

the fact that  $f_{(\text{NaCl})} = 0.657$  and  $f_{(\text{NaClO}_4)} = 0.629$  at  $\mu = 1.0$ . Actually, very little difference would be observed if it was assumed that the activity coefficients of chloride and perchlorate were constant over the range of solutions investigated.

Values of  $F_1(X)$  listed in column 7 of Table V were obtained using the activity coefficients just outlined and the value of  $(E^{0,1/2})_s$  obtained earlier (after correction for the 40 mv. difference between the s.c.e. and the n.c.e.). No observed values of  $I_{\mu=1.0}/I_{\mu=0}$  are available, and this ratio was assumed to be unity. The  $F_1(X)$  values were plotted vs.  $C_x$  and the value of  $K_1^0$  given by the intercept is 4.5. The slope of the plot was zero, showing no indication of any additional species present.

An alternative procedure based on the formation of a thallos perchlorate complex is possible. Thallos perchlorate solutions have an unusually small stoichiometric activity coefficient and have a  $\beta$  coefficient of  $-0.17$ . Guggenheim and Turgeon<sup>13</sup> have indicated that when  $\beta$  is less than  $-0.1$ , ion association is important in 1:1 electrolytes. Furthermore, Robinson and Davies<sup>15</sup> have reported an association constant of 1.0 for thallos perchlorate on the basis of conductivity data.

In calculating  $F_1(X)$  for thallos chloride assuming the formation of a perchlorate complex, the activity coefficients employed must again be those of the ions of a strong electrolyte, and thus, for reasons expounded earlier, it was assumed that  $f_s = f_{\text{Tl}^+} = f_{\pm(\text{KCl})} = 0.604$  at  $\mu = 1.0$ . The coefficients for chloride and perchlorate ions were those obtained using Harned's rule.

To obtain values of  $F_1(X)$  for  $\text{Tl}^+ - \text{Cl}^-$  association from the data in mixed electrolytes, it is necessary to equate the quantity

$$\{[F_0(X) - 1/f_s - K^0_{\text{TlClO}_4} C_{\text{ClO}_4} f_{\text{ClO}_4}] / C_{\text{Cl}^-} f_{\text{Cl}^-}\}$$

with  $F_1(X)$ . These quantities have been calculated using Robinson and Davies' value of the association constant for thallos perchlorate, and they

(15) R. A. Robinson and C. W. Davies, *J. Chem. Soc.*, 574 (1937).

are listed in column 8 of Table V. A plot of  $F_1(X)$  vs.  $C_x$  yields an intercept of 4.3, corresponding to  $K_1^0$  for  $[\text{TlCl}]$  (aq.).

It is observed that the two values of  $F_1(X)$  in column 8 at the lowest chloride concentration are somewhat high but that for the remainder of the solutions, no trend appears in the value of  $F_1(X)$ . This situation might arise if  $(E^{0,1/2})_s$  were too positive or if  $f_s$  were too large. Both of these factors would have their greatest effect in the region of low chloride concentration.

The data obtained using gelatin as a maximum suppressor yielded similar results for  $K_1^0$  of thallos chloride association.

For thallos chloride, the value of  $\log K_1^0 = 0.46$  determined from data in varying ionic strengths is in agreement with most of the values determined conductometrically which range from 0.48 to 0.52 with one higher value at 0.61, but it is lower than those determined from potentiometric and solubility data which range from 0.59 to 0.68.<sup>16</sup> The value of  $\log K_1^0 = 0.64$  determined at constant ionic strength of 1.0 is in excellent agreement with these latter values. The reason for the apparent grouping of association constants by different methods and the reason for the two different polarographic values are not immediately apparent. The latter difference could conceivably be due to liquid junction potentials being handled inadequately. Vlcek corrected his data by means of the Henderson equation. The liquid junction potentials for the chloride data at constant ionic strength were estimated to be 1 millivolt or less, and since these estimations are very approximate, no correction was made.

In conclusion, the polarographic method of studying complex formation does yield for relatively simple systems equilibrium constants comparable to those obtained by other methods when activity coefficients are included.

More complicated systems, where consecutive equilibria occur, have not as yet been studied but will be the subject of a future investigation.

(16) Ref. 10, p. 106.

[CONTRIBUTION FROM THE MELLON INSTITUTE,<sup>2</sup> PITTSBURGH, PA.]

## Sn<sup>119</sup> Nuclear Magnetic Resonance Spectra<sup>1</sup>

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RECEIVED MAY 9, 1960

The Sn<sup>119</sup> spectra of a number of organic and inorganic tin compounds have been obtained. Chemical shifts of over 1800 parts per million were found and indirect spin-spin couplings with protons in alkyl groups were observed to be of the order of 50 to 100 cycles per sec. The spectra of mixtures of SnCl<sub>4</sub>, SnBr<sub>4</sub> and SnI<sub>4</sub> were examined, and all of the twelve possible mixed tin (IV) halides, including the preciously unreported SnBr<sub>3</sub>I, SnBr<sub>2</sub>I<sub>2</sub> and SnBr<sub>3</sub>I, and SnClBrI<sub>2</sub>, SnClBr<sub>2</sub>I and SnCl<sub>2</sub>BrI, were found to be present in the concentrations expected for random halogen exchange. The average lifetimes of the halide molecules in the mixtures were found to be between 10<sup>-2</sup> and 10 seconds. Solvent effects upon the Sn<sup>119</sup> chemical shifts of various tin compounds were observed and the Sn<sup>119</sup> chemical shift of SnCl<sub>2</sub>·2H<sub>2</sub>O in aqueous solution was found to be dependent upon the concentration of added hydrochloric acid.

