

X-ray study.⁹ This structure for the DMA adduct in solution is further established as a result of these studies. The thermochemical data are indicative of extensive rehybridization of the acid upon coordination. In general, it is found that as the enthalpy of a donor-acceptor interaction increases the entropy becomes more negative. In contrast to an enthalpy of -9.5 kcal. mole⁻¹ and an entropy of -17 e.u. for the DMA-ICl adduct, values of -7.7 kcal. mole⁻¹ and

(9) R. Hulme, *J. Chem. Soc.*, 1524 (1963); I. R. Beattie, G. P. McQuillan, and R. Hulme, *Chem. Ind. (London)*, 1429 (1962).

-23 e.u. are obtained for the trimethyltin chloride adduct. The larger negative entropy for this latter adduct is attributed to a large extent to the extensive rearrangement of the methyl groups in going from a C_{3v} structure for the free acid to a trigonal bipyramidal adduct. There is no evidence, under these experimental conditions, for a six-coordinate species.

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Electromotive Force, Raman, and Nuclear Magnetic Resonance Studies on the Interaction of Chloride and Bromide Ions with the Dimethyltin(IV) Ion. Inner- and Outer-Sphere Complexes¹

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The complexing of (CH₃)₂Sn²⁺(aq) by Cl⁻ and Br⁻ in aqueous solution has been studied by e.m.f., Raman, and proton n.m.r. measurements. By the use of the cells, glass electrode|0.2 M H⁺, 2.8 M Na⁺, 3 M ([ClO₄⁻] + [X⁻])|AgX|Ag (X = Cl⁻ and Br⁻), the halide ion concentrations were determined in solutions containing (CH₃)₂Sn²⁺. The following values for the stability constants of the chloro complexes were obtained at 25° by least-squares refinement: log β₁ = 0.380 ± 0.001 and log β₂ = -0.14 ± 0.01. Little of the 2:1 complex could have been present, and its existence is not definitely established. The interaction with Br⁻ was very weak, and log β₁ < -0.5. The values of the ¹¹⁷Sn and ¹¹⁹Sn methyl proton spin-spin coupling constants and the integrated Raman intensities for tin-chloride bond stretching in solutions as a function of chloride ion concentration indicated that both inner- and outer-sphere complexes are formed. Only in concentrated chloride solutions are appreciable concentrations of the inner-sphere complex present. The Raman spectra show that inner-sphere complexing also occurs in concentrated bromide solutions. The dimethyltin(IV) ion is characterized by a high affinity for water molecules, and in many respects the solutions of (CH₃)₂SnCl₂ and (CH₃)₂SnBr₂ resemble those of oxonium chloride and bromide. The hypothetical free linear (CH₃)₂Sn²⁺ can be regarded as an extremely "hard" acid which forms very stable complexes with bases of low polarizability and gives large crystal-field effects in lattices.

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Introduction

There are many organometallic cations which are stable in aqueous solution ranging from diamagnetic alkyl and aryl derivatives of groups III-V-B to paramagnetic π -cyclopentadienyl cations of the transition metals. The solution chemistry and structure of these ions have been little studied, although the ions have some unique properties.

In many respects, the chemistry of the complexes of organometallic cations containing small alkyl groups should resemble that of other complexes of the particular metal under consideration. On the other hand, there are instances where the study of an organometallic ion can be particularly advantageous. This would appear to be especially true in the case of ions of the post-transition metals which are diamagnetic and which lack electronic transitions which are of much use for obtaining information on the structure and bonding of complexes of the ions. While complexes of these metals with most ligands are generally quite labile, the metal-carbon bonds are often inert, so that the thermodynamically favorable hydrolysis proceeds at an infinitesimal rate. Studies on complexes of these organometal ions by vibrational and n.m.r. spectroscopy often can provide structural information on metal-ligand interactions not easily obtainable for complexes of the simple metal ions.

