Nuclear Quadrupole Coupling in Organotin Chlorides. II. Dichlorides[1]

Paul J. Green and Jack D. Graybeal[2]

Contribution from the Department of Chemistry, West Virginia University, Morgantown, West Virginia. *Received January 16, 1967*

Abstract: As an effort to further the understanding of the nature of bonding to tin, the nuclear quadrupole coupling in 11 organotin chlorides was investigated and resonance frequencies were measured at 77, 200, and 303°K where possible. The data show that (1) there is a larger increase in the coupling constant relative to that of the tetrahalide with organic substitution than with analogous carbon and silicon compounds; (2) the ratios of the coupling constants for analogous carbon and tin compounds are not close to being constants as is the ratio for carbon and silicon compounds; (3) an abnormal temperature coefficient exists for dimethyl-, dipropyl-, and dibutyltin dichlorides. The observed data indicate an appreciable change of either ionic or π character of the Sn–Cl bond with organic substituent, and while evidence favors a change in the latter no definite conclusions can be established.

In a previous paper[3] it was pointed out that various estimates of the π bonding and ionic character in the Sn–Cl bond differed by considerable amounts. This study is an extension of the earlier work and attempts to produce more evidence as to the nature of the bonding.

Experimental Section

The compounds studied were obtained from Metallomer Laboratories, Inc., or Alfa Inorganics, Inc., and were used without further purification. For room-temperature measurements samples were sealed in 2-dram vials. For lower temperature measurements samples were sealed in 1-dram vials. For the former samples the vial was placed directly into the spectrometer coil while for the latter the vial was surrounded with a small dewar flask and the entire assembly placed into the coil.

The resonances were found using a Zeeman modulated superregenerative spectrometer which was a modification of the design of Peterson.[4-6]

Identification and frequency measurement of the resonances were made by modulating the quench frequency at a rate of 10–20 Hz, thereby allowing the center frequency of the oscillator to be distinguished on a radio receiver. A stable external oscillator was then zero-beat with the center frequency, using the receiver as a detector, and the frequency of the external oscillator was measured with a Hewlett-Packard 524D frequency counter. While quench modulation suppressed the side-band signals enough to allow the center frequency to be recognized, there was enough leakage of quench signal to prevent a direct measure of the superregenerative oscillator frequency with the counter, hence the use of the external oscillator. The measurements were aided by the fact that the patterns obtained on the recorder were exceptionally symmetrical enabling an unambiguous setting of the oscillator at the point where it was the center frequency rather than a side band which was interacting with the sample. This symmetry is illustrated by the room-temperature quartet of $(C_6H_5)_2SnCl_2$ as shown in Figure 1. A spectrum analyzer was used to confirm the intensity relationships between the recorder output and oscillator spectrum. Frequency measurements are accurate to ± 0.1 kHz. The observed line widths were 6–8 kHz, and the over-all accuracy of the measurements was limited to ± 2 kHz by the uncertainty associated with setting the spectrometer on a line peak. The coherence of this system was superior to that of the externally quenched spectrometer used in earlier work,[3] and the resolution was much better. The latter factor is shown by the increased number of resonances which were found for some compounds.

The differences in measured frequencies between this work and the earlier work are due to two factors. The reference oscillator used for beating with the superregenerative oscillator and hence measurement of frequencies in the earlier work was found to have a parasitic oscillation that would vary from approximately 0.5 to 1.5 MHz below the primary oscillation frequency. The exact location of the parasitic oscillation was irregular and would change with time in an irregular manner. In the earlier work the frequencies were always measured by approaching the oscillator frequency with the reference oscillator frequency from the high side; hence the parasitic oscillation would beat with the oscillator before the primary frequency but the primary frequency of the reference oscillator would be recorded. The present work employed a different reference oscillator and is free of this problem. A second factor which would cause a difference in recorded resonances of the order of a few (less than six) quench frequencies (at 25 kHz) was the fact that the multiple resonances observed in the present work were unresolved in the earlier work; hence the earlier recordings were a composite of several resonances in some cases. Hence they did not show the symmetry of the present ones and the choice of the center of the pattern was more difficult. This lack of resolution was due to the incoherence of the former oscillator operation.

