

STUDY OF THE CHEMICAL BOND IN METHYLTIN HALIDE-PYRIDINE COMPLEXES BY PMR SPECTROSCOPY

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INTRODUCTION

Methyltin halides are known to form molecular complexes with organic bases such as pyridine, the composition of which depends on the number of halogens in the alkyltin halide molecule; the complexes, $\text{CH}_3\text{SnCl}_3 \cdot 2 \text{Py}$, (I), $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2 \text{Py}$, (II) and $(\text{CH}_3)_3\text{SnCl} \cdot \text{Py}$, (III) have been described. IR absorption¹ and X-ray diffraction studies² have indicated an octahedral structure, probably with sp^3d^2 hybridization around tin, for (I) and (II). A trigonal bipyramidal structure involving sp^3d hybrid orbitals of tin seems, however, to have been accepted for (III). In many recent investigations, the value of indirect spin-spin coupling constants, $J(\text{Sn}-\text{C}-\text{H})$, in deriving information about the orbital hybridization around the tin nucleus has been demonstrated. All previous investigations have been confined mainly to tetra-coordinated tin and the investigations reported in this paper were undertaken to show that similar useful information can be obtained also for five- and six-coordinated tin.

EXPERIMENTAL

Synthesis of compounds

The $(\text{CH}_3)_3\text{SnX} \cdot \text{Py}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) compounds were obtained by treating liquid $(\text{CH}_3)_3\text{SnX}$ with the stoichiometric amount of pyridine. The resulting solids can be purified by vacuum sublimation at 30° to yield pure white crystals.

The $(\text{CH}_3)_2\text{SnX}_2 \cdot 2 \text{Py}$ and $\text{CH}_3\text{SnX}_3 \cdot 2 \text{Py}$ complexes precipitated when carbon tetrachloride solutions of methyltin halide and pyridine were mixed in the molar ratio of 1 : 2. The stoichiometry of the compounds was confirmed by potentiometric titration of the halogen content of the crystals with standard AgNO_3 solution in water.

Spectra

The spectra were recorded with a V-4300-B spectrometer at 56.44 MHz. TMS was used as an external reference. As most of the shifts observed were rather low we prefer to give them in cps downfield of TMS rather than as τ -values (notation Δ TMS). Δ complex is the chemical shift difference between the complexed and uncomplexed $(\text{CH}_3)_n\text{SnX}_{4-n}$. The tin-proton coupling constants over two bonds with ^{117}Sn and ^{119}Sn are given the symbols $J(\text{Sn}-\text{C}-\text{H})$ (1) and $J(\text{Sn}-\text{C}-\text{H})$ (2), respectively. The results are presented in Tables 1-3. The solubilities of the $\text{CH}_3\text{SnX}_3 \cdot 2 \text{Py}$ complexes

TABLE 1

PMR SPECTRAL PARAMETERS OF SOLUTIONS OF $(CH_3)_nSnX_{4-n} \cdot mPy$ IN $CHCl_3$

X	$(CH_3)_3SnX$			$(CH_3)_3SnX \cdot Py$			Δ complex		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
Δ TMS	37	45	55	37	45	55	0	0	0
$J(Sn-C-H)(1)$	56	56	56	56	56	56	0	0	0
$J(Sn-C-H)(2)$	58.5	58.5	58.5	58.5	58.5	58.5	0	0	0

X	$(CH_3)_2SnX_2$			$(CH_3)_2SnX_2 \cdot 2Py$			Δ complex		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
Δ TMS	70	79	93	79	75	97	+ 9	+ 7	+ 4
$J(Sn-C-H)(1)$	67	63.5	60	87	80	64	+ 20	+ 16.5	+ 4
$J(Sn-C-H)(2)$	69.5	66	63	90	83	67	+ 20.5	+ 17	+ 4

TABLE 2

PMR SPECTRAL PARAMETERS OF $(CH_3)_nSnX_{4-n} \cdot mPy$ IN AQUEOUS SOLUTION

X	$(CH_3)_3SnX$			$(CH_3)_3SnX \cdot Py$			Δ complex		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
Δ TMS	47	34	32	30	30	30	- 17	- 4	- 2
$J(Sn-C-H)(1)$	67.5	67.5	67.5	65	65	65	- 2	- 2	- 2
$J(Sn-C-H)(2)$	70.5	70.5	70.5	68	68	68	- 2	- 2	- 2

