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THE EFFECT OF THE SOLVENT UPON THE RATES AND MECHANISMS OF ORGANOMETALLIC REACTIONS

V. PMR SPECTRA AND STRUCTURES OF MOLECULAR COMPLEXES OF METHYLTIN HALIDES IN SOLUTIONS

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Summary

The complexation of methyltin halides in electron-donating solvents such as acetone, dioxane, dimethoxyethane, pyridine, dimethylformamide, dimethyl sulfoxide, hexamethylphosphoric triamide, and tetramethylethylenediamine has been studied by means of PMR spectroscopy. Equilibrium constants have been evaluated for $\text{Me}_3\text{SnHal}\cdot\text{D}$ (D = donor) complexes. The concentration and temperature dependences of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ in methyltin halides suggest some conclusions on the electron and spatial structures of complexes in solutions.

Introduction

In the first paper in this series [1] it was emphasised that the problem of the effect of solvent upon the rates and mechanisms of organometallic reactions may be only successfully approached through a study of both the kinetics of the reactions in various solvents and the structures of the complexes formed by the organometallic and solvent molecules in the crystalline phase and in solution. In earlier papers we discussed the synthesis [2], NQR [3] and Mössbauer [4] spectra and the structures of molecular complexes of methyltin halides in the crystalline phase.

In the present work PMR spectroscopy has been used to study the same complexes in solutions, due regard being taken of the fact that the structures of the complexes may change on going from the crystalline phase to solution.

Results and discussion

It is well known [5-9] that equilibria exist between the free and complexed molecules of methyltin halides in solution. In the case of trimethyltin halides and monodentate solvent molecules, only equilibrium (1) exists whereas in the

TABLE I
LIMITING VALUES OF ρ ($^{119}\text{Sn}-\text{C}-\text{H}$) FOR $\text{Me}_3\text{SnHal}\cdot\text{D}$, $\text{Me}_2\text{SnHal}_2\cdot\text{D}$ AND $\text{MeSnHal}_3\cdot\text{D}$ SYSTEMS

Donor	Acceptor					
	Me_3SnCl	Me_3SnBr	Me_2SnCl_2	Me_2SnBr_2	MeSnCl_3	MeSnBr_3
Acetone	66.0	65.5	91.5 (-50°) ^a	88.7 (-50°) ^a	129.4 (-50°) ^a	113.9 (-50°) ^a
Dioxane	62.6 (28°) 63.0 (-10°)	62.2 (28°) 62.6 (-10°)	73.5 (+28°) ^a	76.2 (+28°) ^a	117.3 (-10°) ^a	106.2 (-10°) ^a
DME	62.4 (28°) 64.5 (-30°) 65.3 (-50°)	61.9 (28°) 64.2 (-30°) 64.7 (-50°)	96.4 (-70°)	95.2 (-70°)	131.0	119.5
Pyridine	68.0	67.6	b	b	b	b
TMED	69.7	68.5	b	b	b	b
DMF	70.0	69.6	109.8 (-50°) ^a	112.0	133.5	129.5
DMSO	70.1	69.6	114.8 (+28°) ^a	115.3 (+28°) ^a	139.0	128.5
HMPT	71.8	71.3	121.1 (-50°) ^a	119.5	146.0	139.6

^a Maximal values observed are given. The limiting values could not be measured (see text). ^b Insoluble AD_2 complexes are formed in all cases.

cases of dimethyltin dihalides and methyltin trihalides it is essential to consider equilibrium (2) as well.



Spin-spin coupling constants, $J(^{119}\text{Sn}-\text{C}-^1\text{H})$, observed for the solutions of methyltin halides are expressed by eq. (3) for Me_3SnHal and by eq. (4) for $\text{Me}_2\text{SnHal}_2$ and MeSnHal_3 .

$$J_{\text{obs}} = p(A) \cdot J(A) + p(AD) \cdot J(AD) \quad (3)$$

$$J_{\text{obs}} = p(A) \cdot J(A) + p(AD) \cdot J(AD) + p(AD_2) \cdot J(AD_2) \quad (4)$$

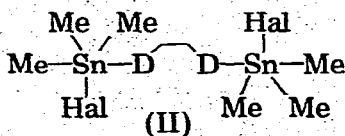
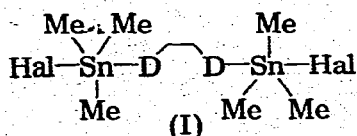
where $p(A)$, $p(AD)$ and $p(AD_2)$ are molar fractions of the free acceptor, the 1/1 complex, and the 1/2 complex and $J(A)$, $J(AD)$ and $J(AD_2)$ are $^{119}\text{Sn}-\text{C}-^1\text{H}$ spin-spin coupling constants for the same molecules.

