PROTON MAGNETIC RESONANCE AND INFRARED SPECTRAL PARAMETERS FOR THE TIN–HYDROGEN BOND IN SOME ALKYL- AND PHENYLSTANNANES[*]

M. L. MADDOX, N. FLITCROFT AND H. D. KAESZ
Chemistry Department, University of California, Los Angeles, California 90024 (U.S.A.)
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INTRODUCTION

Recent demonstration of increased coordination number of the metal in adducts of alkyltin compounds[1,2], an alkylsilicon compound[3], and the more surprising five-coordinate adducts of aluminum alkyls[4], has prompted us to investigate the same possibility for stannane and the alkylstannanes. Such a change in coordination number would cause changes in the electronic structure around the central metal atom. This would reasonably be expected to result in changes in spectroscopic parameters dependent on these such as the coupling constant between the metal and the protons in magnetic resonance spectra, or the force constant (and the stretching frequency) in infrared absorptions. We have measured both those parameters in alkylstannanes in neat liquid, solutions, and in the presence of potential coordinating agents. We have also investigated the possibility of a regular relationship between these two parameters.

During the course of these studies, which followed our earlier work in this area[5], several reports[6-8] have appeared containing data on alkyl- and arylstannanes; this has been included in our treatment of the data.

EXPERIMENTAL

Organotin halides were prepared from the tetra-alkyl derivative by treatment with $SnCl_2$[9] or by disproportionation with $SnCl_4$[**,11]. The phenyltin chlorides were purchased from M & T Chemicals, Inc. All volatile hydrides were handled on a conventional vacuum line, others under dry and oxygen-free nitrogen. The organotin hydrides were obtained by reduction with aqueous borohydride[12] or by a modification of the method of Finholt[13] *et al.* which deserves special mention as it enabled us to obtain and handle even those hydrides which were reported[14] to be unstable, such as $n\text{-}C_3H_7SnH_3$.

$LiAlH_4$ (2 g) was placed in a nitrogen-filled 50-ml three-necked flask fitted with dropping funnel, magnetic stirrer and vacuum take-off. Anhydrous diethyl ether (10 ml) was added and the mixture stirred for five min. The alkyltin chloride (approx. 2 g)

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[*] Contribution No. 1732.
[**] See for example the review of ref. 10.

in anhydrous diethyl ether (10 ml) was slowly added from a dropping funnel while cooling the flask to —78°. The cooling and stirring were continued for 5–10 min after addition was complete (25–30 min total). Two cold traps (—78° and —196°) were attached in series with the vacuum take-off and vacuum applied. After about 5 min the cooling bath was removed from the reaction mixture and pumping continued until the mixture became dry. The —78° trap was then transferred to a high vacuum line and ether removed from the product by fractional distillation. This method proved satisfactory for the synthesis of the highly unstable[14] n-$C_3H_7SnH_3$ and also iso-$C_3H_7SnH_3$. Samples of these compounds in tubes sealed under vacuum decomposed at room temperature in one day but could be kept for several days at —78°.

Proton magnetic resonances were observed on a Varian A60 spectrometer equipped with a Varian V6040 variable temperature probe (used for measurements on SnH_4 at —50°). Frequencies were calibrated with a Hewlett-Packard 200CD wide-range oscillator and a Hewlett–Packard 5233L electronic counter. For the ethyl and higher alkyl derivatives the coupling constants are accurate to ± 0.3 cps. Spin–spin coupling constants in the stannanes were measured on neat liquids or in diethyl ether solution; chemical shifts were measured in 7 % solution in cyclopentane or diethyl ether using the methyl resonance of toluene (τ = 7.68) or hexamethyldisiloxane (τ = 9.95) as internal reference. Amberger *et al.*[7] have shown that the coupling constants in the series of phenylstannanes are essentially independent of solvent, and we have corroborated this.