### Introduction

As part of a program in this Laboratory for the study of the nuclear magnetic resonance (n.m.r.)

(1) Presented in part at the 133rd meeting of the American Chemical Society in San Francisco, April 15, 1958.

spectra of compounds of the Group IV b elements, C<sup>13</sup> spectra<sup>3,4</sup> and Si<sup>29</sup> spectra<sup>5</sup> have been investigated

(2) Multiple Fellowship on Silicones sustained by Dow Corning Corporation and Corning GlassWorks.

(3) P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).

previously. This paper now presents a survey of the  $\text{Sn}^{119}$  spectra of a number of organic and inorganic tin compounds and describes, as examples of the use of such spectra in chemical studies, an investigation of the redistribution reactions in mixtures of tin(IV) halides and a brief study of the dependence of the  $\text{Sn}^{119}$  chemical shift in  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  solution upon the concentration of added hydrochloric acid.

Numerous papers listing the chemical shifts of the more common elements in a wide variety of their compounds have appeared,<sup>6-12</sup> usually with some tentative theoretical discussion. The compounds studied have been of such diverse types, however, that it has been difficult to know where to begin with theoretical calculations or how to compare various possible systems of simplifying assumptions. The closest approaches to calculations of shifts from first principles, for elements other than hydrogen, have been those of Saika and Slichter,<sup>13</sup> who calculated the shift between  $\text{F}_2$  and  $\text{HF}$ , and those of Griffith and Orgel<sup>14</sup> and of Freeman, Murray and Richards<sup>15</sup> on cobalt complexes. Even in the case of fluorine, the shifts do not follow any simple pattern, and it is apparent that other parameters besides the ionic characters of the bonds are needed to interpret the results.

The need for complete sets of data on groups of closely related simple compounds can best be met by measurements on the tetrahedral and nearly tetrahedral compounds of such elements as carbon, silicon, germanium, tin and lead. Great numbers of these are either available or can be readily prepared, and the effects of replacing one substituent group or element by another can be measured while retaining the essentially tetrahedral geometry of the simpler compounds. It has been shown in studies of carbon<sup>3,4</sup> and silicon<sup>5</sup> derivatives that the chemical shift is a smooth function of composition in series of the type  $\text{MX}_n\text{Y}_{4-n}$ . In these series, as in similar series of phosphoryl and thiophosphoryl compounds,<sup>16</sup> it was also noted that the shifts in mixed compounds were always to lower fields than would be predicted by a linear interpolation between  $\text{MX}_4$  and  $\text{MY}_4$  (or  $\text{APX}_3$  and  $\text{APY}_3$ ). In one case only, the replacement on carbon of chlorine by bromine, was a strictly linear relationship found.

Although it must be admitted that linear variations in the properties of halogen compounds are not difficult to find, it is certainly desirable to see if this surprising simplicity shows up in other series of carbon halides and in the halides of the remaining elements in the Group. One goal of our study of  $\text{Sn}^{119}$  n.m.r. spectra, the first part of which is presented here, is to obtain just such data for tin compounds. The theoretical implications of these results will be discussed more fully in succeeding papers.

In the course of this work the redistribution reactions in mixtures of tin (IV) halides were studied. The existence of the mixed halides has long been a subject for controversy. Early reports<sup>17-19</sup> of their isolation have been shown to be in error,<sup>20-22</sup> and in recent years it has been shown that the Raman spectra of the halide mixtures contain new lines which can be assigned to the various mixed halides containing chlorine and bromine<sup>23,24</sup> and chlorine and iodine.<sup>25</sup> The various species are in fairly rapid equilibrium, apparently with a random Calingaert<sup>26,27</sup> distribution. It was thought that, in addition to providing data on the chemical shifts of the mixed halides, a study of the  $\text{Sn}^{119}$  n.m.r. spectra of the mixtures might confirm the Raman data, provide quantitative data on the distributions and allow the identification of the compounds containing three different halogens. These latter should exist, but they have not previously been reported.

Solutions of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  containing various concentrations of  $\text{HCl}$  were also studied. The formation of tin(II) complexes with chloride ion has been investigated by other methods,<sup>28-30</sup> and it was thought that n.m.r. might prove useful in the study of such complexes.

Three of the ten stable tin isotopes have non-zero spins and magnetic moments.<sup>7</sup> Of these, all of which have spin  $1/2$ ,  $\text{Sn}^{116}$  has too low an abundance (0.35%) to be readily observable. The other two,  $\text{Sn}^{117}$  and  $\text{Sn}^{119}$ , have similar abundances (7.6% and 8.68%, respectively) and only slightly different magnetic moments. The  $\text{Sn}^{119}$  isotope gives slightly stronger resonances and has, therefore, been used exclusively in this work, since no additional chemical information can be obtained from observations on the other isotopes.

