrates at 25°C ($n=1, 2, 3$, and 4)

Substrate	$k_{2(obs)}\times10^4$ ($l.mole^{-1}sec^{-1}$)	$k_{2(obs)}/n$ [a]
Et_4Sn	no reaction	—
Et_3SnMe	3.5	3.50
Et_2SnMe_2	7.0	3.50
$EtSnMe_3$	6.8	2.26
$SnMe_4$	8.1	2.02

[a] n=Number of methyl groups in each substrate.

The flask containing known amounts of tetraalkyltin (from 1 to 10 ml) and of Me_2SnCl_2 (from 1 to 3 ml of the standard solutions) in 50 ml total volume of methanol, and salt ($NaClO_4$) in order to make a constant salt concentration equal to 0.01, were put into a thermostat at the desired temperature (±0.01°). At known intervals, quantities of the solution were taken off for analysis of the unreacted Me_2SnCl_2. All runs were made in duplicate. Reproducibility was approximately 2-3%.

Results and Discussion

Effect of Varying the R Group on the Substrates R_3SnMe. We have observed that, under the experimental conditions employied, the reactions occured only for those substrates where at least one R is a methyl group. The reactivity order of the examined substrates is as follows (cfr. Table II):

$$Me_3SnMe > Et_3SnMe > n\text{-}Pr_3SnMe > n\text{-}Bu_3SnMe > iso\text{-}Pr_3SnMe \quad (5)$$

In view of the above observations that only the methyl group is cleaved, we have measured the reaction rates of a series of substrates $Et_{4-n}SnMe_n$ ($n=1,2,3$) in order to establish whether reactivity is statistically dependent upon the number of the methyl groups. The rate constants $k_{2(obs)}$ for these substrates are listed in Table III with that for tetramethyltin. It may be seen that statistics can not be the main factor because, as it is shown in the third column of the Table III, the values $k_{2(obs)}/n$ (n=number of methyl groups in each substrate) slowly decrease on increasing the number of methyl groups.

Salt Effect. The reaction rates decrease on adding NaCl; for a NaCl solution of about 0.15 *M*, the reactions are nearly stopped. Table IV shows the $k_{2(obs)}$-values, as obtained for the reaction, $Me_4Sn+Me_2SnCl_2=2Me_3SnCl$ (6), on varying the chloride concentration in the range $1-10\times10^{-3}\,M$ and keeping the total salt concentration equal to 0.01 *M* at 30°. One can see that the $k_{2(obs)}$-values appreciably decrease on increasing the chloride ions concentration.

Table IV. Effect of varying Cl^- concentration for the reaction, $Me_4Sn+Me_2SnCl_2\rightarrow2Me_3SnCl$, at 30°C. $[Me_2SnCl_2]=5\times10^{-4}$; $[Me_4Sn]=3\times10^{-2}$. Total salt concentration, $[Me_2SnCl_2]+[NaCl]+[NaClO_4]=0.01$

$[Cl^-]\times10^3$ [a]	$k_{1(obs)}\times10^6$ (sec^{-1})	$k_{2(obs)}\times10^4$ ($l.mole^{-1}sec^{-1}$)
1.0	38.0	12.6
2.0	20.0	6.6
4.0	11.0	3.7
6.0	7.2	2.4
7.0	6.1	2.0
10.0	4.3	1.4

[a] $[Cl^-]=[NaCl]+2[Me_2SnCl_2]$.

A positive salt effect is observed on adding salt not containing chloride ions (cfr. Table V). The values α, obtained from the relation $\log k_{2(obs)} = \log k_{2(obs)0} + \alpha\sqrt{\mu}$, are 0.57 and 0.9 for Et_2SnMe_2 and Me_3SnMe substrates respectively.

Table V. Salt effect for the reactions: $R_2SnMe_2 + Me_2SnCl_2 \rightarrow R_2SnMeCl + Me_3SnCl$ (R = Me and Et) $[Me_2SnCl_2] = 5 \times 10^{-4}$; $[R_2SnMe_2] = 4.3 \times 10^{-1}$

Substrate	$[NaClO_4]$	$k_{2(obs)} \times 10^4$ (l.mole^{-1}sec^{-1})	α [a]
Et_2SnMe_2 (30°)	0	9.1	0.57
	0.01	9.8	
	0.05	12.5	
	0.083	13.8	
	0.150	15.0	
Me_3SnMe (25°)	0	7.5	0.9
	0.01	8.1	
	0.05	11.0	
	0.10	12.5	
	0.16	15.1	

[a] Calculated from the relation $\log k_{2(obs)} = \log k_{2(obs)0} + \alpha\sqrt{\mu}$.