Infrared measurements were obtained for cyclohexane solutions on a Perkin-Elmer 421 or on a Beckman IR-4 equipped with LiF optics. Both spectrophotometers were calibrated using the 5.029 and 5.412 micron (1988.5 and 1847.7 cm^{-1}) bands of atmospheric water. The values reported are the average of at least three runs and are accurate to ± 1 cm^{-1}. Matched NaCl cells (0.4 mm thickness) were used for all IR measurements. The results of these studies and related data which have appeared in the literature[11–17] are given in Table 1. Table 2 gives the values of spin–spin coupling constants obtained from approximately 50/50 mixtures by volume of two tin hydrides with various phosphines and an amine.

DISCUSSION

It has been shown[7] that solvent effects alone may cause changes of up to 0.5 % in observed Sn–H coupling constants. It was therefore necessary that changes larger than this must be expected from increased coordination around the tin atom in mixtures of stannanes with donors. We observed no significant change in $J(^{119}Sn–H)$ for mixtures of $(CH_3)_2SnH_2$ with $(CH_3)_2PH$, $[(CH_3)_2PCH_2]_2$ or 2,2′-bipyridine, or for SnH_4 with $(CH_3)_2PH$ at —50° as shown in Table 2 and assume no strong interactions between donor solvent and tin atom exist in these derivatives. Without some positive charge on the tin atom as in the alkyltin chlorides, there is apparently no tendency for the tin atom to attract electron donors. Even the presence of only one chlorine atom seems to give acceptor properties to the tin atom. For instance trimethyltin chloride will form derivatives such as $(CH_3)_3SnCl \cdot$pyridine or the anionic species arising in solutions with $(CH_3)_4N^+Cl^-$ which could be $(CH_3)_3SnCl_2^-$ (five-coordinate) or $[(CH_3)_3SnCl_2]_2^{2-}$ (bridging chlorine atoms, six-coordinate, *cf.* Seyferth and Grim[18]). In these the tin atom has expanded its coordination number and a significant change

TABLE I

PROTON MAGNETIC RESONANCE AND INFRARED SPECTRAL PARAMETERS FOR THE TIN–HYDROGEN BOND IN SOME ALKYL- AND ARYLSTANNANES[a]

Compound	*NMR*					*IR*		
	τ(Sn–H) ppm	*Solvent*[b]	*J(¹¹⁷Sn–H) cps*	*J(¹¹⁹Sn–H) cps*	*Ref. or footnote*	*ν(Sn–H) cm⁻¹*	*Solvent*[b]	*Ref. or footnote*
SnH_4	6.11	CS_2	1842	1933	6	(1906)	n-Bu_2O	6
	6.15	C_5H_{10}	1846	1931	5b	1898	C_6H_{14}	[d]
CH_3SnH_3	5.86	C_5H_{12}	1770	1852	5b	1870	C_6H_{12}	[d]
						1875	Gas(?)	14
$(CH_3)_2SnH_2$	5.55	C_5H_{12}	1717[c]	1797[c]	[d]	1850	C_6H_{12}	[d]
			1717.4	1797.1	8	(1856)		15
$(CH_3)_3SnH$	5.27	C_5H_{12}	1664	1744	5b	1833	C_6H_{12}	[d]
	5.39		1677	1755	[e]			
$C_2H_5SnH_3$	5.66	C_5H_{10}	1710.8	1790.1	[d]	1853	C_6H_{12}	[d]
						(1869)	Gas(?)	14
						(1869)	C_6H_{12}	16
$(C_2H_5)_2SnH_2$	5.25	C_5H_{10}	1616.2	1691.1	[d]	1822	C_6H_{12}	[d], 16
$(C_2H_5)_3SnH$	5.00	C_5H_{10}	1539.9	1611.3	[d]	1797	C_6H_{12}	[d]
						1800	C_6H_{12}	16
n-$C_3H_7SnH_3$	5.83	Et_2O	1710.5	1790.2	[d]	1860	C_6H_{12}	[d]
$(n$-$C_3H_7)_2SnH_2$	5.48	neat	1614.7	1689.4	[d]	1833	C_6H_{12}	[d]
$(n$-$C_3H_7)_3SnH$	5.21	neat	1533.5	1605.0	[d]	1811	C_6H_{12}	[d]
			1530	1600	6	1795	n-Bu_2O	6
						1820		17
iso-$C_3H_7SnH_3$	5.46	Et_2O	1672.5	1750.0	[d]	1853	C_6H_{12}	[d]
(iso-$C_3H_7)_2SnH_2$	5.07	C_5H_{10}	1540.3	1612.1	[d]	1820	C_6H_{12}	[d]
(iso-$C_3H_7)_3SnH$	4.82	C_5H_{10}	1439.4	1505.8	[d]	1794	C_6H_{12}	[d]
n-$C_4H_9SnH_3$	5.98	CS_2	1720	1800	6	1865	n-Bu_2O	6
			1716.5	1796.1	[d]	1862	C_6H_{12}	[d]
						1855	C_6H_{12}	16
$(n$-$C_4H_9)_2SnH_2$	5.23	CS_2	(2119)	(2219)	6	1842	n-Bu_2O	6
			1618.6	1639.9	[d]	1835	C_6H_{12}	[d], 16
$(n$-$C_4H_9)_3SnH$	(7.93)	CS_2	(1650)	(1722)	6	1808	n-Bu_2O	6
	5.22		1532	1609	[e]	(1820)		17
			1539.0	1610.6	[d]	1813	C_6H_{12}	[d]
$C_6H_5SnH_3$	4.98	Et_2O	1836.7	1921.5	7	1880	C_6H_{12}	16
$(C_6H_5)_2SnH_2$	3.98	Et_2O	1842.0	1927.8	7	1855	C_6H_{12}	16
$(C_6H_5)_3SnH$	3.16	Et_2O	1850.8	1935.8	7	1843	C_6H_{12}	[d]