## Experimental

**Apparatus.**—All of the spectra were obtained with a Varian 4300B High Resolution N.M.R. Spectrometer, operating at

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8.5 Mc/sec., combined with a Varian 12-inch electromagnet, flux stabilizer and slow sweep unit. Additional batteries were installed in the latter to allow the generation of the faster sweeps needed for this work. At the 8.5 Mc/sec. frequency,  $\text{Sn}^{119}$  resonances are found at about 5,360 gauss. It should perhaps be pointed out that these conditions are not optimum for  $\text{Sn}^{119}$  spectra. Magnetic fields of over 10,000 gauss can be obtained with this magnet, and the use of a higher frequency at such a field would give much better  $\text{Sn}^{119}$  signals. A Hewlett-Packard 200 AB oscillator was used to generate modulation side-bands, and its frequency was set by comparison with the nominal 60 cycle/sec. line frequency or determined by a Hewlett-Packard 521C Electronic Frequency Counter.

**Measurements of Shifts.**—The recorder chart (on a Varian G-10 recorder) was calibrated by generating 900 cycle/sec. side bands<sup>31</sup> on a strong resonance, usually that of  $(\text{CH}_3)_4\text{Sn}$  or  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ . Shifts were measured during the first part of this study by the sample replacement method and later by the use of a 3 mm. o.d. capillary containing  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  enriched to  $64.4 \pm 1\%$  in  $\text{Sn}^{119}$ . Measurements made with increasing and decreasing sweep fields were always averaged to eliminate errors caused by asymmetry of the peaks. All of the shifts are reported as parts per million (p.p.m.) relative to the resonance of  $(\text{CH}_3)_4\text{Sn}$ , although some were measured relative to  $\text{SnBr}_4$  or an aqueous solution of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and then reduced to the  $(\text{CH}_3)_4\text{Sn}$  scale. Shifts to higher field than the reference are given positive numbers. At least two sets of measurements, and usually more, were made on each compound, and most of the shifts are believed to be accurate to within about  $\pm 2$  p.p.m.

**Resonance Conditions.**—Depending on the relaxation times and experimental conditions, the resonances were recorded as rapid passage signals<sup>32,33</sup> (e.g.,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) slow passage dispersion mode signals<sup>32</sup> (e.g.,  $\text{SnCl}_4$ ) or absorption mode signals<sup>32</sup> (e.g.,  $\text{SnBr}_4$ ). Most of the samples could be made to give rapid passage signals with oscilloscope observation, dispersion mode tuning and high radio-frequency power ( $H_1$ ). The strength of  $H_1$  was usually between 2 and 50 milligauss.

**Sample Preparation.**—The samples were all contained in 15 mm. outside diameter Pyrex tubes and were run at room temperature (27°). The capillary containing  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  enriched in  $\text{Sn}^{119}$  was used as a secondary standard. This sample was made up by reducing  $\text{SnO}_2$  to Sn with  $\text{NH}_3$  and dissolving the metal in concentrated HCl.  $\text{SnBr}_4$ , which melts at about 30°, was undercooled.  $\text{SnSO}_4$  and sodium and potassium stannates were used as saturated aqueous solutions. The  $\text{SnI}_4$  sample was a saturated solution in  $\text{CS}_2$ , and the equimolar mixture of  $\text{SnBr}_4$  and  $\text{SnI}_4$  was made liquid by the addition of a few drops of  $\text{CS}_2$ . The  $\text{Sn}^{119}$  shifts of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in acetone and ethanol were measured in both saturated and dilute solutions. The dialkyltin dichlorides were measured as saturated solutions in either acetone or  $\text{CS}_2$ , as indicated. The mixtures of  $\text{SnCl}_4$  and  $\text{SnBr}_4$  were prepared by mixing the two liquids and allowing the solutions to stand at room temperature for several hours. The mixtures of halides containing  $\text{SnI}_4$  were heated in a boiling water bath until all of the iodide had dissolved.

The  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} + \text{HCl}$  samples were made up by mixing 5.00 grams of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  with 3.00 ml. of HCl of various concentrations. No attempt was made to eliminate  $\text{O}_2$  from these  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  samples. In all cases, a small amount of precipitate formed and was centrifuged out of the solution. The measurements were made on the clear supernatant solutions.

The anhydrous  $\text{SnCl}_2$  was run as a saturated tetrahydrofuran solution.

**Sources of Samples.**—The organic derivatives of tin were all donated by the Metal and Thermit Co., as were anhydrous  $\text{SnCl}_2$  and  $\text{SnF}_2$ .  $\text{SnCl}_4$ ,  $\text{SnI}_4$ ,  $\text{SnSO}_4$  and sodium stannate were obtained from the Fisher Scientific Co. The  $\text{SnI}_4$  was "technical grade," and a small amount of dark solid remained when it was dissolved in  $\text{CS}_2$  or mixed with other tin (IV) halides. The  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was obtained