X	$(CH_3)_2SnX_2$			$(CH_3)_2SnX_2 \cdot 2Py$			Δ complex		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
Δ TMS	65	58	54	49	49	49	- 16	- 9	- 6
$J(Sn-C-H)(1)$	103	103	103	85	85	85	- 18	- 18	- 18
$J(Sn-C-H)(2)$	108	108	108	89	89	89	- 18	- 18	- 18

in $CHCl_3$, H_2O and pyridine are too low for NMR measurements. Also, the melting points of the compounds, $(CH_3)_2SnX_2 \cdot 2Py$ and $CH_3SnX_3 \cdot Py$, are above 160° so that they could not be studied in the liquid state. The solubility of $(CH_3)_2SnX_2 \cdot 2Py$ in pyridine is insufficient to yield useful NMR spectra. The PMR spectral data for free $(CH_3)_nSnX_{4-n}$ molecules are taken from ref. 3.

DISCUSSION

 $(CH_3)_3SnXPy$ ($X = Cl, Br, I$)

Chloroform solution (Table 1). The NMR data of these complexes in chloroform solution are identical with those of the separate components in the same solvent. An attempt to establish the stoichiometry of the complexes by the Job method by UV absorption spectrometry failed for the same reason. The complex is obviously completely dissociated in this solvent.

TABLE 3

PMR SPECTRAL DATA FOR $(\text{CH}_3)_3\text{SnX}_{4-n} \cdot m\text{Py}$ IN PYRIDINE SOLUTION AND IN THE LIQUID STATE

$(\text{CH}_3)_3\text{SnBr} \cdot \text{Py}$			
	<i>in CHCl₃</i>	<i>in Py</i>	<i>liquid</i>
Δ TMS	45	14	52
$J(\text{Sn}-\text{C}-\text{H})(1)$	56	64	62
$J(\text{Sn}-\text{C}-\text{H})(2)$	58.5	67	65

$(\text{CH}_3)_3\text{SnI} \cdot \text{Py}$			
	<i>in CHCl₃</i>	<i>in Py</i>	<i>liquid</i>
Δ TMS	55	20	62
$J(\text{Sn}-\text{C}-\text{H})(1)$	56	64	62
$J(\text{Sn}-\text{C}-\text{H})(2)$	58.5	67	65

Water solution (Table 2). The chemical shifts as well as the coupling constants of all three complexes are identical, regardless of the halogen. Both parameters are slightly lower than those for the pure trimethyltin halides in water. This could be explained on the assumption that the trimethyltin groups are bonded in a complex ion, $[(\text{CH}_3)_3\text{SnNC}_5\text{H}_5]^+$. Kraus and Greer⁴ have already postulated the formation of such a complex ion to explain the increase of the electrical conductivity of trimethyltin halide solutions in ionizing solvents on the addition of pyridine. On the other hand, it was shown in a previous report⁵ that trimethyltin halides in water ionize to yield the $(\text{CH}_3)_3\text{Sn}^+$ ion, which is weakly hydrated to $[(\text{CH}_3)_3\text{SnH}_2\text{O}]^+$. As pyridine is a better donor than water, the coordinated water will most likely be replaced by pyridine, thus yielding the same complex ion, $[(\text{CH}_3)_3\text{SnNC}_5\text{H}_5]^+$, for all three trimethyltin halide complexes. As pyridine will be bonded more firmly, the Sn-C bonds will have less sp^2 character (which they have in free $(\text{CH}_3)_3\text{Sn}^+$) and more sp^3 character, and the shielding of the protons will be increased. This hypothesis therefore readily explains the slight decrease of $J(\text{Sn}-\text{C}-\text{H})$ and the upfield chemical shifts observed.

