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Solvent Effect on the Proton Magnetic Resonance Spectra of Dimethyltin Dichloride, Trimethyltin Chloride and Trimethyllead Chloride

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The chemical shifts of methyl protons (τ(M–CH$_3$) values) and the coupling constants between the methyl protons and the metal atom $J_{\text{M-CH}_3}$ values for dimethyltin dichloride, trimethyltin chloride, and trimethyllead chloride have been measured in thirty-two organic solvents. From the relation between the τ(M–CH$_3$) and the $J_{\text{M-CH}_3}$ values, the solvents used here have been classified into four groups. Carbon tetrachloride is representative of the first groups. The second group consists of usual polar organic solvents which can coordinate to the metal atom. The third consists of nitrobenzene, benzonitrile, pyridine, and its derivatives among the solvents studied here. The fourth consists of alkyl- or halogen-substituted aromatic solvents. The configurations of trimethyltin chloride in these solvents have been discussed on the basis of the $J_{^{119}\text{Sn-CH}_3}$ values and the intensity of the Sn–C symmetric stretching band relative to that of the asymmetric one. The effects of the temperature and the concentration of the solute on the τ(Sn–CH$_3$) and the $J_{^{119}\text{Sn-CH}_3}$ values of trimethyltin chloride have been examined in several solvents.

The configuration of organometallic compounds in solution is of much chemical interest. The proton magnetic resonance spectra of methyltin[1-3] and methyllead[2,4] compounds have been measured and discussed on the basis of their configurations, particularly in some strongly-coordinating solvents, by several workers. When methyltin and methyllead halides are coordinated by polar solvent molecules, the coupling constant between the methyl protons and the metal atom increases; this coupling constant is correlated with the configurational change of the compounds.

The effects of benzene, *p*-xylene, and mesitylene on the chemical shifts of the methyl protons were examined for $(CH_3)_nMX_{4-n}$ ($n=1, 2, 3, 4$), where M is a group IVB element and X is a halogen, and discussed on the basis of a dipole-induced dipole interaction.[5]

In order to investigate further the interaction of organometallic halides with organic solvents, we have chosen dimethyltin dichloride, trimethyltin chloride, and trimethyllead chloride, because their configurations have already been widely studied.[1-11]

The chemical shifts of the methyl protons (τ(M–CH$_3$) values) and the coupling constants between the methyl protons and the metal atom ($J_{\text{M-CH}_3}$ values) have been measured in thirty-two organic solvents. The effects of the temperature and the concentration of the solute on the τ(Sn–CH$_3$) and the $J_{\text{M-CH}_3}$ values of trimethyltin chloride have been measured in several organic solvents. The infrared spectra of the Sn–C stretching region have been measured to obtain some information about the configuration of trimethyltin chloride in several solvents.

Experimental

Materials. Dimethyltin dichloride was supplied by Nitto Kasei, Ltd., and was purified by sublimation. Trimethyltin chloride was prepared by the disproportionation of tin tetrachloride and tetramethyltin,[12] and purified by distillation. Trimethyllead chloride was prepared by the chlorination of tetramethyllead in a mixed solvent of ether and toluene at about −60°C.

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[1] E. V. van der Berghe and G. P. van der Kelen, *Ber. Bunsen Geselsch. Phys. Chem.*, **68**, 652 (1964).

[2] N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964).

[3] M. M. McGrady and R. S. Tobias, *ibid.*, **3**, 1157 (1964).

[4] H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.*, **1**, 297 (1964).

[5] T. L. Brown and K. Stark, *J. Phys. Chem.*, **69**, 2679 (1965).

[6] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).

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[8] W. F. Edgell and C. H. Ward, *J. Mol. Spectry.*, **8**, 343 (1962).

[9] R. Hulme, *J. Chem. Soc.*, **1963**, 1524.

[10] I. R. Beattie and G. P. McQuillan, *ibid.*, **1963**, 1519.