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[a] We considered some data less reliable since they differed widely from the numerical analysis presented in the text; these have been placed in parentheses. [b] Solvents: Et_2O, diethyl ether; n-Bu_2O, dibutyl ether; C_5H_{10}, cyclopentane; C_5H_{12}, neopentane; C_6H_{12}, cyclohexane; C_6H_{14}, n-hexane. [c] The measurements in the methylstannanes reported earlier[5b], were repeated using improved calibration as described in the experimental section, following a slight disagreement (3%) with data on $(CH_3)_2SnH_2$ published later[8]. The earlier coupling constants for dimethylstannane were in fact too low; the present values agree well with the later published ones[8]. However, the earlier published coupling constants for stannane and the other methylstannanes[5b] are correct as reported. Apparently there was an error only for the value of the one derivative. [d] This work. [e] H. C. CLARK and L. W. REEVES, University of British Columbia, personal communication.

in coupling constant (Sn–CH_3) is observed. These values and that for neat trimethyltin chloride are presented in Table 3.

Coupling constant and stretching frequency in Sn–H bonds

It has previously been suggested[5], that the trends in the coupling constants of the tin-bonded proton(s) to active isotopes of tin and to other protons in the methylstannanes could be explained by changes in the hybridisation of the heavy metal atom. While investigating these trends in other alkyl stannanes other work has appeared[6,7,8] containing relevant data (included in condensed form in Table 1) but with no indication of any underlying relationship between stretching frequency and chemical shift and/or coupling constant for the SnH moiety as the number and type of the substituent is varied. This was surprising since it would be expected that by attaching groups of varying electronegativity to the tin atom, second order changes in hydridisation would occur which would affect both J(Sn–H) and ν(Sn–H) in a small though regular manner. In Table 1 our own data are presented as well as the data from several other sources. We have discovered that some useful relationships appear.