In one instance, $(n\text{-}C_4H_9)_2SnCl_2$ at 77°K, a previously found resonance could not be relocated. Because of the differences in the spectrometer arrangement used at low temperatures in the two studies, the sample size was one-half and the coil filling factor was one-fourth that of the earlier work. A check of the spectrometer with *p*-dichlorobenzene which has a very intense resonance showed the sample size necessary to produce the minimum detectable signal (signal-to-noise (S/N) ratio = 2) was 0.4 g (0.2 g of Cl) at room temperature employing the low-temperature coil and dewar arrangement and at a sweep speed equal to that used for S/N ratios reported in Table I. The weights of Cl present in the samples of $(n\text{-}C_4H_9)_2SnCl_2$, $(n\text{-}C_8H_{17})_2SnCl_2$, and $(C_6H_5)_3SnCl$ which were used were about 1.6, 0.8, and 0.5 g, respectively. Since the intensities of the observed resonances decrease with decreasing temperatures, as is shown in Figure 2, and the observed resonances for these compounds, as shown in Figures 2–4, are quite weak at room temperature, it is not surprising that their low-temperature resonances were not observed. The absence of observed resonances in $(CH_2{=}CH)_2SnCl_2$ is due either to insufficient sensitivity or to disorder in the crystal structure. The latter is highly probable since aging of other samples for several days at temperatures just below their melting points was often necessary to obtain resonances. Aging produced no effect in this case however.

Results

The observed nuclear quadrupole resonance frequencies of ^{35}Cl in the compounds investigated are given in Table I. Where possible, measurements were made at three temperatures. The coupling constants listed in Table I were calculated from the average of the multiplets due to nonequivalent crystalline sites by using

---

[1] Supported by National Science Foundation Grant GP-4192. P. J. G. acknowledges receipt of a NASA Traineeship.

[2] To whom inquiries should be addressed.

[3] E. D. Swiger and J. D. Graybeal, *J. Am. Chem. Soc.*, **87**, 1464 (1965).

[4] G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instr.*, **35**, 698 (1964).

[5] R. P. Croston and J. D. Graybeal, *ibid.*, 37, 376 (1966).

[6] J. D. Graybeal and R. P. Croston, *ibid.*, **38**, (1967).

Table I. Observed Nuclear Quadrupole Resonance Frequencies and Coupling Constants of Organotin Chlorides

Compounds	Mp, °C	Obsd frequency, MHz[a] 77°K	200°K	303°K	Calcd e^2Qq_{zz}, MHz	$\Delta\nu/\Delta T$, kHz/°K
$(CH_3)_2SnCl_2$	90	15.466 (6)	15.620 (10)	15.714 (50)	31.428	+1.10
$(C_2H_5)_2SnCl_2$	85	15.520 (6)	15.490 (10)	15.487 (29)	31.014	−0.15
		15.740 (6)	15.595 (10)	15.536 (20)		−0.90
$(n\text{-}C_3H_7)_2SnCl_2$	81	14.930 (2)	15.125 (3)	15.309 (10)	30.618	+1.68
$(n\text{-}C_4H_9)_2SnCl_2$	43	NO[b]	15.820 (2)	15.982 (8)	31.974	+1.57
		NO	15.948 (2)	15.992 (8)		+0.43
$(n\text{-}C_8H_{17})_2SnCl_2$		NO	NO	15.136 (2)	30.272	
$(C_6H_5)_2SnCl_2$	42	17.440 (2)	17.390 (3)	17.337 (6)	35.687	−0.45
		17.902 (2)	17.798 (3)	17.724 (6)		−0.79
		18.020 (2)	17.985 (3)	17.995 (6)		−0.29
		18.722 (2)	18.530 (3)	18.340 (6)		−1.69
$(C_6H_5)_3SnCl$	106	NO	NO	16.750 (2)	33.736	
		NO	NO	16.985 (2)		
$(C_6H_5)SnCl_3$	150[c]	20.112 (6)	19.925 (10)	Liquid	40.836	−1.52
		20.632 (3)	20.339 (6)	Liquid		−2.38
		21.279 (6)	20.991 (10)	Liquid		−2.34
$(n\text{-}C_4H_9)SnCl_3$		20.012 (3)	Liquid	Liquid	40.654	
		20.448 (3)	Liquid	Liquid		
		20.521 (3)	Liquid	Liquid		
$(CH_2{=}CH)_2SnCl_2$		NO	NO	Liquid		

[a] Intensities given as signal-to-noise ratios are in parentheses following the frequencies. [b] NO compound searched but no resonance found. [c] Approximate.