[11] P. Taimsalu and J. L. Wood, *Spectrochim. Acta*, **20**, 1357 (1964).

[12] L. G. A. Luijiten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Research Institute," Greenford, Middlesex (1955).

The solvents used in the spectral measurements were purified by distillation.

Proton Magnetic Resonance Spectra. The proton magnetic resonance measurements were made with a Japan Electron Optics model JNM-3H-60 spectrometer operating at 60 Mc/sec. The chemical shifts were measured relative to tetramethylsilane as an internal standard. The τ(M–CH$_3$) values are accurate to ±0.01 ppm. The $J_{\text{M-CH}_3}$ values were determined by the side-band technique and are reproducible to within ±0.6 cps. The sample temperature was approximately 23°C.

Infrared Spectra. The infrared spectra were measured using a Hitachi EPI-2G grating spectrometer. The intensity of the Sn–C symmetric stretching band relative to that of the asymmetric one for solutions of trimethyltin chloride of about 3 wt% was measured with 0.5 mm fixed cells.

Results and Discussion

The chemical shifts of the methyl protons (τ(Sn–CH$_3$) and τ(Pb–CH$_3$) values) and the coupling constants between the methyl protons and the tin or the lead atom ($J_{^{119}\text{Sn-CH}_3}$ and $J_{^{207}\text{Pb-CH}_3}$ values) for dimethyltin dichloride, trimethyltin chloride, and trimethyllead chloride in various solvents are summarized in Table 1. The dependence of the τ(M–CH$_3$) and the $J_{\text{M-CH}_3}$ values on the concentration of the solute (1—10 wt%) was very small, within the limits of experimental error in coordinating polar solvents. In aromatic solvents, however, a small concentration-dependence of the τ(Sn–CH$_3$) values was observed. The τ(M–CH$_3$) and the $J_{\text{M-CH}_3}$ values in Table 1 are those obtained for solutions with about 3 wt% of the solute.

Figures 1, 2, and 3 show the relationships between the τ(M–CH$_3$) and the $J_{\text{M-CH}_3}$ values of these molecules. As can be seen from these figures, the solvents used here can be classified into four groups. Carbon tetrachloride is representative of the first group. The second group consists of usual polar

TABLE 1. THE CHEMICAL SHIFTS OF THE METHYL PROTONS AND THE COUPLING CONSTANTS BETWEEN THE METHYL PROTONS AND THE METAL ATOM AT 23°C

No.	Solvent	$(CH_3)_2SnCl_2$		$(CH_3)_3SnCl$		$(CH_3)_3PbCl$	
		τ(Sn–CH$_3$) ppm	$J_{^{119}\text{Sn-CH}_3}$ cps	τ(Sn–CH$_3$) ppm	$J_{^{119}\text{Sn-CH}_3}$ cps	τ(Pb–CH$_3$) ppm	$J_{^{207}\text{Pb-CH}_3}$ cps
1	Carbon tetrachloride	8.84	68.9	9.34	58.2		
2	Chloroform	8.80	67.7	9.35	57.8		
3	1, 2-Dichloroethane	8.80	70.4	9.38	58.4	8.52	67.8
4	Benzene	9.66	69.3	9.78	58.9		
5	Toluene	9.60	68.9	9.73	58.3		
6	*p*-Xylene	9.58	68.5	9.73	57.3		
7	Mesitylene	9.55	69.5	9.72	58.3		
8	α-Chloronaphthalene	9.63	66.8	9.77	57.7		
9	Chlorobenzene	9.25	69.0	9.55	58.1		
10	Bromobenzene	9.20	67.8	9.54	58.1		
11	Iodobenzene	9.13	67.2	9.52	57.5		
12	*o*-Dichlorobenzene	9.03	68.1	9.45	58.1		
13	*p*-Chlorotoluene	9.20	68.9	9.56	58.2		
14	Thiophene	9.43	68.0	9.67	57.6		
15	Furan	9.22	71.3	9.58	58.9		
16	*N*, *N*-Dimethylaniline	9.36	71.7	9.69	58.2		
17	Anisole	9.26	72.4	9.59	58.0		
18	Aniline			9.52	64.5		
19	Nitrobenzene	8.55	75.6	9.21	60.5	8.30	70.5
20	Benzonitrile	8.54	79.1	9.21	63.3	8.39	73.8
21	α-Picoline	8.47	93.9	9.21	64.6	8.39	76.6
22	γ-Picoline			9.16	67.4		
23	Pyridine			9.06	68.0	8.35	81.4
24	Dioxane			9.41	61.6	8.57	73.6
25	Acetonitrile	8.81	81.6	9.40	64.7	8·58	77.8
26	Tetrahydrofuran	8.87	85.4	9.41	65.8	8.60	78.9
27	Acetone	8.78	86.5	9.36	66.2	8.58	80.0
28	Methanol	8.83	93.7	9.39	67.0	8.56	78.6
29	*N*, *N*-Dimethylacetamide	8.84	102.6	9.42	69.5		
30	*N*, *N*-Dimethylformamide	8.81	106.1	9.37	69.6	8.55	81.8
31	Water		110.2		69.3		76.6
32	Dimethylsulfoxide	8.91	117.1	9.46	70.0	8.60	81.8