An increase in the concentration of donor molecules and a decrease of the temperature favours an increase of AD and AD_2 concentrations and in many cases shifts the equilibria towards the complexed forms. In these cases J_{obs} reflect the electronic and spatial structures of AD and AD_2 complexes. Thus it is possible to obtain $J(AD)$ and $J(AD_2)$ for some complexes by studying the concentration and temperature dependences of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ for solutions of methyltin halides in various solvents.

I. $J(AD)$ for $\text{Me}_3\text{SnHal} \cdot D$ complexes

We have studied the intermolecular coordination of Me_3SnCl and Me_3SnBr with acetone, dioxane, dimethoxyethane (DME), pyridine (Py), dimethylformamide (DMF), dimethyl sulphoxide (DMSO) and hexamethylphosphoric triamide (HMPT) in methylene chloride. It was shown firstly that $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ values for solutions of Me_3SnHal in neat CH_2Cl_2 do not change on altering the Me_3SnHal concentration from 0.1 mol/l up to 0.5 mol/l and the temperature from +28 down to -50° . These data may be indicative of the absence of any association of Me_3SnHal with CH_2Cl_2 .

We also studied the concentration and temperature dependences of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ for solutions of Me_3SnHal in CH_2Cl_2 , to which the electron-donor solvents mentioned above have been added. A typical plot of such dependences is shown in fig. 1. The measurements in most cases were carried out at +28, -30 and -50° ; the highest ratio $[D]/[A]$ corresponds to the solutions in neat solvents. Limiting values of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$, which conform in most cases to $J(AD)$, are given in Table 1. For bidentate ethers (dioxane and DME) it was shown that for different temperatures there are different limiting values of J_{obs} (Table 1). We believe that such anomalous character of these values is due to the coexistence in solution of complexes such as $\text{Me}_3\text{SnHal} \cdot D$ and $2\text{Me}_3\text{SnHal} \cdot D$. In this case the latter complex can exist not only in the form of a trigonal bipyramid (I) but in the form of a trigonal bipyramid (II) as well.



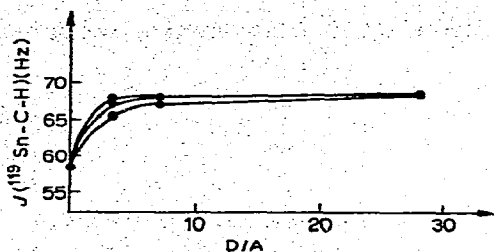


Fig. 1. Concentration and temperature dependence of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ for the Me_3SnCl -pyridine system.

It is reasonable to assume that $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ constants for the structures (I) and (II) are different and since there is an equilibrium between these two structures which depends on the temperature only, at different temperatures one should observe different limiting values of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$, characteristic of the relative content of structures (I) and (II) in the mixture. This hypothesis seems to be supported by the NQR spectra of Me_3SnBr solutions in DME [3].

Analysis of the data given in Table 1 shows that $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ values for Me_3SnHal increase in the sequence: Acetone < pyridine < TMED < DMF ~ DMSO < HMPT, in good agreement with data for the respective systems [5-9]. In our opinion this sequence reflects the comparative strengths of the donor-acceptor bonds between the solvent and the organotin molecules, i.e. it represents the relative solvating abilities of these solvents.