Solutions containing organometallic cations are most often obtained by dissolution of the halides. Among the best-known examples are the organotin halides. Aquation of these compounds with displacement of halide ion occurs very rapidly, and it has been suggested that the mechanism is a synchronous displace-

ment in the case of the trialkyltin chlorides.⁴ Association of the alkyltin cations and the halide ions is not extensive, for it has long been known that aqueous solutions of the compounds R_3SnX_2 and R_3SnX behave like 2:1 and 1:1 electrolytes, respectively. It has also been noted that the solvent must be a good electron donor if electrolyte behavior is to occur. In dimethylformamide solutions, for example, these compounds are nonelectrolytes.^{5,6}

In order to obtain some information on the nature and extent of the interaction between organotin cations and ligands, a study of halide complexing of the dimethyltin(IV) cation was undertaken. Earlier Raman spectroscopic studies had indicated that some chloride complexing of $(CH_3)_2Sn^{+2}$ occurs in concentrated aqueous solution.⁷ Since the halide ion complexing constants of tin(II) are accurately known, it should be possible to make precise comparisons of the stability of complexes of $(CH_3)_2Sn^{+2}$ and Sn^{+2} . It has been noted previously that analogous compounds of these two ions often have similar properties.⁸

An earlier attempt to study the coordination of ligands like acetylacetonate, picolinate, and 1,10-phenanthroline with $(CH_3)_2Sn^{+2}$ in aqueous solution was not especially successful, because these ligands do not compete very effectively with hydroxide ion.^{9,10} Apparently this cation has a very high affinity for water molecules, since a variety of these chelate complexes can be prepared and studied in nonaqueous systems.¹¹ Also, because the hydrolysis reactions of the dimethyltin ion must be taken into consideration in the calculations of the complexing, it is not feasible to use mixed water-organic solvent systems in order to form appreciable concentrations of the uncharged complexes.

Experimental Section

Preparation of Reagents and Solutions. Dimethyltin oxide was prepared by hydrolysis of the chloride. Dimethyltin dichloride obtained from M and T Chemicals was dissolved in water, and the solution was filtered and shaken with benzene to extract a colored impurity. The oxide was precipitated by adding ammonia, collected on a filter, and washed. The first product was dissolved in dilute perchloric acid and reprecipitated as the oxide. This procedure was repeated two more times, and no chloride could be detected in the perchlorate solutions. The final precipitate was washed 15 times with water and dried.

Sodium perchlorate used for the ionic medium was prepared by neutralizing A.R. grade sodium carbonate with A.R. grade perchloric acid, and the CO_2 was expelled by boiling. The solution was neutralized to pH 7 with carbonate-free NaOH, and the silica which precipitated was filtered off using a sintered glass funnel. The solution was acidified with $HClO_4$, boiled, neu-

tralized, and filtered again. The product $NaClO_4$ was recrystallized three times at 90° as the anhydrous salt. Finally the salt was dissolved in distilled water to give a nearly saturated solution and filtered through a fine sintered glass funnel. The solution was standardized by drying aliquots to constant weight at 120° .

Perchloric acid solutions were prepared from A.R. grade 70% acid. Standardization was accomplished vs. Na_2CO_3 and $KHCO_3$. The potassium hydrogen carbonate was prepared by recrystallizing A.R. grade $KHCO_3$ from water saturated with CO_2 at 55° . Hydrochloric acid solutions were prepared from A.R. grade hydrochloric acid as follows. Concentrated acid was diluted to about 20% by weight with distilled water. About 0.1 mole of $KMnO_4$ was added to 4 l. of the diluted acid in 25 aliquots, the chlorine being boiled off after each addition in order to remove traces of bromide in the HCl. This procedure was necessary, since traces of Br^- are known to have a pronounced effect on silver-silver chloride electrodes.¹² The solution was boiled for some time to expel chlorine and the acid was distilled through a column packed with glass chips. The first and last 25% of the distillate was rejected, and the middle fraction was redistilled with the first and last fractions again being rejected. The acid stock solutions were standardized volumetrically using $KHCO_3$ and gravimetrically by precipitation of $AgCl$. Sodium bromide (A.R.) was recrystallized twice from water and dried.

The distilled water used in the preparation of all of the solutions was obtained by distillation of demineralized water from an alkaline $KMnO_4$ solution in an all-glass still.

Apparatus and Procedure for Solution Measurements.