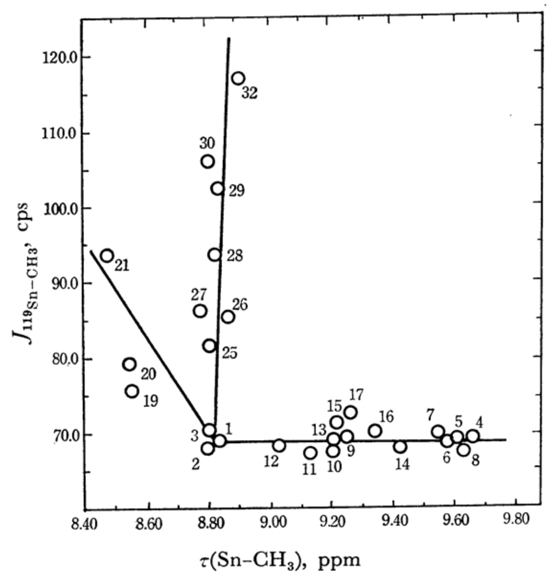


Fig. 1. Plots of the $J_{^{119}Sn-CH_3}$ values *vs.* the τ(Sn-CH$_3$) values of dimethyltin dichloride in various solvents. The concentration of the solute is about 3 wt% in each solvent. The numbers for the plots indicating solvents are referred to Table 1.

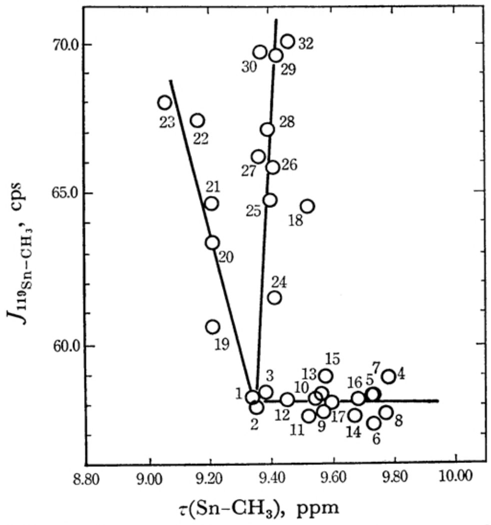


Fig. 2. Plots of the $J_{^{119}Sn-CH_3}$ values *vs.* the τ(Sn-CH$_3$) values of trimethyltin chloride in various solvents. The concentration of the solute is about 3 wt%.

organic solvents which can coordinate to the metal atom. The third consists of nitrobenzene, benzonitrile, pyridine, and its derivatives. The fourth consists of alkyl- or halogen-substituted aromatic solvents.

