On the Sn–H Bond in Some Organotin Hydrides

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Many investigations have been carried out with organometallic compounds by the method of nuclear magnetic resonance in order to study the effect of alkyl groups on the shielding of a metal nucleus or of hydrogen bound directly to a metal. The effect of the alkyl group in trialkylsilane or dialkylmercury has been found to be somewhat complicated. In the case of dialkylmercury,[1] the effect of the alkyl group on the shielding of the ^{199}Hg nucleus cannot be explained by a simple mechanism, such as the inductive or the hyperconjugation effect. It has been found that the apparent shielding of the ^{199}Hg nucleus is a function of the number of the β protons of the alkyl group; the shielding increases in the order $CH_3 < n\text{-}C_3H_7 < C_2H_5 < i\text{-}C_3H_7$, and the spin-spin coupling of the ^{199}Hg nucleus with the β protons was greater than that of the α protons or γ protons. The same effect of the alkyl group was found on the shielding of the (Si–)H proton in the trialkylsilane.[2] On the contrary, however, in trialkylphosphines[3] the shielding value of the ^{31}P nucleus decreases with an increase in the number of the β protons of the alkyl group.

In the case of dialkyltin dichloride, the increasing shielding value of the ^{119}Sn nucleus has been reported[4] to be $n\text{-}C_4H_9 < C_2H_5 < CH_3$. This order is different from that of the dialkylmercury or trialkylsilane. In the NMR spectrum of alkyltin compounds, therefore, hyperconjugation seems to be a predominant factor. In order to clarify the effect of the alkyl group in the alkyltin compounds, we studied the proton magnetic resonance and the infrared spectra of the Sn–H bond of some alkyltin hydrides.

Experimental

Material.—All the organotin hydrides were prepared from the corresponding chlorides by reduction with lithium aluminum hydride in ethyl ether or in dioxane. The chlorides were kindly supplied by the Nitto Kasei Co., Ltd. The properties of the alkyltin hydrides used in our experiments are given in Table I.

Nuclear Magnetic Resonance Spectra. — The measurements were made at a fixed frequency of 60 Mc./sec. on two spectrometers, a Varian model

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[1] R. E. Dessy, T. J. Flautt, H. H. Jaffe and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).

[2] D. E. Webster, *J. Chem. Soc.*, **1960**, 5132.

[3] W. A. Henderson and S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 5794 (1960).

[4] J. J. Burke and P. C. Lauterbur, ibid., **83**, 320 (1961).

Table I. Boiling points and analyses

	Boiling point, °C/mmHg		Anal. Calcd., %			Anal. Found, %		
			Sn	C	H	Sn	C	H
$(CH_3)_3SnH$	59—61/760	(59/760)*						
$(C_2H_5)_3SnH$	73—75/72	(79—81/92)**		34.83	7.80		34.87	7.10
$(n\text{-}C_3H_7)_3SnH$	108—109/37	(80—81/12)**		43.41	8.90		44.18	9.08
$(n\text{-}C_4H_9)_3SnH$	112.5—113.5/8	(76/0.7 81/0.9)**	40.78	49.52	9.69	40.25	49.44	9.41
$(i\text{-}C_3H_7)_3SnH$	68—69/16			43.41	8.90		43.23	8.90
$(C_6H_5)_3SnH$	177.5—178.5/2	(168—170/0.5)**	33.81	61.59	4.60	33.87	61.25	4.69
$(n\text{-}C_3H_7)_2SnH_2$	46.5—47.5/35	(39—40.5/12)**						
$(n\text{-}C_4H_9)_2SnH_2$	61—62/7	(75—76/12)**		40.93	8.58		41.01	8.53
$n\text{-}C_4H_9SnH_3$		(99—101)**						

* A. E. Finholt, A. C. Bond and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

** J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute Utrecht (1958).

Table II. The nuclear magnetic resonance shielding value for Sn-H proton (τ value) in organotin hydrides

	$RSnH_3$		R_2SnH_2		R_3SnH	
	τ Sn-H	Solvent	τ Sn-H	Solvent	τ Sn-H	Solvent
R=H	6.11[*1]	a				
	6.15[7)]	b				
CH_3			5.55[*2]	c	5.36	a
	5.86[7)]	c	5.24[7)]	c	5.27[7)]	c
C_2H_5					5.24	a
	5.66[*2]	b	5.25[*2]	b	5.00[*2]	b
$n\text{-}C_3H_7$			5.42	a	5.23	a
$n\text{-}C_4H_9$	5.71	a	5.43	a	5.22	a
	5.98[*1]	a	5.23[*1]	a	7.93[*1]	a
$i\text{-}C_3H_7$					4.85	a
			5.07[*2]	b	4.82[*1]	b
C_6H_5					3.03	a
	4.98[*3]	d	3.98[*3]	d	3.16[*3]	d

[*1] P. E. Potter, L. Platt and G. Wilkinson, *J. Chem. Soc.*, **1964**, 524.