Bearing in mind that Me_3SnHal gives only the 1/1 complexes with monodentate solvent molecules we can estimate in these cases the equilibrium constants K_{eq} using eqn. (5). Table 2 contains K_{eq} values at different temperatures for some of the systems studied.

$$K_{\text{eq}} = \frac{P(\text{AD})}{\{1-p(\text{AD})\} \{[\text{D}_0] - p(\text{AD})[\text{A}_0]\}} \quad (5)$$

$$\text{where } p(\text{AD}) = \frac{J_{\text{obs}} - J(\text{A})}{J(\text{AD}) - J(\text{A})}$$

TABLE 2

K_{eq} VALUES FOR COMPLEXES OF Me_3SnHal WITH SOME MONODENTATE SOLVENTS

Complex	K_{eq} ($\text{l}\cdot\text{mol}^{-1}$)			
	+ 28°C	-10°C	-30°C	-50°C
$\text{Me}_3\text{SnCl}\cdot\text{Acetone}$			0.8 ± 0.1	1.3 ± 0.2
$\text{Me}_3\text{SnBr}\cdot\text{Acetone}$			0.6 ± 0.1	1.1 ± 0.2
$\text{Me}_3\text{SnCl}\cdot\text{DMSO}$	2.2 ± 0.3	3.0 ± 0.5		
$\text{Me}_3\text{SnBr}\cdot\text{DMSO}$	2.8 ± 0.3	3.1 ± 0.3		
$\text{Me}_3\text{SnCl}\cdot\text{DMF}$	1.4 ± 0.2		2.3 ± 0.4	4.3 ± 0.6
$\text{Me}_3\text{SnBr}\cdot\text{DMF}$	1.5 ± 0.2		3.1 ± 0.5	4.9 ± 0.6
$\text{Me}_3\text{SnCl}\cdot\text{pyridine}$	3.4 ± 0.5		36 ± 8	
$\text{Me}_3\text{SnBr}\cdot\text{pyridine}$	3.4 ± 0.5		28 ± 3	
$\text{Me}_3\text{SnCl}\cdot\text{HMPT}$	103 ± 4		231 ± 9	360 ± 12
$\text{Me}_3\text{SnBr}\cdot\text{HMPT}$	99 ± 4		232 ± 9	360 ± 12

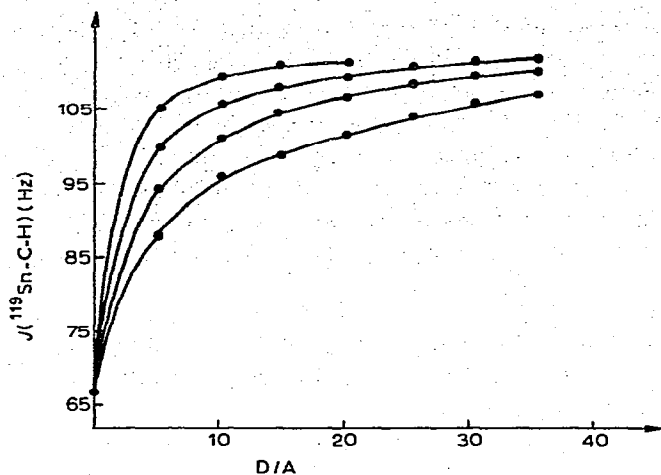


Fig. 2. Concentration and temperature dependence of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ for the Me_2SnBr_2 -DMF system.

II. $J(\text{AD}_2)$ for $\text{Me}_2\text{SnHal}_2 \cdot 2\text{D}$ and $\text{MeSnHal}_3 \cdot 2\text{D}$ complexes

We studied the PMR spectra of $\text{Me}_2\text{SnHal}_2$ and MeSnHal_3 (Hal = Cl, Br) in CH_2Cl_2 containing acetone, dioxane, DME, DMF, DMSO, and HMPT. It was impossible to study the systems with Py and TMED, since insoluble complexes were immediately formed.

Figures 2 and 3 show that in the cases of $\text{Me}_2\text{SnHal}_2$ and MeSnHal_3 $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ values increase with an increase of the $[\text{D}]/[\text{A}]$ ratio and a decrease of the temperature. These facts are in good agreement with the usual rationalization of equilibria such as (1) and (2) between free and complexed molecules of methyltin halides.