In the solvents of the first group, trimethyltin and trimethyllead chlorides have the configuration (I) of a C_{3v} symmetry[7] around the central metal atom.

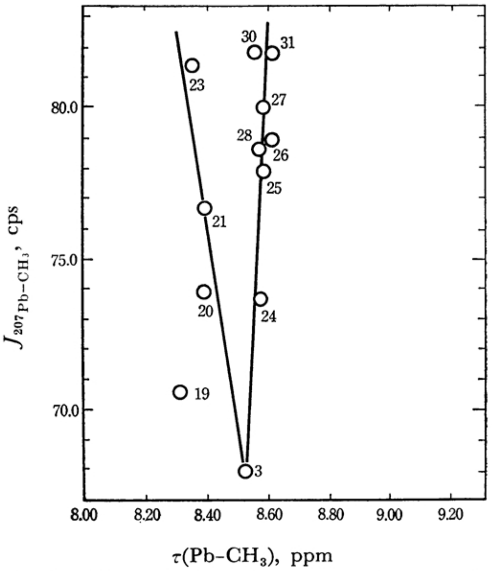
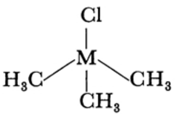


Fig. 3. Plots of the $J_{^{207}Pb-CH_3}$ values *vs.* the τ(Pb-CH$_3$) values of trimethyllead chloride in various solvents. The concentration of the solute is about 3 wt%.



(I) (M=Sn and Pb)

According to the relationship postulated by Holmes and Kaesz,[13] trimethyltin chloride has about a 27% *s*-character in the tin orbitals used to bind the methyl carbons in carbon tetrachloride. Solvents of both the second and the third groups have the ability to coordinate to the metal atom, and some of them are known to form stable 1 : 1 or 1 : 2 adducts with alkyltin chlorides[9-11,14] and tin tetrahalides.[15] In dimethylsulfoxide, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, pyridine, and water, the $J_{^{119}Sn-CH_3}$ values of trimethyltin chloride are about 70 cps. This indicates that the tin orbitals directed to the methyl carbons are sp^2 hybrid orbitals as deduced from the relationship postulated by Holmes and Kaesz.[13] On the other hand, infrared spectra show that the intensity of the Sn–C symmetric stretching band relative to that of the asymmetric one of trimethyltin chloride (I_{sym}/I_{asym}) is much smaller in dimethylsulfoxide and pyridine than in any other solvent (see Table 2). Therefore, one of the interpretations of these results

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13) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961).

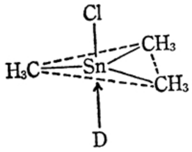
14) T. F. Bolles and R. S. Drago, *ibid.*, **87**, 5015 (1965); H. G. Langer and A. H. Blut, *J. Organometal. Chem.*, **5**, 291 (1966).

15) I. R. Beattie, *Quart. Rev.*, **17**, 382 (1963); I. R. Beattie and L. Rule, *J. Chem. Soc.*, **1965**, 2995; T. L. Brown and M. Kubota, *J. Am. Chem. Soc.*, **83**, 331 (1961); J. J. Myher and K. E. Russell, *Can. J. Chem.*, **42**, 1555 (1964).

TABLE 2. THE Sn–C SYMMETRIC AND ASYMMETRIC STRETCHING FREQUENCIES OF TRIMETHYLTIN CHLORIDE AND THEIR RELATIVE INTENSITIES IN VARIOUS SOLVENTS

Solvent	ν_{sym}(Sn–C) cm^{-1}	ν_{asym}(Sn–C) cm^{-1}	Relative intensity I_{sym}/I_{asym}
Carbon tetrachloride	515	544	0.24
Benzene	515	545	0.23
p-Xylene	515	544	0.21
Mesitylene	515	545	0.18
Acetonitrile	516	549	0.16
Tetrahydrofuran	514	546	0.15
α-Picoline	513	545	0.10
Pyridine	508	545	0.03
Dimethylsulfoxide	512	548	0.03

is that trimethyltin chloride has a penta-coordinated trigonal bipyramidal configuration (II) containing an almost planar SnC_3 group in these solvents.