$(\text{CH}_3)_3\text{SnX} \cdot \text{Py}$ complexes in the molten state (Table 3). In the liquid state at temperatures well above their melting point, these complexes exhibit NMR spectra that are clearly different from the solution spectra. Both tin-proton coupling constants and chemical shifts are sharply increased and there is a net difference depending on the halogen. The trigonal bipyramidal structure established for $(\text{CH}_3)_3\text{SnCl} \cdot \text{Py}$ has already been mentioned. If the structure in the liquid state is assumed to be the same as in the solid state, then the trend in the PMR spectra data shows that the same structure may be accepted for the bromo- and iodo-derivatives. The changes in the PMR spectral parameters of the trimethyltin group in the pure liquid complexes compared with those for the trimethyltin halides in chloroform solution, should then be ascribed to this change in orbital configuration around tin. Theoretical calculations of Daude⁷ and Bucher⁸ have shown that for atoms with complete lower d -orbitals (e.g. tin), hybridization of one s , three p - and one d -orbital with the same quantum number into sp^3d hybrid orbitals, results in a trigonal bipyramidal configuration. These theoretical considerations are apparently in agreement with the experimental data and therefore support the above assumption. Although the percent s -character in the sp^3d hybrid

orbitals is undoubtedly lower than in sp^3 or sp^2 orbitals, the $J(\text{Sn}-\text{C}-\text{H})$ values have nevertheless increased and it seems that the empirical relations between percent s -character of the central atom, X , and coupling constants, $J(\text{X}-\text{H})$ or $J(\text{X}-\text{C}-\text{H})$, only hold for sp^n -type orbitals. The changes of the chemical shift are less easily interpreted, as the volume susceptibility of the media is quite different.

Pyridine solutions (Table 3). The tin-proton coupling constants of the compounds in pyridine solution are markedly higher than in the liquid state. This is probably due to the fact that at 60–70° there might be a slight dissociation, whereas this should be impossible in pyridine solution. The very drastic change of the chemical shift stems mostly from the bulk susceptibility effect of the pyridine solvent.

$(\text{CH}_3)_2\text{SnX}_2 \cdot 2 \text{Py}$ ($X = \text{Cl}, \text{Br}, \text{I}$)

Chloroform solution. It can be seen in Table 1 that the $J(\text{Sn}-\text{C}-\text{H})$ values as well as the chemical shifts of the complexed dimethyltin compounds are markedly higher than for free $(\text{CH}_3)_2\text{SnX}_2$ in chloroform solution. Also, both parameters tend to increase in the order $\text{I}, \text{Br}, \text{Cl}$. The obvious explanation for these observations is first, that the complex compounds, $(\text{CH}_3)_2\text{SnX}_2 \cdot 2 \text{Py}$, do not dissociate to any appreciable extent in chloroform solution and second, that their stability increases in the order, $\text{I} < \text{Br} < \text{Cl}$. These facts are in sharp contrast to the situation for the $(\text{CH}_3)_3\text{SnX} \cdot \text{Py}$ complexes. A clear picture of these relations is given in Fig. 1.

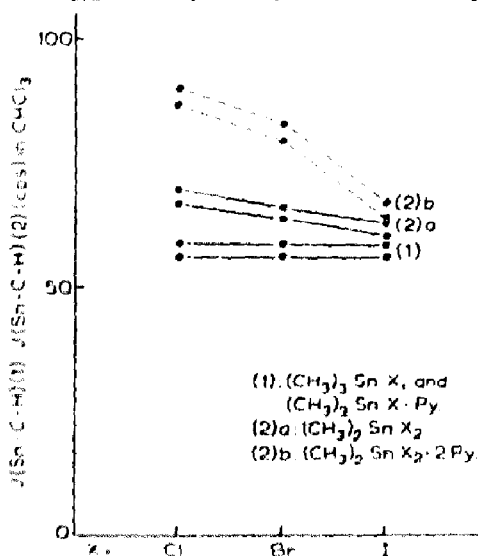


Fig. 1

In a previous paper³ on the PMR spectra of the methyltin halides, $(\text{CH}_3)_n\text{SnX}_{4-n}$ ($X = \text{Cl}, \text{Br}, \text{I}$), we had ascribed the deviation from the additivity relation for the $J(\text{Sn}-\text{C}-\text{H})$ values as a function of n and of the nature of X , in terms of increasing distortion of the atomic orbitals of Sn with increasing number and increasing electronegativity of the substituents. The effect of the electronegative substituents is to increase the effective nuclear charge of the central atom and contract the empty upper d -orbitals of this central atom⁷. The formation of, for example, sp^3d^2 hybrid orbitals then yields atomic hybrid orbitals (of tin) that are sufficiently dense to allow effective overlap with filled orbitals of the ligand (pyridine), to yield a stable complex molecule.

