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Preliminary communication

Me_3SnCl/solvent interaction studied through heteronuclear double magnetic ^1H–$\{^{119}Sn\}$ resonance

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The first paper[1] on the ^{119}Sn chemical shifts in organotin compounds mentioned that the shifts were strongly dependent on the solvent used. Later, a dependence of the shifts on concentration was found[2] for compounds of the type Alk_3SnX. However, direct recording of the ^{119}Sn NMR spectra as used in both the papers cited above did not permit the ^{119}Sn chemical shifts to be studied at low concentrations.

The ^1H–$\{^{119}Sn\}$ heteronuclear double magnetic resonance (HDMR) technique enabled us to find the ^{119}Sn chemical shifts for Me_3SnCl at low concentrations[3]. The solvent effect was determined for 5% *M* concentrations of organotin compounds. The shifts varied from −179.3 (in Me_2CO) to −44.5 ppm (in MeOH). This may be explained by assuming that the organotin compounds can form complexes with donor solvents.

The present paper deals with a study of the ^{119}Sn shifts as a function of concentration and temperature in various solvents. Me_3SnCl was chosen as the object of the study.

The ^{119}Sn chemical shift observed, $\delta_{obs.}$, is an averaged quantity:

$$\delta_{obs} = (1 - \alpha)\,\delta_o + \alpha\delta_c \qquad (1)$$

where δ_o is the ^{119}Sn chemical shift for the uncomplexed Alk_3SnX, δ_c is the same for the complexed Alk_3SnX, and α is the extent of complex formation.

Formation of an equimolar complex may be written as follows:

$$Alk_3SnX + D \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Alk_3SnX : D \qquad (2)$$

where D is a donor solvent.

In this case, the equilibrium constant, *K*, may be calculated[2] from the concentration dependences found for the chemical shifts,

$$K = \frac{k_1}{k_2} = \frac{\delta_o(\delta_c - C\,\delta_o)}{\delta_o^2(1 - C) + C\,\delta_o^2 - \delta_o\,\delta_c} \qquad (3)$$

where C is the initial molar fraction of Alk_3SnX.

The ^{119}Sn chemical shifts were measured with the aid of the $^1H-\{^{119}Sn\}$ HDMR technique on a JEOL C–60HL instrument which recorded the proton spectra. Frequency sweep and internal lock were used throughout. The ^{119}Sn spectrum was irradiated at 22.37 MHz with a Ch1–9 synthesizer. The frequency was set accurately to within ±1 Hz. Other details of the experiment may be found elsewhere[3].

We have studied solutions of Me_3SnCl in acetone, dioxane, methanol, ethanol, carbon tetrachloride and methylene chloride, as well as solutions of Et_3SnCl in acetone or acetonitrile. Tables 1–7 summarise the ^{119}Sn chemical shifts obtained at various

TABLE 1

^{119}Sn CHEMICAL SHIFTS, δ (PPM), FOR Me_3SnCl DISSOLVED IN ACETONE [a]

Concentration (molar percent)	Temperature (°C)					
	−55	−34	−2	+20	+37	+50
20	−84.8	−92.7	−104.3	−113.2	−121.3	−125.5
15	−82.5	−91.3	−102.7	−111.8	−119.8	−124.1
10	−80.8	−90.4	−101.5	−110.3	−118.5	−122.9
5	−79.0	−89.0	−100.4	−109.3	−117.4	−121.7
2	−77.8	−87.5	− 98.4	−108.5	−116.4	−121.0
δ_c^b	−74±6	−77±5	−76±4	−78±4	−79±3	−78±3
K^c	12.6±3	7.1±2	2.5±0.6	1.7±0.4	1.1±0.2	0.9±0.15

[a] ^{119}Sn chemical shifts are given in ppm relative to tetramethyltin, [b] δ_c is the ^{119}Sn chemical shift for the complexed Alk_3SnX, [c] K is the calculated value of the equilibrium constant.

TABLE 2

^{119}Sn CHEMICAL SHIFTS, δ (PPM), FOR Me_3SnCl DISSOLVED IN ACETONITRILE [a]

Concentration (molar percent)	Temperature (°C)					
	−20	−5	+20	+40	+60	+70
40	−107.3	−114.7	−118.9	−129.3	−135.6	−137.5
20	−101.7	−108.7	−116.2	−126.1	−130.9	−133.5
10	− 98.2	−105.0	−113.2	−123.6	−128.7	−131.1
5	− 95.2	−103.4	−111.5	−120.4	−127.1	−129.6
3	− 92.7	−101.6	−110.8	−119.5	−126.4	−129.0
δ_c	−84±6	−86±5	−87±5	−87±5	−88±4	−85±5
K	6.2±2	3.5±0.8	2.1±0.5	1.2±0.2	0.8±0.1	0.7±0.1

[a] See remarks to Table 1.

TABLE 3

^{119}Sn CHEMICAL SHIFTS, δ (PPM), FOR Me_3SnCl DISSOLVED IN DIOXANE[a]

Concentration (molar percent)	Temperature (°C)				
	+20	+37	+50	+68	+82
20	−125.3	−129.1	−135.2	−139.6	–
15	−124.3	−128.0	−134.1	−138.3	−141.9
10	−123.8	−127.6	−133.7	−137.9	−141.4
5	−121.5	−126.3	−132.5	−136.9	−140.7
2	−120.4	−125.5	−131.6	−136.4	−140.1
δ_c	−104±4	−103±4	−105±4	−104±3	−106±4
K	2.1±0.4	1.5±0.3	1.0±0.2	0.7±0.1	0.5±0.1

[a] See remarks to Table 1.

