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NMR and IR studies of dialkyltin halide hydrides

In order to obtain information on tin–hydrogen bonding, organotin hydrides have been studied spectroscopically by several groups[1-7].

Diorganotin chloride hydrides were reported for the first time in 1961[8], and the chemical shifts of the proton attached directly to the tin atom and the frequencies of Sn–H bonding of di-n-butyltin halide hydrides were measured by Sawyer *et al.*[9]. On the other hand, their use in synthesis was reported by Neumann and Pedain[10].

In this paper we report the NMR and IR data of dialkyltin halide hydrides and discuss the influence of halogen substituents on the spectral parameters with reference to the case of the organotin hydrides.

Table 1 shows the observed values for the chemical shift of the proton attached directly to the tin atom, the spin–spin coupling constants, $J(^{117}\text{Sn–H})$ and $J(^{119}\text{Sn–H})$ and the stretching frequencies for a series of dialkyltin halide hydrides and, for comparison, the values found in the literature for dialkyltin dihydrides.

Sawyer, Brown and Hanson[9] have reported τ(Sn–H) and ν(Sn–H) values (included in Table 1) for di-n-butyltin halide hydrides. Although a slight difference is found between their data and ours, this is not a serious one and may be due to the fact that they obtained their data on neat compounds while we made measurements in 20 mole % cyclohexane solutions.

For the first row elements in the periodic table, Bent[12] proposed a theory that for electropositive substituents, the hybrid orbitals of the central atom increase in *s*-character. The *s*-character of the bonding orbital determines the Fermi contact term, which, in turn, decides the values of coupling constants. Thus, the coupling constant $J(^{13}\text{C–H})$ reflects very well the changes of the hybridization of the C-atom[13]. This idea was extended to organotin compounds and has been used to estimate the rehybridization effect of the tin atom[14]. Organotin hydrides in particular, were studied systematically in this way and the spectral parameters were tabulated by Maddox, Flitcroft and Kaesz[5].

As Table 1 shows, regular changes occur in the coupling constants, $J(^{117}\text{Sn–H})$ and $J(^{119}\text{Sn–H})$ for a series of dialkyltin halide hydrides. For instance in R_2SnHX they increase in the order of X = H, I, Br and Cl. If one changes the alkyl groups R for a given X, then the coupling constants increase from isopropyl to methyl. In Fig. 1 is given the correlation between the coupling constant $J(^{119}\text{Sn–H})$ and the sum of the Taft's σ^* constants of all R and X for the various types of organotin hydride. This correlation reflects the σ type electron withdrawing power, and shows qualitatively good relationships between these two values. Table 1 shows that the same correlation is observed for the values of the Sn–H stretching frequencies.

In the previous paper we proposed that for the case of trialkyltin hydrides, the p_π–d_π interaction was the predominant factor influencing τ values of the protons bound directly to the tin atom[7]. In the case of dialkyltin halide hydrides τ(Sn–H) decreases as the electronegativities of halogen atoms increase, for instance, for the methyltin compounds, 5.55, 3.92, 3.31 and 2.88 for X = H, I, Br and Cl respectively. On the other hand the τ(Sn–H) values increase as the electron withdrawing powers of alkyl groups increase. Thus, dimethyltin halide hydrides show the largest τ(Sn–H)

TABLE 1

NMR AND IR SPECTRAL DATA AND THE SUM OF TAFT'S σ^* CONSTANTS FOR DIALKYLTIN HALIDE HYDRIDES R_2SnHX

R	*X*	σ^*	$\tau(Sn\text{-}H)$ (ppm)	$\nu(Sn\text{-}H)^c$ (cm^{-1})	$J(^{117}Sn\text{-}H)$ (cps)	$J(^{119}Sn\text{-}H)$ (cps)	$\frac{J(^{119}Sn\text{-}H)}{J(^{117}Sn\text{-}H)}$	*Solvent*^{c}
CH_3	H^a	0.98	5.55	1850	1717	1797	1.046	neopentane
	I	2.87	3.92	1862	2032	2128	1.047	
	Br	3.29	3.31	1874	2082	2178	1.046	
	Cl	3.43	2.88	1877	2128	2228	1.047	
C_2H_5	H^a	0.78	5.25	1822	1612	1691	1.047	cyclopentane
	I	2.67	3.79	1843	1823	1908	1.047	
	Br	3.09	3.18					
	Cl	3.23	2.67	1859	1940	2031	1.047	
n-C_3H_7	H^a	0.75	5.42	1833	1615	1689	1.046	neat
	I	2.64	3.63	1841	1836	1926	1.049	
	Br	3.06	3.15	1844	1862	1954	1.049	
	Cl	3.20	2.68	1852	1914	2002	1.046	
n-C_4H_9	H^a	0.71	5.43	1835^d	1619	1690	1.044	CS_2
	I^b	2.60	3.92	1836				neat
	I		3.85	1838	1817	1902	1.047	
	Br^b	3.02	2.91	1847				neat
	Br		3.13	1845	1875	1964	1.047	
	Cl^b	3.16	2.58	1853				neat
	Cl		2.69	1852	1890	1983	1.049	neat
	Cl		2.66	1855	1911	2002	1.048	
	Cl		2.69	1845	1956	2045	1.046	$(C_2H_5)_2O$
	Cl		2.90	1835	2019	2113	1.047	THT^e
	Cl		2.78	1852	2049	2145	1.047	dioxane
	Cl		2.80	1848	2108	2208	1.047	THF
	F^b	3.30	2.44	1875				methanol
iso-C_3H_7	H^a	0.60	5.07	1820^d	1540	1612	1.047	cyclopentane
	I	2.49	3.56	1830	1663	1736	1.044	
	Br	2.91	3.13	1830	1706	1786	1.047	
	Cl	3.05	2.70	1830	1745	1828	1.046	

[a] Ref. 5. [b] Ref. 9. [c] 20 mole % cyclohexane solution unless otherwise noted. [d] Cyclohexane solution. [e] Tetrahydrothiophene.

values and diisopropyltin analogues the smallest values, although the differences are small in the cases of dialkyltin bromide hydrides and chloride hydrides. This is the reverse of the trend expected on the basis of electron withdrawing power of alkyl groups. This experimental result suggests to us that the hyperconjugation between methyl groups and the tin atom also plays the predominant role in determining τ(Sn–H) values in a series of dialkyltin halide hydrides.

