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AN INVESTIGATION OF THE CHEMICAL BEHAVIOUR IN BINARY SYSTEMS $(CH_3)_{4-n}SnX_n/(CH_3)_{4-n}Sn(SCH_3)_n$ (X = Cl, Br, I) BY ^{1}H AND ^{119}Sn NMR

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Summary

Binary systems of type $(CH_3)_{4-n}SnX_n$ / $(CH_3)_{4-n}Sn(SCH_3)_n$ (X = halogen, n = 1, 2, 3, 4) have been investigated in solution by ^{1}H and ^{119}Sn NMR spectroscopy At room temperature the existence of a rapid exchange of the halogen and SCH_3 substituents on the methyltin moiety was established, the rate of exchange being slowest with iodine. Low-temperature measurements provide additional evidence for the proposed exchange mechanism.

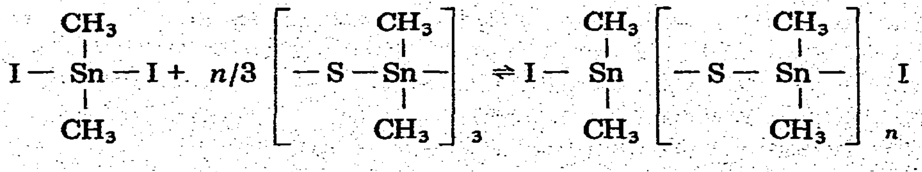
Introduction

Halogenating agents are reported [1] to cleave the Sn—SCH_3 bond with subsequent formation of an Sn—Hal bond. Thus trimethyl(alkylthio)stannanes react with CH_3I [2, 3] even at room temperature according to eqn. (1) and molecular bromin reacts with trimethyl(phenylthio)tin [2] according to eqn. (2). Analogous reactions occur with silicon and germanium compounds [4].

$$R_3SnSR' + CH_3I \rightarrow R_3MI + R'SCH_3 \qquad (1)$$

$$2(CH_3)_3SnSC_6H_5 + Br_2 \rightarrow 2(CH_3)_3SnBr + (C_6H_5)_2S_2 \qquad (2)$$

It has been shown by ^{1}H NMR spectroscopy that trimeric dimethyltin sulfide shows rapid interchange of halogen atoms with formation of sulfur bridges [5]. The exchange rate was higher with chlorine than with iodine. The three broad ^{1}H resonance signals observed with this substituent were interpreted in terms of equilibria of type (3).



$$\mathrm{I}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Sn}}}-\mathrm{I} + n/3\left[-\mathrm{S}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Sn}}}-\right]_3 \rightleftharpoons \mathrm{I}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Sn}}}\left[-\mathrm{S}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\mathrm{Sn}}}-\right]_n \mathrm{I} \qquad (3)$$

It is relevant [6] that $(C_4H_9)_2SnCl(SC_4H_9)$ is the only monomeric halogenoalkyltin mercaptide isolated from reaction (4).

$$(C_4H_9)_2SnCl_2 + (C_4H_9)_2Sn(SC_4H_9)_2 \rightarrow 2(C_4H_9)_2SnCl(SC_4H_9) \qquad (4)$$

In this study we wish to report on a study of solution of a series of binary systems, $(CH_3)_{4-n}SnX_n/(CH_3)_{4-n}Sn(SCH_3)_n$ with $n = 1, 2, 3, 4$ and X = halogen, which were investigated by ^1H and ^{119}Sn NMR spectroscopy.

Two possibilities may be considered for the reactions between the components. First, a complete redistribution of the non-alkyl ligands resulting in the formation of an equilibrium mixture containing the halogenated methyl(methylthio tin compound, as represented for $n = 2$ by reaction (5), from which all three components could be isolated, and second, rapid exchange between the SCH_3 groups

$$(CH_3)_2Sn(SCH_3)_2 + (CH_3)_2SnX_2 \rightleftharpoons 2(CH_3)_2SnSCH_3X \qquad (5)$$

and X atoms on the alkyltin moiety according to reaction (6), from which the separate components cannot normally be isolated.

$$(CH_3)_2Sn(SCH_3)_2 \rightleftharpoons (CH_3)_2SnSCH_3X \rightleftharpoons (CH_3)_2SnX_2 \qquad (6)$$

Experimental

The methyl(methylthio)stannanes were synthesised as described by Abel and Brady [2] from aqueous solutions of the corresponding methyltin chloride and gaseous CH_3SH. The $Sn(SCH_3)_4$ compound was prepared as described by Merohtra et al. [7] and modified by us [8] for R = CH_3 [eqn. (7)].