[*2] N. Flitcroft and H. D. Kaesz, Private Communication.

[*3] E. Amberger, H. P. Fritz, C. G. Kreiter and M. Kula, *Chem. Ber.*, **96**, 3270 (1963).

a) Carbon disulfide b) Cyclopentane c) Neopentane d) Diethylether

A-60 and a Japan Electron Optical Laboratory Co., Ltd., model 3H-60. Carbon disulfide was used as the solvent and the tetramethylsilane as the internal standard throughout. Measurements in a cyclohexane solution or in a neat liquid were also carried out in order to check the solvent effect.* The sample with a 2—10% concentration and with 1% tetramethylsilane was mixed in a Pyrex tube 5 mm. in diameter. The temperature was maintained at 20°C. The position of the peak was measured to the nearest 0.1 cycle/sec., the average of at least two determinations being used for each value recorded.

Infrared Absorption Spectra.—The infrared spectra were recorded by using a Perkin-Elmer (model 21) double-beam spectrophotometer equipped with sodium chloride optics, or a Hitachi EPI-2G infrared spectrophotometer equipped with gratings. The neat sample was used, and all spectra were calibrated by using known peaks of a polystyrene film.

Results and Discussion

The observed shielding values, in parts per million (p. p. m.), of the resonance of the proton attached directly to the tin atom in various organotin hydrides are shown in Table II together with the values in the literature. The results show that the shielding of the (Sn-)H proton increases in the order of $i\text{-}C_3H_7 < n\text{-}C_4H_9 \simeq n\text{-}C_3H_7 \simeq C_2H_5 < CH_3$ in trialkyltin hydrides. These results may be interpreted by considering such contributions as that of II in the ground state of the molecule, in which a considerable amount of d_π-p_π bonding may take part:

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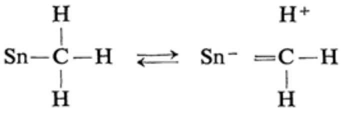
* Carbon tetrachloride, a usual solvent in the proton magnetic resonance measurement. cannot be used because of its reactivity toward organotinhydrides (D. H. Lorenz and E. I. Becker, *J. Org. Chem.*, **27**, 3370 (1962)).

TABLE III. THE INFRARED SPECTRA OF THE Sn-H STRETCHING VIBRATIONS: POSITIONS OF BANDS (in cm^{-1})

	$RSnH_3$		R_2SnH_2		R_2SnH	
	ν Sn-H	Solvent	ν Sn-H	Solvent	ν Sn-H	Solvent
R=H	1906[*1]	a				
	1898[*2]	b				
CH_3	1876[*4]		1858		1830	
	1870[*2]	c	1845[*2]	c	1833[*2]	c
C_2H_5	1869[*4]				1809	
	1869[*4]	c	1822[*3]	c	1800[*3]	c
n-C_3H_7			1835		1809	
			1835[*5]		1820[*5]	
			1842[*1]	a	1795[*1]	a
n-C_4H_9	1870		1832		1807	
	1865[*1]	a	1842[*1]	a	1808[*1]	a
	1855[*3]	c	1835[*3]	c	1820[*5]	
i-C_3H_7					1792	
			1820[*2]	c	1792[*2]	c
C_6H_5					1838	
	1880[*3]	c	1855[*3]	c	1843[*3]	c

[*1] P. E. Potter, L. Platt and G. Wilkinson, *J. Chem. Soc.*, **1964**, 524.
[*2] N. Flitcroft and H. D. Kaesz, Private Communication.
[*3] E. Amberger, H. P. Fritz, C. G. Kreiter and M. Kula, *Chem. Ber.*, **96**, 3270 (1963).
[*4] H. J. Emeleus and S. F. A. Kettle, *J. Chem. Soc.*, **1958**, 2444.
[*5] R. Mathis-Noel, M. Lesbre and I. S. de Roche, *Compt. rend.*, **243**, 257 (1956).
a) Di-*n*-butylether b) *n*-Hexane c) Cyclohexane



$$\mathrm{Sn-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H \rightleftarrows Sn^-\ =\overset{\displaystyle H^+}{\underset{\displaystyle H}{C}}-H}$$

(I) (II)