TABLE I  
 $\text{Sn}^{119}$  CHEMICAL SHIFTS

Compound	Solvent	Shift (p.p.m.)
$\text{SnI}_4$	$\text{CS}_2$	1701 $\pm$ 2
$\text{SnSO}_4$	$\text{H}_2\text{O}$	909 $\pm$ 2
$\text{SnBr}_4$		638 $\pm$ 1
$\text{Na}_2\text{Sn}(\text{OH})_6$	$\text{H}_2\text{O}$	592 $\pm$ 2
$\text{K}_2\text{Sn}(\text{OH})_6$	$\text{H}_2\text{O}$	590 $\pm$ 2
$\text{SnCl}_2$	Tetrahydrofuran	236 $\pm$ 1
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{OOCCH}_3)_2$		195 $\pm$ 1
$\text{SnCl}_4$		150 $\pm$ 2
$(n\text{-C}_4\text{H}_9)_3\text{Sn}$		12 $\pm$ 1
$(n\text{-C}_4\text{H}_9)_2\text{SnCl}_3$		3 $\pm$ 1
$(\text{CH}_3)_4\text{Sn}$		0
$(\text{CH}_3)_2\text{SnCl}_2$	$(\text{CH}_3)_2\text{CO}$	- 36 $\pm$ 2
$(\text{C}_2\text{H}_5)_2\text{SnCl}_2$	$(\text{CH}_3)_2\text{CO}$	- 62 $\pm$ 1
$(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$	$(\text{CH}_3)_2\text{CO}$	- 71 $\pm$ 2
$(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2$	$\text{CS}_2$	-114 $\pm$ 2
$(n\text{-C}_4\text{H}_9)_2\text{SnS}$		-124 $\pm$ 2
$(n\text{-C}_4\text{H}_9)_3\text{SnCl}$		-143 $\pm$ 2
$(\text{C}_2\text{H}_5)_3\text{SnCl}$		-151 $\pm$ 2

from the J. T. Baker Chemical Co., the  $\text{SnBr}_4$  from City Chemical Corporation and potassium stannate from K & K Laboratories. The  $\text{Sn}^{119}\text{O}_2$  used to make up the capillary of  $\text{Sn}^{119}\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  was obtained from the Oak Ridge National Laboratory.

**Chemical Shifts in Pure Compounds and Solutions.**—The  $\text{Sn}^{119}$  chemical shifts in a miscellaneous lot of compounds are given in Table I.

**Indirect Spin-Spin Couplings.**—Protons in alkyl groups attached to tin have coupling constants with  $\text{Sn}^{119}$  of about 50 to 100 c.p.s. For example, the  $\text{Sn}^{119}$  spectrum of  $(\text{CH}_3)_3\text{Sn}$  consists of thirteen peaks (of which nine have been observed) with separations of 54 c.p.s. These couplings are usually best measured in the proton spectra. These couplings between methyl protons and tin are functions both of the other substituents and of the solvent used. For example, the  $\text{Sn}^{119}$  coupling in  $(\text{CH}_3)_3\text{SnCl}_2$  in acetone solution is 80 c.p.s. and in water solution is 98 c.p.s. Both of the above measurements were also made on the proton spectra.

If larger alkyl groups are present on the tin, couplings occur with more distant protons as well. These longer range interactions are comparable in size to the shorter range ones and are sometimes considerably greater. Such a phenomenon has been observed in  $(\text{C}_2\text{H}_5)_3\text{Pb}$  by Baker<sup>34</sup> and in some dialkylmercury compounds by Dessy, *et al.*<sup>11</sup> Its effects on  $\text{Sn}^{119}$  spectra is to split the resonance into a great many closely spaced components so that it appears to be a very broad peak. The resonances of such compounds as  $(n\text{-C}_4\text{H}_9)_3\text{Sn}$  are thus difficult to measure accurately, and the usefulness of the spectra in the study of organotin compounds is impaired. The effective removal of the splitting by double resonance techniques<sup>35</sup> would greatly increase the sensitivity and accuracy of measurements on such compounds.

**Line Widths.**—The widths of the  $\text{Sn}^{119}$  resonances are extremely variable. The effects of the indirect spin-spin coupling with protons in alkyl derivatives have been discussed above. The width of each individual line in the  $(\text{CH}_3)_3\text{Sn}$  rapid passage spectrum, measured at half height, was about 25 c.p.s. at the power levels normally used. The limiting width at low power, measured with absorption mode tuning, was about 10 c.p.s., and was undoubtedly determined by the magnetic field inhomogeneity over the large sample. Under the same conditions, the width of the  $\text{SnBr}_4$  peak was 56 c.p.s. After addition of about 10 mole % of  $\text{AlBr}_3$  to form a purple solution, the width was found to be 52 c.p.s. In a 3:1 molar mixture with  $\text{SnCl}_4$  it was 51 c.p.s. The widths are accurate to about  $\pm 10\%$ , so there were no significant changes. On the other hand, a solution of 40% by volume  $\text{SnBr}_4$  in  $\text{CS}_2$  gave a line width of 130 c.p.s. The  $\text{SnCl}_4$  peak behaved similarly on dilution. In