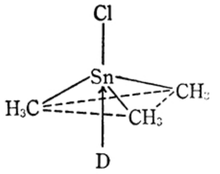


(II)

(M = Sn and Pb ; D = solvent molecule)

This configuration is consistent with the results of the X-ray crystallographic analysis of the trimethyltin chloride-pyridine complex.[9]

In acetonitrile, the $J_{^{119}Sn-CH_3}$ value of trimethyltin chloride is 64.7 cps, which is intermediate between the value of 70.0 cps in dimethylsulfoxide and that of 58.2 cps in carbon tetrachloride. The τ(Sn–CH_3) and the $J_{^{119}Sn-CH_3}$ values are independent of the solute concentration in acetonitrile (see Table 3). The infrared spectrum of trimethyltin chloride in acetonitrile shows one strong Sn–Cl stretching band at 300 cm^{-1} [11,16] which is lower than that in cyclohexane (345 cm^{-1}),[11] but higher than those found in trimethyltin chloride-pyridine and -dimethylsulfoxide complexes ($\sim$240 cm^{-1}).[17] The intensity of the Sn–C symmetric stretching band relative to that of the asymmetric one (I_{sym}/I_{asym}) in acetonitrile is intermediate between those in carbon tetrachloride and in dimethylsulfoxide (see Table 2).



(III)

TABLE 3. THE EFFECT OF THE CONCENTRATION OF TRIMETHYLTIN CHLORIDE ON THE τ(Sn–CH_3) AND THE $J_{^{119}Sn-CH_3}$ VALUES IN VARIOUS SOLVENTS AT 23°C

Solvent	Concentration of the solute wt%	τ(Sn–CH_3) ppm	$J_{^{119}Sn-CH_3}$ cps
Carbon tetrachloride	1	9.34	58.7
	5	9.33	58.2
	10	9.33	58.2
Benzene	1	9.77	58.9
	5	9.75	58.9
	10	9.71	59.2
Toluene	1	9.74	58.1
	5	9.73	58.4
	10	9.71	58.0
Acetonitrile	1	9.40	64.9
	5	9.40	64.7
	10	9.40	64.7
	25	9.40	64.7
Pyridine	1	9.06	68.0
	5	9.06	68.1
	10	9.06	68.1

From these results, it may be concluded that trimethyltin chloride in accetonitrile has configuration III intermediate between I and II. From similar considerations, trimethyllead chloride and dimethyltin dichloride in acetonitrile must have configurations intermediate between those in carbon tetrachloride and in dimethylsulfoxide.

Thus, the stronger coordination of solvent molecules appears to make the MC_3 moiety more planar or the MC_2 moiety more linear. These configurational changes may be explained by the increase in the *s*-character of the metal orbitals directed to the methyl carbons. As long as the J_{M-CH_3} value depends on the *s*-character of the metal orbitals directed to the methyl carbons, the larger J_{M-CH_3} value means a stronger coordination of solvent molecules to the metal atom.

As may be seen from the J_{M-CH_3} values in Table 1, the relative coordinating ability of solvent molecules is :

$$(CH_3)_2SO \sim (CH_3)_2NCHO \sim H_2O \sim (CH_3)_2NCOCH_3 > C_5H_5N > CH_3OH > (CH_3)_2CO \sim (CH_2)_4O > CH_3CN > C_6H_5CN.^{18)}$$

This order is similar to that observed for dimethylthallium compounds.[19] In pyridine and its derivatives the order of coordinating ability is ; pyridine > γ-picoline > α-picoline.