the usual relationship for the spin $^3/_2$ case[7]

$$\nu = \frac{e^2Qq_{zz}}{2}\left[1 - \frac{\eta^2}{3}\right]^{1/2}$$

and assuming $\eta = 0$. This assumption is justified since considerable asymmetry is necessary before it affects the magnitude of the calculated coupling constant appreciably. The calculated values of the coupling constants are for 303° or the next lower temperature where no measurement was made at 303°. The temperature dependency of the frequencies were calculated by dividing the difference between available frequency extremes by the corresponding temperature difference and are listed in Table I. A rapid decrease of intensity with the organic group chain is noted. The intensities given as signal-to-noise ratios are in Table I. It is to be pointed out that for these compounds which were reported previously[3] and remeasured in this work the magnitudes of the changes in the measured frequencies are insufficient to invalidate the deductions of the earlier work and that furthermore they are in a direction such as to add increased weight to those and the present deductions. The new measurements place the coupling constants of the phenyltin chlorides above those of the aliphatic compounds which is as expected from other work on carbon and silicon compounds.

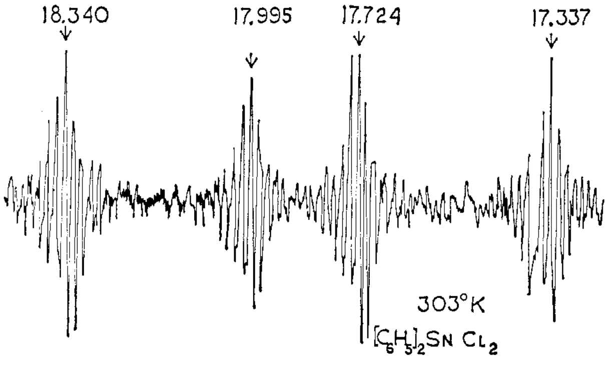


Figure 1. Diphenyltin dichloride spectrum at 303°K.

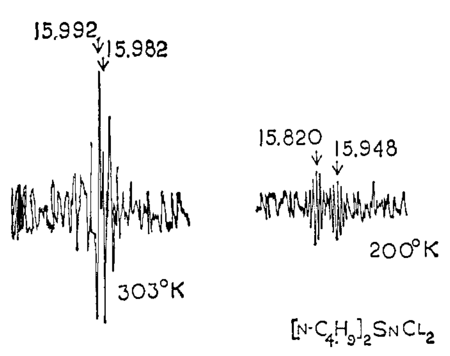


Figure 2. *n*-Dibutyltin dichloride spectrum at 303 and 202°K.

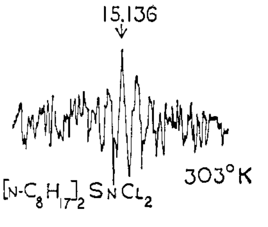


Figure 3. *n*-Dioctyltin dichloride spectrum at 303°K.

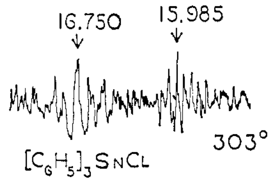


Figure 4. Triphenyltin chloride spectrum at 303°K.

[7] T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press Inc., New York, N. Y., 1958, p 14.

Discussion

As in the previous study, there is a larger decrease in the coupling constant relative to that of the tetrahalide with organic substitution than with carbon and silicon compounds. The lack of consistency in the ratio of the coupling constants between analogous tin and carbon compounds is again noted. This investigation has pointed up two additional facts of interest. (1) There is a greater variation of the coupling constant with aliphatic chain length in the case of tin than with carbon. (2) Three of the compounds have a positive temperature coefficient, and the temperature coefficients for different crystallographic sites in the same compound are of widely varying magnitudes.

A comparison of the decrease in coupling constant with substitution of two methyl groups into the tetrahalides of carbon, silicon, and tin is shown in Table II.

Table II. Changes of e^2Qq_{33} with Methyl Substitution

		$\Delta\lvert e^2Qq_{zz}\rvert$					
Compound	$\lvert e^2Qq_{zz}\rvert$, MHz	Abs, MHz	%	U_p	$I_a \times 100$	$\Delta I_a \times 100$	I_b
CCl_4	81.9			0.75	10		12
$(CH_3)_2CCl_2$	69.8	12.1	6.8	0.64	23	13	12
$SiCl_4$	40.8			0.37	55		56
$(CH_3)_2SiCl_2$	35.5	5.3	13	0.32	61	7	56
$SnCl_4$	48.2			0.44	47		56
$(CH_3)_2SnCl_2$	31.4	16.8	35	0.29	65	18	56