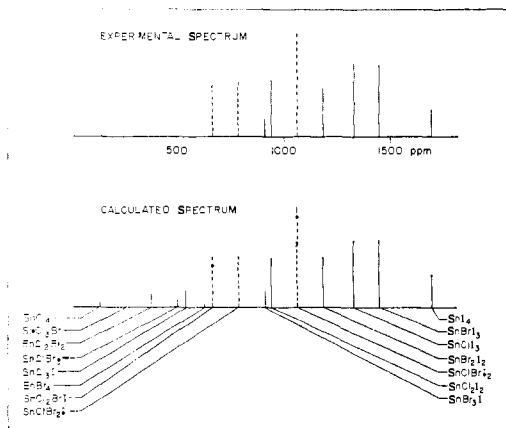
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Fig. 1.—Sn<sup>119</sup> spectrum of a 1:1 molar mixture of SnBr<sub>4</sub> and SnI<sub>4</sub>.Fig. 2.—A comparison of the calculated and observed spectra for a 2:1:1 molar mixture of SnI<sub>4</sub>, SnBr<sub>4</sub> and SnCl<sub>4</sub>. (Dotted lines represent the three new peaks found in the mixture.)

the pure state, the peak-to-peak width of the dispersion curve was about 640 c.p.s., and when diluted to 40% in CS<sub>2</sub> it was about 820 c.p.s. The widths of the resonances in both solutions decreased as the radiofrequency power level was lowered. SnI<sub>4</sub> in CS<sub>2</sub> solutions and in halide mixtures, gave peaks narrower than that of pure SnBr<sub>4</sub>, although no exact measurements were made.

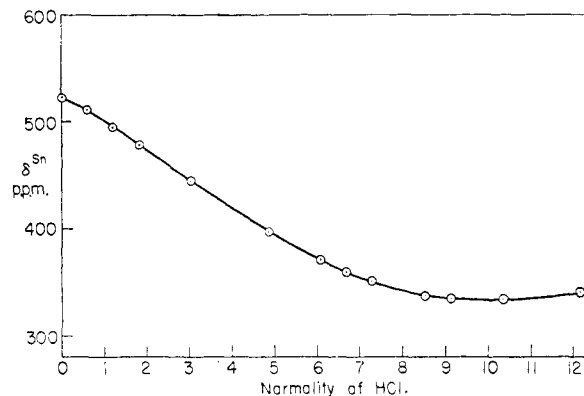
**Mixed Tin(IV) Halides.**—Three new peaks are found in the Sn<sup>119</sup> spectra of mixtures of SnCl<sub>4</sub> and SnBr<sub>4</sub>. They are almost equally spaced between the resonances of the pure compounds, and their intensities are approximately those predicted for each mixture if a random redistribution reaction is taking place. Mixtures of SnCl<sub>4</sub> and SnI<sub>4</sub> and of SnBr<sub>4</sub> and SnI<sub>4</sub> (Fig. 1) give the same type of spectrum. Samples made up from various proportions of all three simple halides gave spectra with three new peaks. They were assigned by comparing their intensities in the three mixtures and by the agreement of the shifts with those predicted by assuming each halogen atom to contribute an amount to the shift equal to one-fourth the shift of the corresponding pure halide. The predicted and observed shifts are compared in Table II. The shifts are those measured on the

Table II

PREDICTED AND OBSERVED Sn<sup>119</sup> CHEMICAL SHIFTS IN SnI<sub>2</sub>BrCl, SnIBr<sub>2</sub>Cl AND SnIBrCl<sub>2</sub>

Halide	Shift (p.p.m.)	
	Calcd.	Obsd.
SnClBrI <sub>2</sub>	1046	1068
SnClBr <sub>2</sub> I	781	796
SnCl <sub>2</sub> BrI	659	672

2:1:1 molar mixture of SnI<sub>4</sub>, SnBr<sub>4</sub> and SnCl<sub>4</sub>, since these are believed to be the most accurate. The shifts in the simpler mixed halide series are not perfectly linear, and the deviations from linearity are such that, if they were taken into account, the calculated and observed shifts would be in better agreement. Table III gives the positions of all of the peaks observed in all of the mixtures and shows that solvent effects are unimportant in halide mixtures and in carbon disulfide solutions. Those compounds not observed were present in low concentrations or give broad lines if moderately abundant. The peaks of polychloro

Fig. 3.—Plot of the Sn<sup>119</sup> shifts in aqueous solutions of SnCl<sub>2</sub>·2H<sub>2</sub>O and HCl vs. the normality of the added HCl.

compounds in particular often proved to be too broad to detect at low concentrations.

The correctness of both the assignments and the assumption of a random redistribution is supported by the agreement between the relative intensities in a calculated spectrum of the 2:1:1 molar SnI<sub>4</sub>, SnBr<sub>4</sub>:SnCl<sub>4</sub> mixture and the average intensities measured in eight such spectra. Table IV shows the calculated and observed intensities expressed as mole per cents. The observed spectrum has been matched to the calculated one by assuming the theoretical value for the SnI<sub>2</sub>BrCl peak. The observed intensities appear to be reproducible to within about ±10%. They were calculated by multiplying together the peak-to-peak heights and peak-to-peak widths of the dispersion curves. Fig. 2 is a graphical comparison of the calculated and observed spectra.