$$SnCl_4 + 4\ RSH + 4\ NH_3 \xrightarrow{C_6H_6} SnR_4 + 4\ NH_4Cl \qquad (7)$$

The NMR spectra were recorded in the frequency sweep mode with a Bruker-Physik HFX5 spectrometer operating for protons at 90 MHz. The binary systems were studied as equimolar solutions in CH_2Cl_2 or/and benzene. The ^{119}Sn NMR spectra were recorded by use of the INDOR technique [8]. In these binary mixtures only broad ^{119}Sn NMR signals could be observed. It may also be noted that, in contrast with the ^{119}Sn NMR spectra of pure $(CH_3)_{4-n}SnCl_n$ compounds in benzene [8], broadened signals without tin—proton coupling fine-structure were observed in CH_2Cl_2. In the ^{119}Sn NMR spectra of the $(CH_3)_{4-n}Sn(SCH_3)_n$ compounds, however, the multiplicity observed in benzene [8] appeared in CH_2Cl_2 also.

Results and discussion

The different NMR parameters measured in CH_2Cl_2 solution for $(CH_3)_{4-n}SnCl_r$ and for $(CH_3)_{4-n}Sn(SCH_3)_n$ with $n = 1, 2$ and 3 and for equimolar mixtures at room temperature are summarized in Table 1. ^1H and ^{119}Sn chemical shifts (δ) are expressed in ppm with respect to TMS and $Sn(CH_3)_4$ respectively. Positive and negative values indicate shifts to lower and resp. higher field. The $^{117,119}Sn$—C—H and $^{117,119}Sn$—S—C—H couplings are denoted by ^2J and ^3J respectively.

TABLE 1

^1H AND ^{119}Sn NMR PARAMETERS OF THE BINARY SYSTEMS $(CH_3)_{4-n}SnCl_n/(CH_3)_{4-n}Sn(SCH_3)_n$ (1/1 molar ratio) IN CH_2Cl_2 AT ROOM TEMPERATURE

Compound	Before mixing (25°)					After mixing (25°)				
	Chemical shift (δ ppm)			$J(^{119}Sn—H)$		Chemical shift (δ ppm)			$J(^{119}Sn—H)$	
	$^1H(CH_3)$	$^1H(SCH_3)$	^{119}Sn	CH_3	SCH_3	$^1H(CH_3)$	$^1H(SCH_3)$	^{119}Sn	CH_3	SCH_3
$(CH_3)_3SnCl$	+0.60		+152	58.7		+0.46	+0.19	+110	57.6	—
$(CH_3)_3SnSCH_3$	+0.34	+0.19	+ 85.1	56.6	35					
$(CH_3)_2SnCl_2$	+1		+126.6	69.5		+0.72	+2.00	+132	65.6	—
$(CH_3)_2Sn(SCH_3)_2$	+0.59	+2.04	+136.7	60.4	41.2					
CH_3SnCl_3	+1.53		+ 4.4	99.2		+0.90	+2.12	+97.2	78.9	—
$CH_3Sn(SCH_3)_3$	+0.69	+2.14	+155	66,0	51.7					

1. $(CH_3)_{4-n}SnCl_n/(CH_3)_{4-n}Sn(SCH_3)_n (n = 1, 2, 3)$ in CH_2Cl_2

From the data in Table 1 it is apparent that the three binary systems in CH_2Cl_2 solution show similar behaviour at room temperature. For the mixtures there is only one ^{119}Sn resonance signal and one signal for each set of protons (i.e. for CH_3 and SCH_3). The ^3J couplings are absent in the mixtures while the ^2J coupling constants remain clearly observable. The ^1H and ^{119}Sn chemical shifts and the ^2J coupling constants of the binary systems have values intermediate between these of the starting compounds. The ^1H signals remain relatively sharp, thus allowing ^2J to be measured, whereas the ^{119}Sn signals are so broadened that no observation of coupling is possible.

These observations are characteristic of a rapid exchange between SCH_3 groups and chlorine atoms on the methyltin moiety, as represented by eqns. (8), (9) and (10). The disappearance of the ^3J couplings also indicates that the time interval of

$$(CH_3)_3SnCl \rightleftharpoons (CH_3)_3SnSCH_3Cl \rightleftharpoons (CH_3)_3SnSCH_3 \qquad (8)$$

$$(CH_3)_2SnCl_2 \rightleftharpoons (CH_3)_2SnSCH_3Cl \rightleftharpoons (CH_3)_2Sn(SCH_3)_2 \qquad (9)$$

$$CH_3SnCl_3 \rightleftharpoons CH_3SnCl_2SCH_3 \rightleftharpoons CH_3SnCl(SCH_3)_2 \rightleftharpoons CH_3SnCl_3 \qquad (10)$$

interaction of the SCH_3 groups with the Sn nuclei must be short compared to the reciprocal of the ^3J coupling constants expressed in frequency units.