Also shown are the apparent ionic character, I_a, of the M–Cl bond as calculated by assuming 18% s character in the Cl σ-bonding orbital, neglecting π bonding and using the relationship[8]

$$I_a = 1 - \frac{U_p}{(1 - s^2)}$$

where $U_p = (e^2Qq_{zz})_{mol}/(e^2Qq_{zz})_{at}$ and the ionic character, I_b, predicted from electronegativity values using the Townes-Dailey curve. Since the change in the chlorine coupling constant with methyl substitution is much larger for tin compounds and the ionic character based on the assumption of no π bonding shows a larger increase for tin than for carbon this indicates that either the amount of π bonding or the ionic character of the Sn–Cl bond is changing with substitution to a greater extent with tin compounds than with those of carbon or silicon.

Table III is illustrative of the ratios of the observed quadrupole coupling constants for analogous C, Si, and Sn compounds. The work of Hooper and Bray[9] gives an average value of 2.00 ± 0.4 for the coupling constant ratio for seven analogous carbon and silicon compounds. Since the various bonding factors, s hybridization, s^2, ionic character, I, and π bonding, π, can be related to the molecular and atomic coupling constants by the factor[8]

$$(e^2Qq_{zz})_{mol}/(e^2Qq_{zz})_{at} = (1 - s^2 - I - \pi)$$

the ratio for the molecular coupling constants of a chlorine atom in two analogous compounds, where the atom bonded to the Cl atom is designated M or M′, becomes

$$\frac{(e^2Qq_{zz})_M}{(e^2Qq_{zz})_{M'}} = \frac{(1 - s_M{}^2 - I_M - \pi_M)}{(1 - s_M{}^2 - I_M - \pi_M)}$$

It is generally assumed that s^2 has a value of 0.15 regardless of the atom to which the Cl atom is bonded if it differs from chlorine in electronegativity by more than 0.25 unit. Since the carbon atom does not have any valence shell orbitals for π bonding to chlorine in sp^3 hybridization state, $\pi_C = 0$ and the ratio of the coupling constant of chlorine in a carbon compound to its silicon or tin analog becomes

$$\frac{(e^2Qq_{zz})_C}{(e^2Qq_{zz})_M} = \frac{(0.85 - I_C)}{(0.85 - I_M - \pi_M)}$$

Table III. e^2Qq_{zz} Ratios for Analogous Compounds of C, Si, and Sn

Compound (M = C, Si, Sn)	$(e^2Qq_{zz})_C/(e^2Qq_{zz})_{Si}$	$(e^2Qq_{zz})_C/(e^2Qq_{zz})_{Sn}$
MCl_4	1.99	1.69
CH_3MCl_3	1.96	1.86[a]
$(CH_3)_2MCl_2$	1.96	2.22
$(C_6H_5)MCl_3$	2.02	1.87

[a] This value is for the n-butyltin compound relative to the methyl carbon analog.

If the electronegativity of the organic group is transferable from a carbon to silicon atom, the ionic character of the M–Cl bond will depend only on the difference in electronegativity between Si and C. Thus the consistency of the ratio for carbon–silicon compounds indicates that there is little effect on the π bonding in the Si–Cl bond upon changing substituent. The ratio for carbon–tin compounds is quite irregular for those compounds studied to date. This indicates that either (1) the π-bond character of the Sn–Cl bond is quite sensitive to the organic substituent or (2) the π-bond character is relatively constant and the electronegativity of the organic group depends appreciably on the atom to which it is bonded. As was pointed out before,[3] Mossbauer work would tend to confirm the first hypothesis.

The work of Hooper and Bray[9] indicated less than 1% variation in the chlorine quadrupole coupling constant as the aliphatic chain was increased from one to ten carbons. This work shows a 5% variation in the substituted compounds, the change being quite regular with the exception of the dibutyltin dichloride. The latter compound has irregular physical properties also. Since the electronegativity effect of changing substituents is very small, as is indicated by the carbon compounds, this variation is undoubtedly due to the fact that intermolecular interactions contribute more to the coupling constants in the more ionic tin compounds, and as one increases the chain length of the organic substituents the unit cell size and intermolecular distances increase, thereby lowering the coupling constant as observed.

The most interesting feature of the present work is the occurrence of a positive temperature coefficient for the resonances in three compounds and the observed irregularities in the temperature coefficients of different crystalline sites. The normal temperature dependency is negative since increasing thermal motion in a solid will symmetrically average field gradients due to neigh-

---

(8) Reference 7, p 138.