The fact that individual resonances, separated by one to three kilocycles/sec., are found for the halides in the mixtures proves that the lifetimes of the molecules between exchange reactions are greater than about 10<sup>-3</sup> sec.<sup>36</sup> The lack of appreciable broadening suggests that these lifetimes could not be much less than 10<sup>-2</sup> sec. An upper limit to these lifetimes of about 10 sec. was set by the failure of two attempts to follow the course of the redistribution reaction. In the first experiment, equimolar quantities of SnCl<sub>4</sub> and SnBr<sub>4</sub> (as under-cooled liquid) were quickly mixed at room temperature. When the first observation of the SnBr<sub>4</sub> peak was made, about 30 seconds later, it had decreased to its equilibrium height. In the second experiment, a solution of 5 g. of SnI<sub>4</sub> in 3 ml. of CS<sub>2</sub> was shaken with a solution of 1.04 ml. of SnBr<sub>4</sub> in 1 ml. of CS<sub>2</sub>. The deep red-orange color of the SnI<sub>4</sub> solution was immediately replaced by a light orange color, and the SnI<sub>4</sub> peak had reached its equilibrium height by the time of the first observation, 30 seconds later. No precautions were taken to exclude atmospheric moisture or to purify the reagents, so that small amounts of hydrogen halides were probably present. Since these may well catalyze the reactions, it is likely that they are slower in the pure materials.

**SnCl<sub>2</sub>·2H<sub>2</sub>O-HCl Solutions.**—Fourteen solutions, each containing 5.00 grams of SnCl<sub>2</sub>·2H<sub>2</sub>O dissolved in 3.00 ml. of hydrochloric acid were prepared. Only one resonance line was observed in each of these solutions, and it is believed that the position of this line represents an average of the chemical shifts of each of the species, including complex ions, present in the solution.<sup>37-39</sup> A plot of the Sn<sup>119</sup> chemical shift vs. the normality of the added HCl is shown in Fig. 3. The change in chemical shift of 180 ± 0.8 ppm.

(36) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

TABLE III

**<sup>119</sup>Sn CHEMICAL SHIFTS OF SPECIES PRESENT IN MIXTURES OF TIN(IV) HALIDES** (—shows not present in mixtures)

Mole fraction			Sn halide															
SnCl <sub>4</sub>	SnBr <sub>4</sub>	SnI <sub>4</sub>	Cl <sub>4</sub>	Cl <sub>3</sub> Br	Cl <sub>2</sub> Br <sub>2</sub>	ClBr <sub>3</sub>	Cl <sub>3</sub> I	Br <sub>4</sub>	Cl <sub>2</sub> BrI	ClBr <sub>2</sub> I	Br <sub>3</sub> I	Cl <sub>2</sub> I <sub>2</sub>	ClBrI <sub>2</sub>	Br <sub>2</sub> I <sub>2</sub>	ClI <sub>3</sub>	BrI <sub>3</sub>	I <sub>4</sub>	
0	0	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1701
0	0.5	0.5	—	—	—	—	—	—	—	—	916	—	—	1187	—	—	1447	1698
0	0.75	0.25	—	—	—	—	—	638	—	—	919	—	—	1192	—	—	—	—
0	1	0	—	—	—	—	—	638	—	—	—	—	—	—	—	—	—	—
0.25	0.75	0	—	—	384	509	—	634	—	—	—	—	—	—	—	—	—	—
0.5	0.5	0	—	265	387	509	—	635	—	—	—	—	—	—	—	—	—	—
0.75	0.25	0	—	260	386	—	—	—	—	—	—	—	—	—	—	—	—	—
1	0	0	150	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.75	0	0.25	—	—	—	—	551	—	—	—	—	951	—	—	1347	—	—	—
0.5	0	0.5	—	—	—	—	557	—	—	—	—	955	—	—	1342	—	—	1712
0.25	0.25	0.5	—	—	—	—	—	—	672	796	919	947	1068	1189	1330	1449	1696	—
0.25	0.5	0.25	—	—	—	508	—	629	666	789	913	—	1063	1195	—	—	—	—
0.5	0.25	0.25	—	267	—	—	543	—	663	783	—	937	1060	—	—	—	—	—

TABLE IV

CALCULATED AND OBSERVED CONCENTRATIONS OF SPECIES IN A 2:1:1 MOLAR MIXTURE OF SnI<sub>4</sub>, SnBr<sub>4</sub> AND SnCl<sub>4</sub>

Compound	Concentration (mole %)	
	Calcd.	Obsd.
SnCl <sub>4</sub>	0.39	..
SnCl <sub>3</sub> Br	1.56	..
SnCl <sub>2</sub> Br <sub>2</sub>	2.34	..
SnClBr <sub>3</sub>	1.56	..
SnCl <sub>3</sub> I	3.12	..
SnBr <sub>4</sub>	0.39	..
SnCl <sub>2</sub> BrI	9.37	9.4
SnClBr <sub>2</sub> I	9.37	10.2
SnBr <sub>3</sub> I	3.12	3.5
SnCl <sub>2</sub> I <sub>2</sub>	9.37	10.9
SnClBrI <sub>2</sub>	18.76	18.76 <sup>a</sup>
SnBr <sub>2</sub> I <sub>2</sub>	9.37	9.0
SnClI <sub>3</sub>	12.50	13.7
SnBrI <sub>3</sub>	12.50	13.3
SnI <sub>4</sub>	6.25	5.5

<sup>a</sup> Assumed.

in going from pure water ( $521.3 \pm 0.3$ ) to 12.17 *N* HCl ( $341.2 \pm 0.5$ ) is the effect upon the observed average shift due to the change in concentrations of the various tin (II) ionic and molecular species which are present in the solutions.<sup>28-30</sup> It must be mentioned, however, that this graph has only a qualitative value since no attempt was made to determine the exact nature of the solutions nor of the precipitate which was formed and discarded in every case. It is probable that shift measurements of this kind, using more careful technique in the preparation of solutions, will prove valuable in the study of solutions of SnCl<sub>2</sub>·2H<sub>2</sub>O and other similar compounds.