As the *d*-orbital contraction increases with increasing electronegativity of the substituent and with increasing number of these substituents, this hypothesis might also explain the increasing stability of $(\text{CH}_3)_2\text{SnX}_2 \cdot 2 \text{Py}$ in the order $\text{I} < \text{Br} < \text{Cl}$, since it shows why $(\text{CH}_3)_2\text{SnX}_2 \cdot 2 \text{Py}$ molecular complexes should be more stable than the $(\text{CH}_3)_3\text{SnX} \cdot \text{Py}$ complexes.

The question now arises why a dependence of $J(\text{Sn}-\text{C}-\text{H})$ on the nature of X could not be observed for the compounds $(\text{CH}_3)_3\text{SnX} \cdot \text{Py}$, in chloroform solution (no complex formation) or in pyridine solution or in the liquid state at 70° . The answer seems to be that the distortion exerted on the atomic orbitals by only one electronegative substituent is so weak that its effect on physical parameters escapes observation. In fact, tin-proton coupling constants found for the free trimethyltin halides, are the same, regardless of the nature of the halogen. There are also chemical arguments in favour of an increased ligand bond strength in the dimethyltin halide-pyridine complexes. The melting points of the complexes are much higher than for the trimethyltin derivatives and the solubility in polar solvents is lower. The data discussed above show that $J(\text{Sn}-\text{C}-\text{H})$ values for compounds with sp^3d^2 hybridization around tin are higher than those for sp^3d hybridized tin and that in the case of molecular complex compounds the coupling constants can be taken as a measure of the bond strength in the complex. Again, the increase of $J(\text{Sn}-\text{C}-\text{H})$ for sp^3d^n hybridized tin is not proportional to the percent *s*-character of the tin-ligand bonding orbitals as for sp^n hybridized tin.

Water solution. The behaviour of water solutions of $(\text{CH}_3)_2\text{SnX}_2 \cdot 2 \text{Py}$ complexes is completely analogous to that for the $(\text{CH}_3)_3\text{SnX} \cdot \text{Py}$ complexes and the interpretation given for the latter compounds can therefore be assumed to apply for the dimethyl compounds.

General discussion of the relation between $J(\text{Sn}-\text{C}-\text{H})$ and state of hybridization of the tin nucleus

The relation between percent *s*-character of tin orbitals and the tin-proton coupling constant as given by Holmes and Kaesz⁸ and by Van der Kelen⁹ is well known. It is based on the $J(\text{Sn}-\text{C}-\text{H})$ data for $\text{Sn}(\text{CH}_3)_4$, $\text{Sn}(\text{CH}_3)_3^+$ ($(\text{CH}_3)_3\text{SnCl}$ in H_2O), $(\text{CH}_3)_2\text{Sn}^{2+}$ [$(\text{CH}_3)_2\text{SnCl}_2$ in H_2O] and $\text{CH}_3\text{Sn}^{3+}$ (CH_3SnCl_3 in H_2O). The ideas underlying these correlations were based on the isovalent rehybridization theory of Bent¹⁰ and the postulate that the coupling mechanism is governed by Fermi contact interaction. Although this theory is applicable to many data of methyltin compounds, it has been shown that the ions $(\text{CH}_3)_n\text{Sn}^{4-n+}$ are more or less hydrated so that the hybridization state around tin became questionable. This theory can only apply, however, to compounds subject to isovalent rehybridization and therefore would not hold for the complexes studied in this report, where it is shown that sp^3d or sp^3d^2 hybridization around tin is highly probable. A graphical plot of percent *s*-character versus $J(\text{Sn}-\text{C}-\text{H})$ (including the latter compounds together with those cited above) is, therefore, almost linear (Fig. 2). In a theoretical treatment of the electron coupled magnetic spin-spin interaction between X and H over two bonds, characterized by the coupling constant $J(\text{X}-\text{C}-\text{H})$, Klose¹¹ has shown that the coupling constant should be directly proportional to the overlap integrals for the bonds between X and H. The degree of overlap is a function of the direction and concentration of the orbitals. The higher the overlap, the higher the orbital bond strength, and the coupling