Low-temperature measurements on the systems described in this work revealed the expected line-broadening of the separate ^1H signals. However, in neither case could a low-enough temperature be reached to reveal the separate signals of the species taking part in the equilibrium, because either the solute or the solvent crystallized out. This happened for the three systems, $(CH_3)_3SnSCH_3/(CH_3)_3SnCl$, $(CH_3)_2Sn(SCH_3)_2/(CH_3)_2SnCl_2$ and $CH_3Sn(SCH_3)_3/CH_3SnCl_3$ at −50°, −65°, and −95°, respectively. For the system $CH_3Sn(SCH_3)_3/CH_3SnCl_3$, with which the lowest temperature could be reached, the effect of

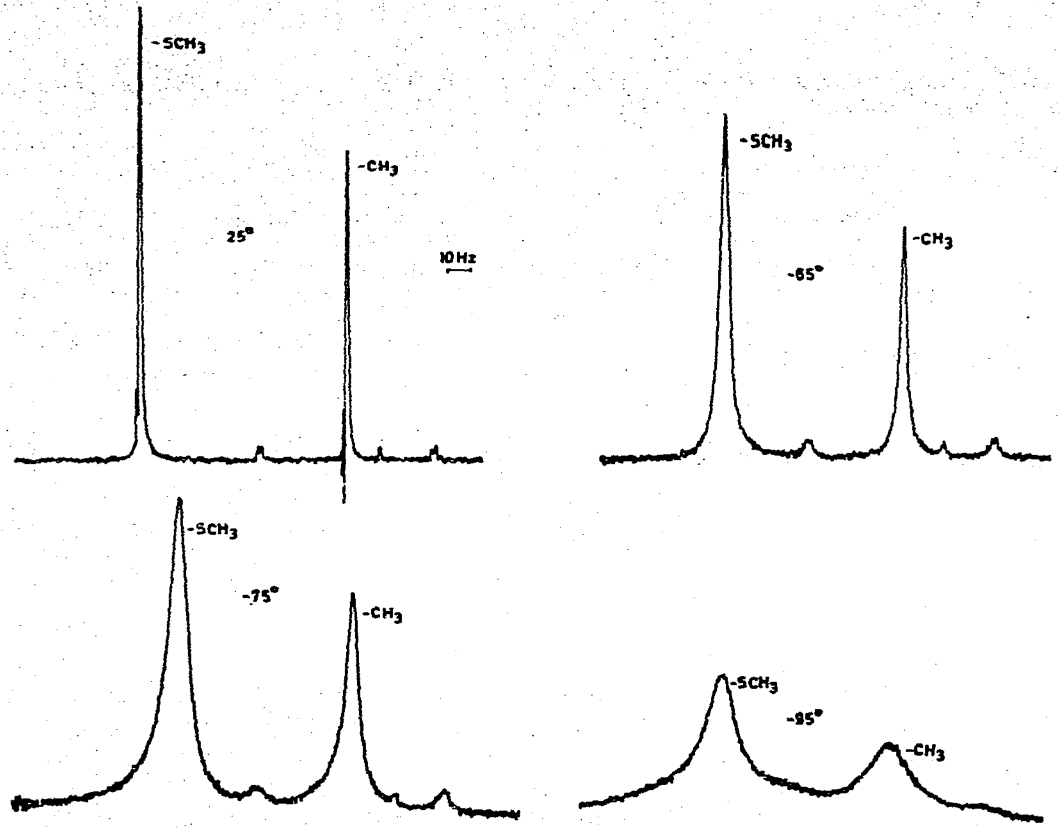


Fig. 1. ^{1}H NMR spectra of the binary system $CH_3SnCl_3/CH_3Sn(SCH_3)_3$ in solution at various temperatures.

line-broadening (Fig. 1) was the most pronounced. These temperature effects were shown to be reversible. Thus the low-temperature studies confirm the occurrence of a rapid exchange of substituents around the alkyltin moiety, and show that complete redistribution to isolable chlorinated alkyl(methylthio)tin compounds does not take place in the temperature range studied.