The data obtained in this investigation also shows that aqueous solutions of SnCl<sub>2</sub>·2H<sub>2</sub>O are of no use as primary standards of reference for shift measurements since the <sup>119</sup>Sn chemical shift in this case is dependent upon the HCl concentration. The SnCl<sub>2</sub>·2H<sub>2</sub>O + HCl capillary which was used in these measurements as a secondary standard gave a value of  $336.6 \pm 0.2$  p.p.m. for the <sup>119</sup>Sn chemical shift.

**Acetone and Ethanol Solutions of SnCl<sub>2</sub>·2H<sub>2</sub>O.**—Effects similar to those noted in the HCl solutions of SnCl<sub>2</sub>·2H<sub>2</sub>O were found in acetone and ethanol solutions of SnCl<sub>2</sub>·2H<sub>2</sub>O. <sup>119</sup>Sn chemical shifts were found to be dependent upon the SnCl<sub>2</sub>·2H<sub>2</sub>O concentration in both acetone and ethanol. Shift differences of approximately 150 p.p.m. were observed in solutions of different SnCl<sub>2</sub>·2H<sub>2</sub>O concentration in ethanol and differences of approximately 100 p.p.m. were found in solutions of different SnCl<sub>2</sub>·2H<sub>2</sub>O concentration in acetone. <sup>119</sup>Sn shifts in saturated, room temperature (27°), SnCl<sub>2</sub>·2H<sub>2</sub>O solutions in both acetone and ethanol were found to change with time and differences of approximately 40 p.p.m. in acetone and 20 p.p.m. in ethanol were observed. These changes in <sup>119</sup>Sn chemical shift in the satu-

rated solutions were accompanied by the formation of crystals in the bottom of the sample tubes.

**Resonances Not Found.**—No <sup>119</sup>Sn resonance could be detected in solid SnBr<sub>4</sub>, although the Cl<sup>13</sup> resonance in solid CBr<sub>4</sub> is strong and fairly sharp.<sup>3</sup> Presumably the self-diffusion rate is slower in the tin compound. Solid SnI<sub>4</sub> gave no observable resonance. The resonance of SnCl<sub>4</sub> in saturated aqueous solution could not be found. It is probably broader than that of liquid SnCl<sub>4</sub>. A saturated aqueous solution of SnF<sub>2</sub> did not have an observable <sup>119</sup>Sn resonance, but a broad, weak F<sup>19</sup> peak was found, indicating that a fairly rapid exchange of fluorines was taking place, broadening the <sup>119</sup>Sn lines.

### Discussion

**Chemical Shifts.**—The first noticeable feature of the shifts is that there is no separation of those of tin(II) compounds from those of tin (IV) compounds. The shifts of SnSO<sub>4</sub>, SnCl<sub>2</sub>·2H<sub>2</sub>O and SnCl<sub>2</sub> are within the range of those found for tin in the higher oxidation state.

A plot of the shifts in the series (Bu)<sub>x</sub>SnCl<sub>4-x</sub> has the usual downward-curving shape of such plots, as was mentioned in the Introduction. The shift for (Bu)<sub>2</sub>SnCl<sub>2</sub> in CS<sub>2</sub> was taken as being the most reliable because no unusual solvent effects upon the shift were observed on the CS<sub>2</sub> solution of SnI<sub>4</sub>. The corresponding plot for the series SnCl<sub>x</sub>Br<sub>4-x</sub> is almost exactly linear, just as it is for the analogous carbon series.<sup>4</sup> The shifts in the SnCl<sub>x</sub>I<sub>4-x</sub> and SnBr<sub>x</sub>I<sub>4-x</sub> series also are nearly linear, but the plots are bowed upward very slightly, the first known example of such behavior. To a very good approximation, however, chlorine, bromine and iodine can be regarded as contributing a fixed amount, independent of the other halogens present, to the chemical shifts of tin in the mixed tin(IV) halides. This is further demonstrated by the good agreement between the calculated and observed shifts, in Table II, of the halides containing three different halogens.

The differences between the shifts of SnCl<sub>4</sub> and SnBr<sub>4</sub> and between those of SnBr<sub>4</sub> and SnI<sub>4</sub> are approximately proportional to the electronegativity differences between the halogens. This is probably not very significant, however. The shift of (CH<sub>3</sub>)<sub>4</sub>-Sn is less than that of SnCl<sub>4</sub>, even though the methyl group is usually assigned a somewhat lower electronegativity than is iodine. It is certain that differences in the diamagnetic part of the shielding<sup>37</sup>

(37) N. F. Ramsey, *Phys. Rev.*, **77**, 567 (1950); **78**, 699 (1950); **83**, 540 (1951); **87**, 243 (1952).

cannot be great enough to account for the large shifts, since it is easy to show that the complete removal of the tin valence electrons would not give shifts of the magnitude observed. The second-order paramagnetic term in Ramsey's shielding expressions<sup>37</sup> must, therefore, be primarily responsible for the observed shifts, but no calculations of this effect in tetrahedrally symmetric molecules have yet been made.