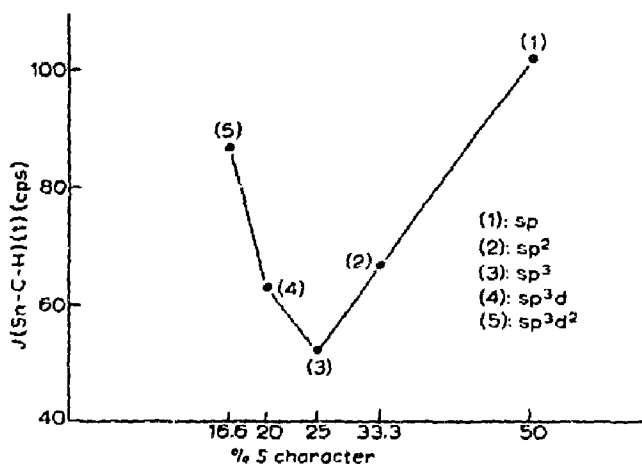


Fig. 2.

constant. Therefore, the values of $J(\text{Sn-C-H})$ in tetravalent tin compounds can be related, through the concept of isovalent rehybridization, with the value of the overlap of the overlap integrals and hence with the bond strength.

Mulliken¹² has shown that, using the proper indices and taking into account the radial as well as the axial energy distribution, the overlap integral for sp^n bonds increases in the sequence $sp^3 < sp^2 < sp$. Although Mullikens' theory was developed for homonuclear bonds between atoms of the first period, it seems reasonable that it should apply also to bonds between atoms of the second and of different periods, the only change being a shift of the whole set of curves (*versus* bond-length) without much change in their mutual position. The bond distances in $(\text{CH}_3)_4\text{Sn}$, $(\text{CH}_3)_3\text{Sn}^+$, $(\text{CH}_3)_2\text{Sn}^{2+}$ and CH_3Sn^+ , regardless of hydration, will certainly be slightly changed as a function of the positive charge of the ion. Nevertheless, it is seen that also in this case, the sequence of increasing values for the overlap integrals would parallel this for the coupling constants. Pauling¹³ has shown that a sp^3 hybrid orbital with a certain amount of d -character, tends to be more concentrated in the bond direction. This means higher overlap, higher bond strength and might also cause higher coupling constants. The data for the methyltin halide-pyridine complexes, showing increasing tin-proton coupling constants with increasing d -orbital contribution, could be explained, qualitatively, in this way.

Consequently, it would probably be more correct to state that the $J(\text{Sn-C-H})$ values are a measure of the tin-carbon bond strength; therefore they are proportional to the percent s -character of the orbitals in sp^n hybrid configurations around tin, but not in sp^3d^n hybrid configurations, the increase in orbital overlap in the latter case being parallel to the increase in orbital bond strength but not with the percent s -character of the orbital.

SUMMARY

In an investigation of the relationship between the Sn-C-H coupling constants and sp^3d , sp^3d^2 orbital hybridization of Sn, the PMR spectra of the pyridine adducts of $(\text{CH}_3)_3\text{SnX}$ and $(\text{CH}_3)_2\text{SnX}_2$ compounds ($X = \text{Cl, Br, I}$) were studied. The relationship between Sn-C-H coupling constants and percent s -character established for

sp^n ($n = 1, 2, 3$) hybridization, does not appear to hold for sp^3d^m ($m = 1, 2$) hybridization states of Sn.

Instead, the increase of the Sn-C-H coupling constants should be directly related with a strengthening of the bondings in the order: $sp^3d^2 > sp^3d > sp^3 < sp^2 < sp$. It was found also that the chlorine substituted complexes are more stable than bromine and iodine substituted complexes in this order. The aqueous solutions of the adducts most probably contain the complex ions, $[(CH_3)_3SnNC_5H_5]^+$ and $[(CH_3)_2Sn(NC_5H_5)_2]^{2+}$.

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