We note a good linear relationship between $J(^{119}\text{Sn–H})$ and ν(Sn–H) for each of the series of alkyl-substituted stannanes, R_nSnH_{4-n}, shown in Fig. 1, using a least squares process to obtain the slopes and intercepts of these lines, given on the left hand side of Table 4. Furthermore, we observed that these parameters are linearly related to σ^* functions of the attached group by the relationship:

$$\nu(\text{SnH}) = 946.2 - 707.1\,\sigma^* + (0.4947 + 0.3691\,\sigma^*)\,J(^{119}\text{SnH}) \qquad (1)$$

The parameters of the straight lines (Fig. 1 and Table 4) may thus be calculated from the σ^* values for each series of alkylstannanes, and these are shown on the right hand side of Table 4.

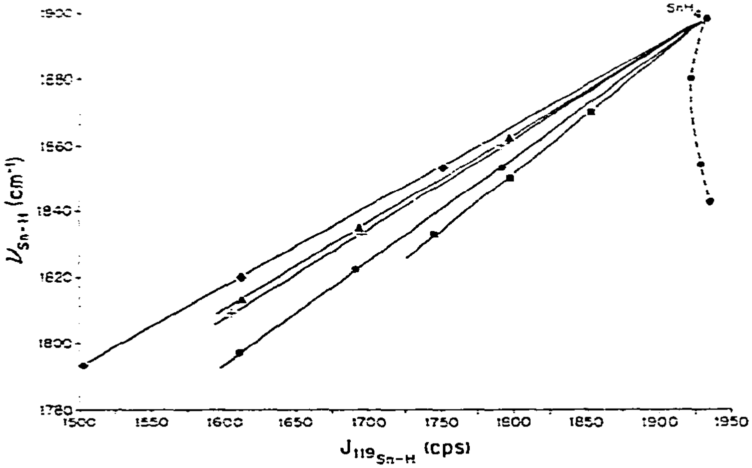

Fig. 1. Coupling constant (cps) and stretching frequency (cm^{-1}) for the Sn–H bond in SnH_4 and in some alkyl- and phenylstannanes: ■, CH_3; ●, C_2H_5; +, n-C_3H_7; ◆, iso-C_3H_7; ▲, n-C_4H_9; ---●---, C_6H_5; the equations for the straight lines are given in Table 4. Starting from the upper right at SnH_4, each of the points within the series going down to the lower left represents increasing number of alkyl groups, such as, $RSnH_3$, R_2SnH_2 and R_3SnH, respectively.

TABLE 2

Sn–H SPIN–SPIN COUPLING CONSTANTS FOR MIXTURES OF TIN HYDRIDES AND DONOR MOLECULES[a]

Sample	$J(^{117}Sn\text{–}H)$ (*cps*)	$J(^{119}Sn\text{–}H)$ (*cps*)
$SnH_4/(CH_3)_2PH$	1845	1931
$(CH_3)_2SnH_2/(CH_3)_2PH$	1714	1794
$(CH_3)_2SnH_2/[(CH_3)_2PCH_2]_2$	1708	1786
$(CH_3)_2SnH_2$/2,2′-bipyridine	1718	1798

[a] All mixtures approx. 50/50 by volume.

TABLE 3

$Sn\text{–}CH_3$ SPIN–SPIN COUPLING CONSTANTS IN TRIMETHYLTIN CHLORIDE AND ITS ADDUCTS CONTAINING INCREASED COORDINATION NUMBER FOR TIN

Sample	$J(^{117}Sn\text{-}CH_3)$ (*cps*)	$J(^{119}Sn\text{-}CH_3)$ (*cps*)	*Temp.* (°*C*)
$(CH_3)_3SnCl$[a]	57.4	59.7	40
$(CH_3)_3SnCl \cdot H_2O$[b]	65.2	68.4	31
$(CH_3)_3SnCl \cdot$ pyridine	64.2[c]	67.0[c]	50
	62.3[d]	65.2[d]	31
$(CH_3)_3SnCl \cdot (CH_3)_4NCl$[e]	64.9	67.9	31

[a] Neat liquid, *cf.* ref. 5a; approximately the same values are obtained in CCl_4 or benzene solutions. [b] *Cf.* ref. 5a. [c] Neat liquid; this work. [d] CCl_4 solution; this work. [e] 33% by weight of each reagent in aqueous solution; this work.