A study of the temperature and concentration dependences of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ constants has made it possible to obtain $J(\text{AD}_2)$ values for some complexes, especially those containing MeSnHal_3 molecules (Table 1). Some experimental difficulties (the limited possibilities of decreasing the acceptor concen-

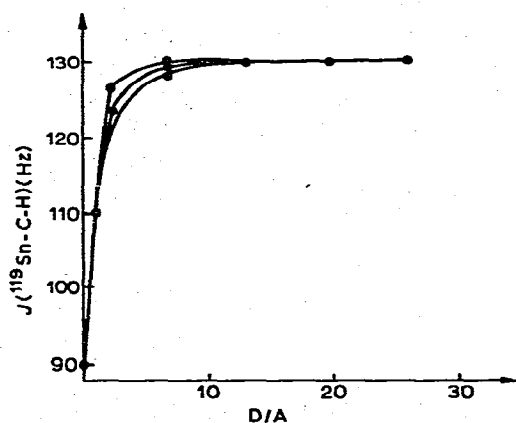
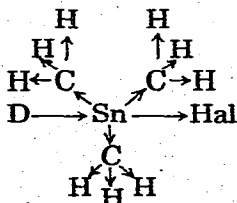


Fig. 3. Concentration and temperature dependence of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ for the MeSnBr_3 -DMF system.

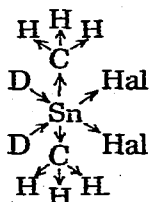
tration and the sample temperature) prevented us from obtaining $J(\text{AD}_2)$ values in other cases, especially those of complexes containing $\text{Me}_2\text{SnHal}_2$ molecules. Data obtained suggest that complexes such as $\text{MeSnHal}_3 \cdot 2\text{D}$ are rather more stable than complexes of the type $\text{Me}_2\text{SnHal}_2 \cdot 2\text{D}$. Unfortunately, we did not succeed in obtaining K_{eq} values for these systems, owing to the coexistence of equilibria (1) and (2) in the solutions under investigation. Nevertheless, the qualitative conclusions derived may be very important in a study of the solvent effect upon the rates and mechanisms of the reactions between these molecules.

III. The changes in tin-carbon and tin-halogen bonds upon coordination

It has been generally accepted [10–13] that the Fermi contact term is the main contribution to $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ constants, and therefore that these are proportional to the s -electron densities on the nuclei coupled. The data given in Table 1 and earlier data [5–13] lead us to conclude that the complexation of methyltin halides with electron-donor solvents is followed by an increase of the relative content of s -electrons in the $\text{Sn}-\text{C}-\text{H}$ site. We emphasise this point because the vast majority of investigators, following Holmes and Kaez [10], conclude that there is an increase in the s -character of the sp^n -hybrid orbitals of the tin atom in tin-carbon bonds. These conclusions are based on the assumption [10] that except for rehybridisation of the tin atom other components of the bonding system $\text{Sn}-\text{C}-\text{H}$ do not change appreciably. It has, however been shown convincingly [14, 15] that $J(^{13}\text{C}-^1\text{H})$ constants in these compounds depend strongly on the nature of the substituents at the tin atom and on the nature of the solvent used. We should like also to draw attention to the fact that as early as 1965 Verdonck and Van der Kelen [11] studied the PMR spectra of ethyltin chlorides (neat and in water solutions), as carried out by Holmes and Kaez [10] for methyltin chlorides and concluded that "a simple relationship between J and percentage s -character is not valid and that other parameters give an important contribution to the coupling". Recently, it was shown in our laboratory [16] that on going from solutions of Et_2Hg in inert solvents to the respective solutions in solvating solvents, $J(^{199}\text{Hg}-\text{C}-^1\text{H})$ changes from 98.0 to 104.5 Hz, whereas the $J(^{199}\text{Hg}-\text{C}-\text{C}-^1\text{H})$ constant does not change and is equal to 127.5 Hz. For ethyltin halides it has been shown recently [13] that on going from the solutions in CDCl_3 to the solutions in $\text{DMSO}-d_6$ the $J(^{119}\text{Sn}-\text{CH}_2)$ constant changes considerably whereas changes in $J(^{119}\text{Sn}-\text{CH}_3)$ are small. On the basis of these observations we have concluded [17] that the complexation which is essentially a $p-d$ donor-acceptor interaction does not disturb the s -electron density on the metal. At the same time, there is an increase of s -electron density on the α -hydrogen atom, owing to the inductive mechanisms shown in structures (III) and (IV).