Solvent Effect. Considering the effects on the reaction rates in several solvents, we found that reactions occur in methanol and ethanol whereas, reactions, in acetone, acetonitrile, and dioxane, are notably slowed up or stopped. A slow reaction is observed in iso-propyl alcohol: as an example reaction (6) in this solvent shows a $k_{2(obs)}$-value of about 4×10^{-5} l.mole^{-1} sec^{-1}, at 30°, so that the relative reactivity in this medium as compared to that in methanol is 1/30.

It has been verified that reactions slow up when water is added to the methanol. In fact, the $k_{2(obs)}$ for the reaction (6) at 25° in methanol-water medium (H_2O, 2 *M*) is 4.5×10^{-4}, in comparison with the value 8.1×10^{-4} obtained in methanol under the same conditions.

Conclusion

On the basis of the experimental findings regarding the use of various solvents, it seems likely to consider that, under the experimental conditions employed, reactions take place only in those media which allow dissociation of the Me_2SnCl_2. In fact, reactions are observed in solvents (S) like methanol, iso-propanol or methanol-water mixture for which dissociation of the Me_2SnCl_2 is known to occur as in the following scheme:[15]

$$Me_2SnCl_2 + xS \rightleftharpoons Me_2SnCl(S)(S)^{+}_{x-1} + Cl^- \qquad (7)$$

$$Me_2SnCl(S)(S)^{+}_{x-1} + S \rightleftharpoons Me_2Sn(S)_2(S)^{2+}_{x-1} + Cl^- \qquad (8)$$

This also agrees (cfr. Table IV) with the decrease of rates on addition of chloride ions which displace to the left the above equilibria (7) and (8) with the formation of undissociated species Me_2SnCl_2.

The reacting species with the substrates investigated may be $Me_2Sn(S)_2(S)^{2+}_{x-1}$ or $Me_2SnCl(S)(S)^{+}_{x-1}$ or both and the reaction rates are depending upon the concentration of these species according to the conditions used, that is, by varying the Me_2SnCl_2 concentration, adding chloride ions or on varying solvent. In addition, it seems likely to assume that the electrophilic strength of the different species decrease in the order $Me_2Sn(S)_2(S)^{2+}_{x-1}$, $Me_2SnCl(S)(S)^{+}_{x-1}$, Me_2SnCl_2-$(S)_x$ and yet on changing the coordinated solvent molecules around the tin centre.

On considering the effect on the observed rates in solvents allowing the Me_2SnCl_2 dissociation, it appears that in iso-propanol alcohol and in methanol-water mixture the reaction rates are slowed up in respect to the methanol. An explanation of this may be found on considering two factors: (a) the different dissociation of the Me_2SnCl_2 related to the different donor strength of the solvent molecules and (b) the mechanism of the reaction involving the substitution of one solvent molecule on the $Me_2Sn(S)_2(S)^{2+}_{x-1}$ ion by an incipient methyl carbanion. Factor (a) is probably important in the case of iso-propanol since this solvent does not allow dissociation as the methanol does, whereas factor (b) may be important in methanol-water medium, water being more strongly bonded to the Me_2Sn^{2+} ion and on considering that the displacement of the water molecules from the first coordination sphere of this ion is very difficult[16] (see later).

The following discussion is based upon the assumption* that the reacting ion is the penta-coordinated species[17] $Me_2Sn(S)_3^{2+}$, and on the findings that Me_2SnCl_2 is largerly dissociated in methanol in the concentration range used.[15]

The observed salt effect (cfr. Table V) more marked for Me_3SnMe than Et_2SnMe_2 in conceivable with a transition state more polar than the reagents in the initial state,[8] and as a consequence it seems likely that the S_E2 transition state is more favourable than a S_F2 one. On examining the possibility that the reaction goes through a transition state S_E2, that is, the occurrence of an activated complex between the substrate and the electrophile, we will take into consideration the obtained reactivity sequence (5) together with the probable significance of the two general factors: steric requirements and inductive effects of the R groups in the substrates R_3SnMe.

Inspection of Table II shows that changing of R group in the order Me, Et, n–Pr, n–Bu has a very small effect in the reaction rates. This behaviour rules out the possibility that steric factors are important, and this is also supported by the fact that the observed activation energies are decreasing in the above order. Moreover, if the inductive effects of the R groups joined to the tin atom were the only

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(15) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, 495 (1960) and references therein.