TABLE 4

LEAST SQUARES PARAMETERS FOR RELATIONSHIP BETWEEN rSnH AND $J(^{119}SnH)$ AND CALCULATED PARAMETERS FROM σ^* VALUE OF ALKYL GROUP IN ALKYL STANNANES[a]

Series	*Observed*		σ^{*b}	*Calculated*[c]	
	A (*cm*$^{-1}$/*cps*)	*B* (*cm*$^{-1}$)		*A* (*cm*$^{-1}$/*cps*)	*B* (*cm*$^{-1}$)
Me_nSnH_{4-n}	0.3477	1226.	−0.49	0.313_9[d]	$1292._7$[d]
Et_nSnH_{4-n}	0.3149	1289.5	−0.59	0.276_9[d]	$1363._4$[d]
$n\text{-}Pr_nSnH_{4-n}$	0.2714	1373.9	−0.605	0.271_4	$1374._0$
$n\text{-}Bu_nSnH_{4-n}$	0.2045	1387.0	−0.62	0.265_3	$1387._6$
iso-Pr_nSnH_{4-n}	0.2437	1427.0	−0.68	0.243_7	$1427._0$

[a] To fit the equation $r(SnH) = A \times J(^{119}SnH) + B$. [b] See ref. 22. [c] See equation (1) in text. [d] Although the calculated slope and intercept do not agree well, the calculated values of r(SnH) are acceptable.

The agreement between observed and calculated values is good to about 1 % in the methyl and ethyl series and 0.2 % in the higher series. These linear relationships first led us to believe that the earlier reported results for two of the butylstannanes[6] were incorrect which was borne out in our subsequent re-investigations shown in Table 1. The accuracy of the correlation between the straight line parameters and the σ^* values is limited by the latter, which are known only to 1 %. This is of course much cruder than our knowledge of stretching frequencies and coupling constants. Even so, equation (1) is still not valid for the phenylstannanes. We feel that this is due to some effects not covered by σ^*. Further work is necessary to clarify this point.

Sn–H coupling constant and the number of substituents in substituted stannanes

For all alkyl-substituted stannanes, the affect of progressively substituting alkyl groups for H on the coupling $J(^{119}\text{Sn–H})$ in SnH_4 is not strictly additive. The coupling for all R_2SnH_2 compounds deviates from the extrapolated SnH_4 to $RSnH_3$ straight line; the coupling for all R_3SnH compounds shows even more deviation. Non-additivity of substituent effects on the coupling constants has been observed in several other instances[19].

One effect for the methylstannanes which has been reported previously has been invalidated; with improved data, the alternation in the change in coupling constants[5b] disappears. However, there is a very definite discontinuity in the change of coupling constant from SnH_4 in the phenylstannanes[7]. There is no doubt that there is a significant difference between these and the alkyl derivatives.

CONCLUSION

Proton magnetic resonance measurements do not indicate any strong donor–acceptor interaction between amines or phosphines and stannane or the alkylstannanes.

The infrared stretching frequency and coupling constants in the Sn–H bond in the alkylstannanes can be correlated with properties of the alkyl groups. These correlations will probably be of most use as a practical guide to the interpretation of the NMR and IR spectra of a wide variety of stannanes. With increasing availability of instruments for the infrared region 900–300 cm^{-1} it should be possible to extend these studies to the Sn–H deformation modes. These by analogy to other systems[20] will probably appear more sensitive to changes in substituents, and might give more meaningful correlations.

It was beyond the scope of the present work to consider any possible regularities in the chemical shift in the present series of derivatives. We have learned, however, of such a study, which was independently motivated, by Kawasaki, Kawakami, Tanaka and Okawara[21] during the preparation of our manuscript.

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SUMMARY

The possibility of donor–acceptor interaction between amines or phosphines and stannane or the alkylstannanes is investigated by proton magnetic resonance; present evidence is in the negative for a strong interaction. A correlation between Sn–H coupling constant and Sn–H stretching frequency and the properties of alkyl groups in alkylstannanes is proposed.

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