Thus, the Sn-C bond would be strengthened, the electron density on the proton bound directly to the tin atom may be increased, and at the same time the Sn-H bond would probably be strengthened. Support for this explanation is found in the recent thermochemical data.[5] The mean dissociation energy, $\bar{D}$(Sn-C), in the tetraalkyltin increases as follows; $C_2H_5 \simeq n\text{-}C_4H_9 \simeq n\text{-}C_3H_7 < CH_3$, which is almost consistent with the above explanation. This order found in organotin hydrides is different from that of the trialkylsilane or dialkylmercury, as has been described already. The low-lying vacant d-orbitals which can accept electrons from the alkyl group through the d_π-p_π bonding are not very different in the tin atom and the silicon atom, although they are a little lower in the former than in the latter. It is not clear why the effect of the hyperconjugation is a predominant factor in the alkyltin hydride but not in the alkylsilane. The τ value in triphenyltin hydride is smaller than that in trialkyltin hydrides; this may be explained in terms of the electronegativity of the phenyl group.[2] The ring current of the phenyl group may also play a role.

In the shielding of the protons bound directly to the tin atom, the successive replacement of the hydrogen of the SnH_4 molecule by an alkyl group results in a progressive decrease in the τ value, as Table II shows. This tendency is smilar to those in hydrocarbons and might have some correlation with the dissociation energy of the carbon and hydrogen concerned, for some electronic strain may be accumulated on the C-H bond by the replacement of the hydrogen with the alkyl group. The dissociation energies of several kinds of C-H bonds are as follows; $\bar{D}$(C-H) = 101, 96, 94 and 89 kcal./mol. for CH_3-H, CH_3CH_2-H, $(CH_3)_2CH$-H and $(CH_3)_3C$-H respectively.[6] The result is parallel to the τ value of the corresponding proton. The same might be true in the alkyltin hydrides. The difference in the τ value of the (Sn-)H or (C-)H protons cannot be explained by the difference in the electronegativities of the tin atom and the carbon atom; for example, the τ values in the $(CH_3)_3XH$ molecule decrease independently of the electronegativity of the X atom; (X-)H=8.46, 6.15, 5.36 and 2.32[7] for

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[5] J. V. Davies, A. B. Pofe and H. A. Skinner, *Trans. Faraday Soc.*, 59, 2233 (1963).

[6] L. L. Cottrell, "The Strength of Chemical Bonds," Butterworths Scientific Publication London, (1958).

[7] N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, 85, 1377 (1963).

X=C, Si, Sn and Pb respectively. One factor which influences these τ values may be the paramagnetic effect of the central atom X, for the paramagnetic effect seems to increase with an increase in the atomic number.

The frequencies of the Sn-H stretching vibration in the infrared absorption spectra of the alkyltin hydrides are given in Table III, together with the values reported in the literature. In the trialkyltin hydride, the positions of the Sn-H stretching vibration bands are in the order of $i\text{-}C_3H_7 < n\text{-}C_4H_9 \simeq n\text{-}C_3H_7 \simeq C_2H_5 < CH_3$, paralleling the order in the nuclear magnetic resonance spectra. This will support the assumption of the hyperconjugation of the alkyl group, which increases the overlap charge between the tin atom and the hydrogen atom. The position of the Sn-H stretching band in triphenyltin hydride, however, is exceptional, as it is in the case of the silicone analogues. In the dialkyltin or monoalkyltin hydride, only one Sn-H stretching band was found,* although two bands may be predicted from the selection rule. This might be due to the overlapping of the two kinds of Sn-H stretching bands as a result of a relatively small coupling between Sn-H vibrations. The Sn-H stretching band in the dialkyltin or monoalkyltin hydride shifts to a wave number relatively higher than that of the trialkyltin hydride. This tendency is parallel to that of the τ value.

Summary

The nuclear magnetic resonance spectra of the proton attached directly to the tin atom in several organotin hydrides (R_nSnH_{4-n}; $n=1, 2, 3$) have been measured. The observed shielding values increase in the order of $i\text{-}C_3H_7 < n\text{-}C_4H_9 \simeq n\text{-}C_3H_7 \simeq C_2H_5 < CH_3$ in trialkyltin hydrides. This order is consistent with that of the hyperconjugation effect of the alkyl group. On the other hand, the change in the shielding of the protons bound directly to the tin atom with a step-by-step substitution of SnH_4 by an alkyl group is similar to that of hydrocarbons or alkylsilanes. The infrared spectra of organotin hydrides show that there is a close correlation between the τ values and the Sn-H stretching frequencies.

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* H. C. Clark et. al. have reported a doublet, but others do not (see Tables III).