Rapid exchange was previously demonstrated in an NMR study [9] on the binary systems $(CH_3)_{4-n}SnX_n$ / $(CH_3)_{4-n}SnY_n$ with X and Y = Cl, Br, I. In those cases, however, the formation of $(C_4H_9)_2SnCl(SC_4H_9)$ by redistribution between $(C_4H_9)_2SnCl_2$ and $(C_4H_9)_2Sn(SC_4H_9)_2$ was clearly established. Furthermore, $(C_4H_9)_2SnClBr$ can be isolated as a pure compound [10], while the existence of analogous methyltin compounds has not been reported. It thus seems that the nature of the alkyl group on tin has an important influence on the formation of stable mixed R_2SnXY compounds.

2. $(CH_3)_2SnX_2/(CH_3)_2Sn(SCH_3)_2$ (X = Br, I)

For the binary systems of disubstituted compounds with halogens other than chlorine we investigated qualitatively the influence of the halogen and of solvent and concentration on the rate of exchange. For X = Cl, Br or I, the NMR behaviour is simular in solvents such as CH_2Cl_2, CCl_4 and C_6H_6. On dilution, line-broadening occurs, indicating a slower rate of exchange. For X = I, however, substantial line-broadening of the CH_3 and SCH_3 ^{1}H resonances is observed even in concentrated solutions, in sharp contrast to the sharp resonance lines found for X = Cl and Br, and so the rate of exchange must be considerably lower with iodine. Thus with the binary system, $(CH_3)_2SnI_2/(CH_3)_2Sn(SCH_3)_2$ in CH_2Cl_2 satellite lines with a separation of 45 Hz appear symmetrically around the SCH_3 ^1H resonance signal at —50° and these can be easily recognized as the ^3J coupling. This value is higher by 3.8 Hz than observed on a solution of pure $(CH_3)_2SN(SCH_3)_2$, giving further evidence for the conversion of the $Sn(SCH_3)_2$ to the $Sn(SCH_3)I$ moiety. It thus appears that because of a slower rate of exchange, the lifetimes of the SCH_3 and iodine substituents on the Sn nucleus became greater than the reciprocal of the ^3J value.

Despite the appearance of the ^3J coupling at temperatures below —50°, the ^1H resonances of the parent compounds could not be detected even at —90°. It is noteworthy that for an analogous silicon system, viz. $(CH_3)_2Si(SCH_3)_2/(CH_3)_2SiCl_2$, no exchange of substituents could be established in solution, only the ^1H signals of the parent compounds being observed throughout. Mixtures of the compounds in the pure state also gave no evidence of exchange of substituents at ambient temperature. However, at elevated temperature a new signal appeared between the original two $(CH_3)Si$ ^1H signals, and its intensity increased with increasing temperature, this being accompanied by a decrease of the $(CH_3)_2Si$ ^1H resonance lines of the starting materials. On cooling the mixture again, the signals remained unchanged. Thus in the silicon case at higher temperatures an equimolecular mixture of the starting pure compounds is subject to redistribution, with formation of a chloro(methylthio)methylsilane. Analogous behaviour must occur in the system $CH_3SiCl_3/CH_3Si(SCH_3)_3$, there being a preference at equilibrium for the mixed species, $CH_3SiCl(SCH_3)_2$ and $CH_3SiCl_2SCH_3$[11].

Thus it may be concluded that the exchange mechanism for substituents around the alkyltin moiety is different from that around the alkylsilicon moiety.

3. $SnCl_4/Sn(SCH_3)_4$

The NMR spectrum of a mixture of $SnCl_4$ and $Sn(SCH_3)_4$ in CH_2Cl_2 shows a single but broadened signal of the SCH_3 protons, without ^{117} ^{119}Sn—S—C—H satellites, although these are clearly observed in the spectrum of pure $Sn(SCH_3)_4$. Apparently a fast exchange of substituents again takes place, as shown in eqn. (11).

$$SnCl_4 \rightleftharpoons SnCl_3SCH_3 \rightleftharpoons SnCl_2(SCH_3)_2 \rightleftharpoons SnCl(SCH_3)_3 \rightleftharpoons Sn(SCH_3)_4 \qquad (11)$$

It can be concluded that monomeric halogenated methyl(methylthio)tin compounds are not produced by the interaction of the two components in the systems studied and work is in progress in this laboratory on the reaction of $(CH_3)_{4-n}Sn(SCH_3)_n$ ($n = 1, 2, 3, 4$) compounds with other potential halogenating agents.

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