(III)



(IV)

In the complexes formed the tin atom has, according to Pauling's primary rehybridisation model [18], five sp^3d (for $\text{Me}_3\text{SnHal}\cdot\text{D}$) and six sp^3d^2 (for $\text{Me}_2\text{SnHal}_2\cdot 2\text{D}$ and $\text{MeSnHal}_3\cdot 2\text{D}$) hybrid atomic orbitals. According to Bent's secondary rehybridisation model [19] the distribution of electrons in the molecules occurs in such a way that the s -electrons are concentrated mainly in the bonds with the more electropositive substituents. Comparison of the $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ constants, infrared spectra [6], NQR spectra [3] and Mössbauer spectroscopy data [4] for the same complexes shows that the increase of the relative content of s -electrons in the $\text{Sn}-\text{C}-\text{H}$ site is followed by an increase of the ionicity of $\text{Sn}-\text{Hal}$ bonds which is in good agreement with Bent's theory [19].

IV. Spatial structures of molecular complexes of methyltin halides in solutions

$J(^{119}\text{Sn}-\text{C}-^1\text{H})$ spin-spin coupling constants are used widely as a criterion for the mutual arrangement of $\text{Sn}-\text{C}$ bonds in complexes of methyltin halides [10, 13, 20]. We believe that such an evaluation of the spatial structure of the complexes on the basis of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ can only be very approximate because, for example, approximately regular tetrahedral molecules Me_3SnCl , Me_2SnCl_2 and MeSnCl_3 [21] differ considerably in their $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ constants (58.5, 70.0 and 100.0 Hz respectively). This, according to Bent, may depend mainly on the secondary rehybridisation of electrons in these molecules.

Comparison of X-ray data for $\text{Me}_3\text{SnCl}\cdot\text{Py}$ [22], which reveal that this complex has trigonal bipyramidal structure (III), with NQR data for complexes such as $\text{Me}_3\text{SnBr}\cdot\text{D}$ [3], which show that in $\text{Me}_3\text{SnBr}\cdot\text{DMSO}$ the charge transfer is greater than in $\text{Me}_3\text{SnBr}\cdot\text{Py}$, and with the present PMR data (Table 1), which show that the secondary rehybridisation of electrons in $\text{Me}_3\text{SnHal}\cdot\text{Py}$ complexes is less effective than in the respective complexes with DMF, DMSO and HMPT, indicates that in solutions the regularity of the trigonal bipyramidal structure of the $\text{Me}_3\text{SnHal}\cdot\text{D}$ complexes depends on the strength of donor-acceptor interaction in these complexes. The same may be observed in complexes such as $\text{Me}_2\text{SnHal}_2\cdot 2\text{D}$ and $\text{MeSnHal}_3\cdot 2\text{D}$, which have the structures of regular or slightly distorted octahedra (IV).

We therefore do not believe that $J(^{119}\text{Sn}-\text{C}-^1\text{H})$ values such as 68.0 Hz for $\text{Me}_3\text{SnHal}\cdot\text{D}$ complexes, 108.0 Hz for $\text{Me}_2\text{SnHal}_2\cdot 2\text{D}$ complexes, and 131.0 Hz for $\text{MeSnHal}_3\cdot 2\text{D}$ complexes are the limiting values [10] which characterise the regular structures of trigonal bipyramids and octahedra, respectively. On the contrary, we believe that the stronger the charge transfer in the complexes the more regular are their structures.

Experimental

Constant concentration of methyltin halides (0.35 mol/l) and variable concentrations of electron-donor solvents were used in the study of concentration and temperature dependences of $J(^{119}\text{Sn}-\text{C}-^1\text{H})$. Methylene chloride was used as a dilution medium.

PMR spectra were measured on a JEOL JNM-C-60HL spectrometer (60 MHz). Frequency sweep mode was employed with CH_2Cl_2 as the internal lock. Spin-spin coupling constants were measured accurately to ± 0.2 Hz. The temperature was adjusted by means of a JEOL T-3 controller and was measured accurately to $\pm 2^\circ$.

The synthesis of methyltin halides and purification of solvents were described previously [2].

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