(9) H. O. Hooper and P. J. Bray, *J. Chem. Phys.*, **33**, 334 (1960).

boring molecules and will hence lower the coupling constants. The occurrence of temperature-dependent intermolecular bonding may account for the positive coefficients. Intermolecular bonding of this form has been observed to exist in $BiCl_3$.[10] In such a case a decrease of intermolecular bonding with increasing temperature compensates or overbalances the normal temperature effect. Such an effect is strongly suggested by the observed data for the dimethyl, dipropyl, and dibutyl compounds. The variation in the magnitude of the temperature coefficients where multiple crystalline sites occur indicates that some sites are more favorably situated for intermolecular bonding than others. The fact that only negative coefficients are observed for the phenyl compounds where large organic groups would tend to prevent close association of a tin atom and a chlorine atom from another molecule tends to substantiate this reasoning also. The crystal structures of the investigated compounds are not known, but these observed temperature effects indicate that the most probable location for a tin atom is in a distorted octahedral site, surrounded by its four singly bonded groups and one or more partial intermolecular bonds to chlorines in neighboring molecules. It is the lowering of the order of these latter bonds with increasing temperatures that would lead to an increase in the asymmetry at the chlorine sites and hence the observed increase in coupling constant with temperature.

From this work it can be concluded that there is both ionic and π character involved in addition to the σ character of the Sn–Cl bond. The occurrence of positive temperature coefficients indicates intermolecular bonding in the solid. While evidence to date tends to favor explaining the changes in the observed coupling constants as being due to changes in π bonding with substituent, the asymmetry parameter and principal axis system for the electric field gradient at the chlorine atoms must be determined in order to settle the issue.

---

(10) H. G. Robinson, *Phys. Rev.*, **100**, 1731 (1955).

Mass Spectra of Silazanes

J. Silbiger,[1a] C. Lifshitz,[1b] J. Fuchs,[1a] and A. Mandelbaum[1c]

Contribution from the Department of Inorganic and Analytical Chemistry and the Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel, and the Department of Chemistry, Israel Institute of Technology, Haifa, Israel.
Received August 29, 1966

Abstract: The 70-v mass spectra of some silazanes and chloro- and methoxysilazanes are presented. The compounds studied include cyclic tri- and tetradimethylsilazanes and newly synthesized linear methoxy- and chlorodisilazanes. Expulsion of stable molecules, such as ammonia, methane, HCl (from the chlorosilazanes), and CH_2O (from the methoxy compound), has been observed. These fragmentations are usually accompanied by metastable transitions.

The information concerning mass spectra of silicon compounds is limited.[2-4] The only silazane which has been studied is hexamethyldisilazane.[5] As mass spectrometry is becoming increasingly important in the analytical determination of chemical compounds, we have studied the spectra of some silazanes: hexamethylcyclotrisilazane (I), octamethylcyclotetrasilazane (I), pentamethylmonochlorodisilazane (III), 1,3-dichlorotetramethyldisilazane (IV), 1,3-dimethoxytetramethyldisilazane (V), and 1,3-bis(dimethylchlorosilyl)-tetramethylcyclodisilazane (VI).

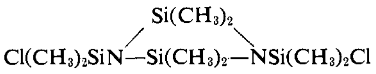
$[(CH_3)_2SiNH]_3$
I

$[(CH_3)_2SiNH]_4$
II

$(CH_3)_3SiNHSi(CH_3)_2Cl$
III

$Cl(CH_3)_2SiNHSi(CH_3)_2Cl$
IV

$CH_3O(CH_3)_2SiNHSi(CH_3)_2OCH_3$
V



VI

The mass spectra will be presented and discussed in terms of the structures of the respective molecules. We were able to assign plausible structures to the major peaks in each spectrum. The structures were in some cases verified by comparing the computed and observed relative abundance of isotopic species of the same fragment ion. The origin of certain fragment ions could be established unambiguously with the aid of metastable ions.

---

(1) (a) Department of Inorganic and Analytical Chemistry, The Hebrew University; part of this work is taken from a Ph.D. thesis to be submitted to the Senate of the Hebrew University by J. F.; (b) Department of Physical Chemistry, The Hebrew University; (c) Israel Institute of Technology.

(2) G. G. Hess, F. W. Lampe, and L. S. Sommer, *J. Am. Chem. Soc.*, **87**, 5327 (1965).

(3) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 155 (1962).

(4) F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, **2**, 46 (1963).

(5) A. G. Sharkey, Jr., R. A. Friedel, and S. H. Langer, *Anal. Chem.*, **29**, 770 (1957).