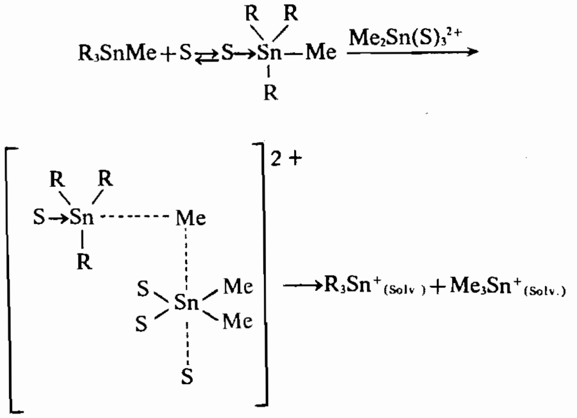
(*) The assumption, that penta-coordinated species $Me_2Sn(S)_3^{2+}$ may be involved in the process, is supported by the fact that penta-coordinated species, $Me_3Sn(S)_2^{2+}$ are formed in the reactions of this type, *e.g.* the aquo-cation,[17,24] $Me_3Sn(OH_2)_2^{2+}$:

(16) R. S. Tobias, *Organometal. Chem. Rev.*, *1*, 1 (1966).

(17) R. Okawara and M. Vada, *Ad. Organometal. Chem.*, 5, 137 (1967).

or the most significant factor, the rate sequence would be inverted in respect to that found (see sequence 5). In fact, as the chain length increases on passing from Me, Et, n–Pr, and n–Bu, the increasing +I inductive effect of the R groups in that order increases the negative charge on the carbon atom of the methyl group and consequently reactivity would increase as above.

From these considerations, it seems likely that the reaction pathway is not dealing with a transition state S_E2. Therefore, we retain that this type of reaction may be better understood assuming that an electrophilic substitution at the saturated carbon centre assisted by the solvent (S_E2), takes place, as pictured below in the scheme. Mechanisms with assistance by the solvent have been proposed for several electrophilic substitutions of substrates of the type R_4M (M=Sn and Pb) with different electrophilic reagents.[18-21]



The tendency of methanol to coordinate to the tin centre of the R_3SnMe substrates is expected to decrease* on increasing the chain length of the R groups as a consequence of the increased negative charge density on the tin atom due to the R groups themselves. In such a way the coordinative step by the solvent is responsible for the decrease of the reaction rates in the series Me, Et, n–Pr, n–Bu, and iso–Pr and explains the observed reactivity sequence (5).

Reactions require the displacement of a solvent molecule on the solvated Me_2Sn^{2+} reagent by an incipient methyl carbanion. The lower reactivity in methanol-water may be due to a relatively high energy being required to break the coordinative bonding between the water molecule and the tin in the aquo-complex $Me_2Sn(OH_2)_3^{2+}$. This energy requirement is not compensated by the energy resulting from the assistance step of the solvent since the coordinative step may statistically be due either to the methanol or the water molecule.

Looking to Table II, the activation parameters ΔE^*_{obs} and ΔS^*_{obs} are, in our opinion consistent with the above mechanism. In fact, the energy requirement becomes smaller on increasing the R chain length of the substrates as a consequence of an increase in the polarity of the R_3Sn—Me bonding, due to the R groups themselves, that is the negative charge on the incipient methyl carbanion increases on increasing the R chain length. In addition, it seems likely to consider that, on increasing the R chain length, the transition state becomes more polar and freezing of the solvent molecules around it is favoured allowing an increasing negative change of the entropic term.

A last point to discuss is the lack of the reactivity, under these particular conditions, of substrates not containing methyl groups. In our opinion, an explanation of this behaviour could be found on considering that the attached bond $\geqslant$Sn—R becomes less polar on passing from R=Me, Et, n–Pr, etc., on the basis of the decrease in electronegativity[25] of those groups in that order. Therefore, it seems likely to retain that the methyl group has a greater ability, thanks to its greater anionic stability,[9,26] to bridge two tin centres and to favour this reaction.

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(*) The decrease in the acceptor properties of the tin centre in organotin compounds on varying the number and the nature of the R groups joined to the tin atoms has been ascertained for $R_{4-n}SnCl_n$ compounds (n=2,3).[22,23]
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