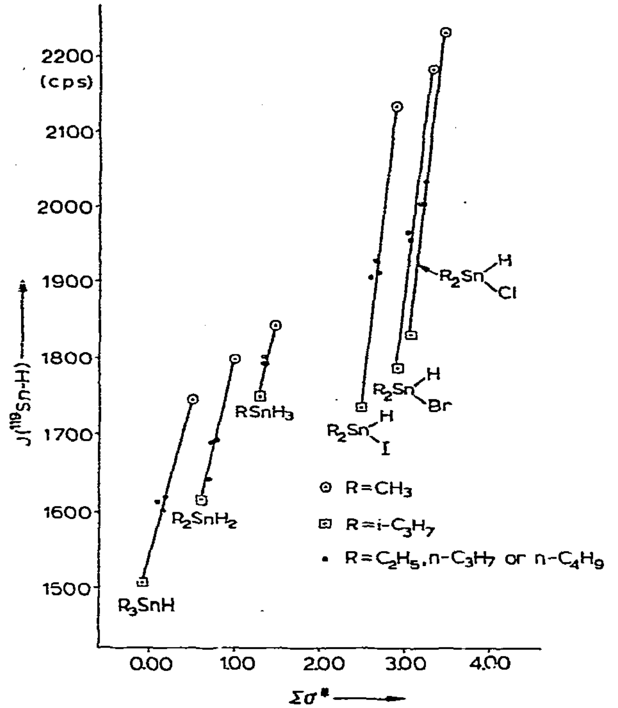
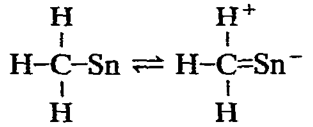


Fig. 1. The correlation between $J(^{119}Sn\text{–}H)$ and the sum of Taft's σ^* constants of all substituents for various organotin hydrides.



$$\begin{array}{ccc} \mathrm{H} & & \mathrm{H^+} \\ | & & | \\ \mathrm{H{-}C{-}Sn} & \rightleftharpoons & \mathrm{H{-}C{=}Sn^-} \\ | & & | \\ \mathrm{H} & & \mathrm{H} \end{array}$$

Acceptor property of dialkyltin halide hydride

It has been shown that for the case of organotin hydrides solvent effects alone may cause changes up to 0.5% in observed Sn–H coupling constants[3]. As shown in Table 1, we have observed significant changes (up to 10%) in $J(^{119}Sn\text{–}H)$ for di-n-butyltin chloride hydride in such polar solvents as tetrahydrofuran, dioxane, diethyl ether and tetrahydrothiophene. These data confirm the strong interactions between donor atoms of solvent molecules and the tin atom in di-n-butyltin chloride hydride. Even the presence of only one chlorine atom gives an acceptor property to the tin atom. Trimethyltin chloride pyridine adduct is a well characterized example of this tendency[15].

Because of this tendency, we could not obtain NMR data in solvents which contained nitrogen atoms. Pyridine, for instance, decomposed the dialkyltin halide hydrides to 1,2-dichlorotetraalkylditins. Amines generally caused this decomposition.

Experimental

Dialkyltin halide hydrides R_2SnHX were prepared by mixing dialkyltin dihydrides and dialkyltin dihalides. Dialkyltin dichlorides were prepared by disproportionation reactions between tetraalkyltin and $SnCl_4$, dialkyltin dibromides from dialkyltin oxides and hydrobromic acid and dialkyltin diiodide by the reaction of dialkyltin dichlorides with sodium iodide in acetone.

In the case of isopropyltin derivatives, the disproportionation reaction gave very low yields of diisopropyltin dichloride. Therefore we prepared diisopropyltin diiodide by the direct method of Matsuda *et al.*[11], which deserves special mention, because it is a convenient method to obtain diisopropyltin derivatives in good yield.

Tin leaf (50 g, 0.42 mole) and isopropyl iodide (178 g, 1.01 mole) were heated at reflux temperature for 3 h with a small amount of magnesium turnings and n-butanol (10 g) as catalysts. After filtration, the reaction mixture was distilled to give diisopropyltin diiodide, (115 g, 60%), b.p. 145–147°/17 mmHg. The chloride and bromide were prepared from the corresponding acids and the oxide obtained by the reaction of the iodide with aqueous ammonia.

Proton magnetic resonance spectra were obtained at 60 Mc. on a Japan Electron Optics Co. Ltd. model 3H-60 spectrometer. All dialkyltin halide hydrides were measured in 20 mole % cyclohexane solution with about 1 vol. % of tetramethylsilane as the internal reference. Methyltin derivatives were handled in a conventional vacuum line and other compounds in an atmosphere of dry nitrogen.

Infrared spectra were obtained in 20 mole % cyclohexane solutions on a Hitachi EPI-2G spectrometer equipped with gratings or on a Hitachi Infracord. Samples were wrapped with polyethylene film in order not to damage the NaCl cells. The results of these studies and related data which have appeared in the literature are given in Table 1. Tetrahydrofuran, dioxane, diethyl ether and tetrahydrothiophene were used to check the solvent effect.

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