**Solvent Effects on Shifts and Indirect Spin-Spin Couplings.**—Except for the observations on the HCl solutions of SnCl<sub>2</sub>·2H<sub>2</sub>O our data on solvent effects are very limited, but in the main it demonstrates that care must be taken in using solutions for shift or coupling measurements. Presumably, the unusually large effects observed in the Sn<sup>119</sup> spectra are the result of the well known tendency of tin compounds to coordinate strongly with many substances. It would seem that n.m.r. spectra should become quite useful in studies of complex

formation by compounds of tin and other elements.

**Line Widths and Relaxation Times.**—The widths of some of the Sn<sup>119</sup> lines are not unprecedented. The P<sup>31</sup> lines in compounds such as PCl<sub>3</sub>, POCl<sub>3</sub> and PSCl<sub>3</sub> are broadened,<sup>38-40</sup> although those in PBr<sub>3</sub>, POBr<sub>3</sub> and PSBr<sub>3</sub> are not.<sup>38,40</sup> The Si<sup>29</sup> lines in chlorosilanes are difficult to observe<sup>5</sup> and the C<sup>13</sup> resonances in CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>CCl<sub>3</sub> and similar compounds are broad and weak,<sup>3</sup> although CBr<sub>4</sub> has a strong resonance and a fairly short spin-lattice relaxation time ( $T_1$ ). It has now been found that the Sn<sup>119</sup> resonance in SnCl<sub>4</sub> is very broad and that the SnBr<sub>4</sub> resonance is slightly broadened and has a  $T_1$  estimated at considerably less than one second. Apparently, some interactions with the halogen nuclei are not completely averaged out by their rapid quadrupole-induced relaxation.

(38) P. C. Lauterbur, unpublished work.

(39) H. Finegold, *Ann. N. Y. Acad. Sci.*, **70**, 875 (1958).

(40) E. Fluck, J. R. Van Wazer and L. C. D. Groenweghe, *THIS JOURNAL*, **81**, 6363 (1959).

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## Molecular Addition Compounds of Tin(IV) Chloride. I. Interaction with Benzonitriles in Benzene Solution

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RECEIVED JULY 11, 1960

Infrared spectra of benzene solutions containing tin(IV) chloride and benzonitriles have been utilized in an evaluation of the equilibria leading to addition compound formation. The results indicate that the formation of the 1:1 addition compound is the most important equilibrium in dilute solutions but that some 2:1 addition compound is also formed. The dependence of the values of the equilibrium constants on the nature of the *meta* or *para* substituent in the benzonitrile has been examined. Dielectric constant data for the tin(IV) chloride-benzonitrile system in benzene have been analyzed in the light of the equilibrium constants obtained from the infrared data to obtain dipole moment values for the 1:1 and 2:1 addition compounds. The moment calculated for the 1:1 addition compound is  $8.4 \pm 0.2D$ ; the moment calculated for the 2:1 compound is about  $3.1D$ . The latter value may, however, be as high as  $5D$  or as low as zero.

The Lewis acid character of tin(IV) chloride, first investigated extensively by Pfeiffer,<sup>1</sup> has been the subject of considerable study. With monofunctional bases which do not undergo a complicating reaction such as dehydrohalogenation<sup>2</sup> the solid compounds obtained are usually of the stoichiometry AB<sub>2</sub>, where A represents SnCl<sub>4</sub> and B represents the base molecule. In cases where solid compounds are not isolated, the formula of the addition compound has been determined by cryoscopic,<sup>3</sup> calorimetric and thermometric<sup>4</sup> or one of a number of other methods.

Despite the considerable literature dealing with tin(IV) chloride (hereinafter abbreviated TC) addition compounds, very little is known about their structures or behavior in solutions. The Lewis acid character of TC is generally pictured as arising from the use of vacant 5d atomic orbitals on the tin atom. In AB<sub>2</sub> the bonding is assumed to sp<sup>3</sup>d<sup>2</sup>, which leads to an octahedral arrangement of hybrid orbitals about the central atom. This

arrangement gives rise to the possibility of *cis-trans* isomerism. This fact was recognized early by Ulich and co-workers,<sup>5</sup> who attempted to determine the geometry of AB<sub>2</sub> species by a combination of freezing point lowering and dielectric constant measurements on benzene solutions of TC with bases such as ethers, ketones and nitriles. Recognizing the possibility of a number of simultaneous equilibria involving the species A, B, AB, (AB)<sub>2</sub> and AB<sub>2</sub>, these workers attempted to evaluate the various equilibrium constants by using the freezing point lowering data. They concluded that in benzene solutions of TC and benzonitrile at 20° the AB<sub>2</sub> species does not exist, that there is a small amount of AB dimer formed and that the principal complex species is AB. The freezing point lowering data on the basis of which the various *K*'s were evaluated do not, however, possess the necessary sensitivity and freedom from random error which is required for precise determination of equilibria.

More recently, Osipov<sup>6,7</sup> has reported dipole

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(b) P. Pfeiffer and O. Halperin, *Z. anorg. Chem.*, **87**, 335 (1913).

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(7) Y. B. Kletenik, O. A. Osipov and E. E. Kravtsov, *Zhur. Obschchei Khim.*, **29**, 11 (1959).