The distinct difference between solvents of the

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16) I. R. Beattie, G. P. McQuillan and R. Hulme, *Chem. Ind.*, **1962**, 1429.

17) T. Tanaka *et al.*, to be published.

18) When this manuscript was near completion, enthalpies of complex formation between trimethyltin chloride and some Lewis bases were measured, and evidence for a linear relation between $J_{^{119}Sn-CH_3}$ and enthalpy of complex formation was found (T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3921, 5730 (1966)).

19) G. D. Shier and R. S. Drago, *J. Organometal. Chem.*, **6**, 330 (1966).

second and the third groups can be seen in the τ(M–CH$_3$) values. In the solvents of the former group, the τ(M–CH$_3$) values become larger with an increase in the coordinating ability of the solvent molecules. The donation of an electron from the solvent molecules to the metal atom reduces the net positive charge on the metal atom; this in turn increases the shielding of the methyl protons attached to the metal atom. As can be seen from Table 1, however, this effect is small. On the other hand, the τ(M–CH$_3$) values in the solvents of the latter group become smaller with an increase in the coordinating ability of the solvent molecules. The large paramagnetic effect due to the ring current of the benzene ring or the pyridine ring of the solvents of the third group may overcome the diamagnetic effect of the coordination described above.

In the solvents of the fourth group, the $J_{\text{M-CH}_3}$ values are almost constant, while the τ(M–CH$_3$) values of the methyl protons vary widely and are observed at a higher magnetic field than in any other solvent. Among the solvents studied here, benzene shows the most remarkable diamagnetic effect for the τ(Sn–CH$_3$) values. The τ(Sn–CH$_3$) values in methyl- and halogen-substituted benzene decrease in the order: benzene, toluene, *p*-xylene mesitylene, chlorobenzene, bromobenzene, iodobenzene, and *o*-dichlorobenzene. These orders for the chemical shifts of the methyl protons of trimethyltin chloride and dimethyltin dichloride are similar to those of acetonitrile in aromatic solvents obtained by Buckingham[20] and by Ledaal[21].

As may be shown in Table 3, the τ(Sn–CH$_3$) value of trimethyltin chloride depends somewhat on the concentration in benzene and in toluene, but not the $J_{^{119}\text{Sn-CH}_3}$ value. The temperature dependence of the τ(Sn–CH$_3$) value of trimethyltin chloride in toluene has also been observed; the value increases with a lowering of the temperature, as may be shown in Fig. 4.

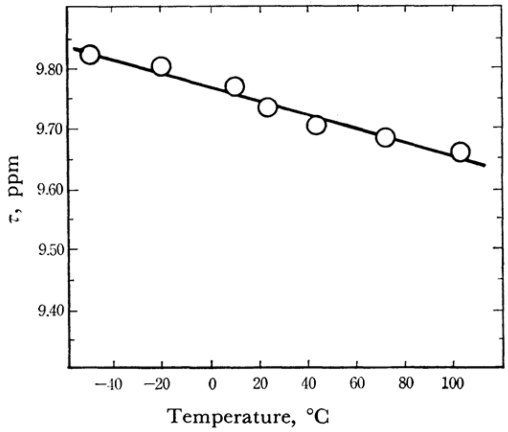

Fig. 4. The effect of the temperature on the τ(Sn–CH$_3$) value of trimethyltin chloride in toluene: the concentration of the solute is 3 wt%.

The $J_{^{119}\text{Sn-CH}_3}$ value in toluene has been observed to be independent of the temperature (58.8 ± 0.3 cps). The dependence of the τ(Sn–CH$_3$) value on the concentration of the solute and on the temperature may indicate some weak solute-solvent interaction. Anisole, thiophene, furan, and *N*,*N*-dimethylaniline belong to the fourth group.

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[20] A. D. Buckingham, T. S. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

[21] T. Ledaal, *Tetrahedron Letters*, **1966**, 1653.