TABLE 4

^{119}Sn CHEMICAL SHIFTS, δ (PPM), FOR Et_3SnCl DISSOLVED IN ACETONITRILE[a]

Concentration (molar percent)	Temperature (°C)				
	−9	+20	+35	+48	+63
90	−146.8	−148.6	−151.8	−153.1	−154.7
75	−139.7	−141.8	−145.4	−147.9	−149.0
50	−127.2	−134.8	−137.2	−139.7	−141.9
25	−115.5	−124.0	−127.6	−130.7	−133.2
10	−111.6	−120.2	−124.8	−127.4	−130.1
δ_c	−84±5	−86±4	−87±4	−86±5	−88±6
K	1.9±0.4	1.2±03	0.9±0.2	0.8±0.1	0.6±0.1

[a] See remarks to Table 1.

TABLE 5

^{119}Sn CHEMICAL SHIFTS, δ (PPM), FOR Et_3SnCl DISSOLVED IN ACETONE[a]

Concentration (molar percent)	Temperature (°C)				
	−20	−10	+20	+35	+48
90	−146.2	−147.5	−149.0	−150.9	−152.7
75	−136.8	−139.7	−147.5	−147.8	−149.4
50	−125.0	−128.3	−134.8	−140.0	−142.3
25	−112.2	−115.9	−125.5	−131.6	−133.7
10	−108.0	−111.7	−121.3	−127.7	−129.2
δ_c	−83±5	−81±6	−84±4	−82±5	−85±4
K	2.1±0.4	1.6±0.3	1.0±0.3	0.7±0.1	0.5±0.1

[a] See remarks to Table 1.

TABLE 6

^{119}Sn CHEMICAL SHIFTS, δ(PPM), FOR Me_3SnCl DISSOLVED IN METHANOL [a]

Concentration (molar percent)	Temperature (°C)				
	−13	+1	+20	+33	+56
20	−36.6	−42.3	−51.1	−54.4	−64.4
12	−34.1	−39.9	−48.2	−52.1	−61.2
7	−30.3	−35.9	−43.0	−45.5	−54.1
4	−29.3	−34.6	−41.7	−44.4	−52.8
2	−28.6	−34.0	−40.9	−43.9	−51.9

[a] See remarks to Table 1

TABLE 7

^{119}Sn CHEMICAL SHIFTS, δ (PPM), Me_3SnCl DISSOLVED IN ETHANOL [a]

Concentration (molar percent)	Temperature (°C)				
	−35	0	+20	+30	+50
20	−27.7	−42.2	−51.8	−60.2	−69.4
15	−26.7	−40.1	−50.7	−57.5	−68.5
10	−24.9	−37.1	−47.9	−54.0	−65.2
5	−22.7	−35.8	−44.6	−52.6	−63.5
2	−21.4	−35.7	−43.7	−51.7	−62.3

[a] See remarks to Table 1.

concentrations and temperatures. Values of δ_c and K are also shown. These are calculated using eqn. (3).

The K *vs.* temperature plot helps to estimate the molar enthalpy of complex formation using eqn. (4):

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2} \tag{4}$$

TABLE 8

ΔH VALUES FOR COMPLEXES OF TRIMETHYL- OR TRIETHYLSTANNYL CHLORIDES WITH ACETONE, ACETONITRILE AND DIOXANE

Complex	ΔH (kcal/mole)
Me_3SnCl with acetone	4.2 ± 1.3
Me_3SnCl with acetonitrile	4.1 ± 1.15
Me_3SnCl with dioxane	5.1 ± 1.5
Et_3SnCl with acetone	3.3 ± 1.4
Et_3SnCl with acetonitrile	2.8 ± 1.25

The results, which are listed in Table 8 are close to those calculated by thermochemical methods[4].

The solvents studied may be subdivided into three groups:

(i) carbon tetrachloride and methylene chloride, which do not significantly affect the ^{119}Sn chemical shifts associated with Me_3SnCl; these solvents may be considered neutral;

(ii) protic polar solvents (acetone, acetonitrile, dioxane), for which the enthalpy of complex formation is 4 to 5 kcal/mole; the enthalpy falls off with an increase in the chain length, (it is equal to 3 kcal/mole in Et_3SnCl);

(iii) alcohols (methanol, ethanol) which probably cause ionisation of the solute.

REFERENCES

1 J.J. Burke and P.C. Lauterbur, *J. Amer. Chem. Soc.*, 83 (1961) 326.
2 B.K. Hunter and L.W. Reeves, *Canad. J. Chem.*, 46 (1968) 1399.
3 A.P. Tupčiauskas, N.M. Sergeyev and Yu.A. Ustynyuk, *Liet. Fiz. Rinkinys.*, 11 (1971) 93.
4 T.F. Bolles and R.S. Drago, *J. Amer. Chem. Soc.*, 88 (1966) 5730.