The e.m.f. measurements for both the chloro and bromo complexing were made in a medium containing 3 M total ($[ClO_4^-] + [Cl^-]$) with 2.8 M Na^+ and 0.2 M H^+ . The presence of the 0.2 M acid is sufficient to prevent any significant hydrolysis of the dimethyltin aquo ion,¹³ and it also allows a glass electrode to be used as a reference electrode for the silver-silver halide electrode used to measure the halide ion concentration. In this way, the complexing could be studied with a cell having no liquid-liquid junctions.

The cell potentials were recorded with the vibrating reed electrometer circuit described earlier.¹³ In order to minimize errors due to drift of the glass electrode asymmetry potential with time, the measurements were made as quickly as possible. The temperature control of the thermostat room was improved so that fluctuations during a run were limited to ca. $\pm 0.1^\circ$. The temperature control of the oil bath was also improved so that the cell temperature did not vary by more than $\pm 0.02^\circ$.

The titration vessel was a seven-neck flask containing two silver halide electrodes and two glass electrodes. A solution volume of 5 ml. covered the electrodes adequately. Two Beckman 40498 electrodes were selected for minimum drift of the asymmetry potential by measurements in acid and buffer solutions. Silver halide electrodes were prepared by electrolysis of 1%

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(9) M. Yasuda and R. S. Tobias, *Inorg. Chem.*, **2**, 207 (1963).

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KAg(CN)₂ to plate silver on platinum electrodes. These were then oxidized by electrolysis of HCl or NaBr solutions.¹⁴

Solutions were made up by weighing standard 1 M HCl or solid NaBr, 1 M HClO₄, ca. 9 M NaClO₄, and solid (CH₃)₂SnO into standard flasks. Densities for all solutions were obtained so volumes delivered could be checked against weights. Approximately 10 ml. of solution was added to the titration flask, two glass and two silver halide electrodes were inserted, and the flask was immersed in the oil bath. Potentials of the four glass-silver electrode combinations were recorded at each point. Differences between the different silver halide electrodes were usually less than 0.05 mv. At times the glass electrodes showed a slight drift in asymmetry potential with time, and the cell voltages were corrected for this.

The potentials of these cells without liquid-liquid junctions and at constant hydrogen ion activity are given by $E = E^\circ - 59.15 \log [X^-]$; $X^- = \text{Cl}^-$ or Br^- in mM and E is in mv. In some of the titrations, the total dimethyltin ion concentration was maintained constant. In these runs, the E° was determined by varying the halide concentration from ca. 1 to 10 mM in the absence of (CH₃)₂Sn²⁺, and then the (CH₃)₂Sn²⁺ was added. In other runs, the halide ion concentration was maintained approximately constant, and the E° was obtained by measurements of the potential with a single standard chloride solution. The values of E were corrected for small differences in [H⁺] between the initial and added solutions and for slight hydrolysis of (CH₃)₂Sn²⁺ at the highest concentrations. These corrections amounted to less than 0.05 mv.

Raman Spectra. The Raman spectra were recorded with a Cary Model 81 spectrophotometer, and the general procedure for the measurements has been described earlier.⁷ All spectra were recorded within a few hours after the preparation of the solution. Cells 7 mm. in diameter constructed with a 48-cm. water jacket were used for the intensity measurements. Water from a thermostat at $25 \pm 1^\circ$ was pumped through the jacket. These cells were used in the spectrophotometer lamp housing designed for gas cells; however, only one lamp was used to excite the spectra. Both ClO₄⁻ and NO₃⁻, 1 M in concentration, were tried as internal standards for the intensity measurements since earlier work had shown that there was no measurable complexing of the (CH₃)₂Sn²⁺ in either 1 M (CH₃)₂Sn(NO₃)₂ or (CH₃)₂Sn(ClO₄)₂.⁷ It was noted that in the solutions which were very strongly acidic the nitrate ion was slowly oxidizing the dimethyltin ion as indicated by a decrease in the intensity with time of both the 1045-cm.⁻¹ line (A₁) of NO₃⁻ and also of the 529-cm.⁻¹ line (A₁) of the (CH₃)₂Sn²⁺. No such reaction was observed with ClO₄⁻ over long periods of time, and the 932-cm.⁻¹ ClO₄⁻ line (A₁) was used for all intensity measurements.

The solutions were prepared from (CH₃)₂SnO, HClO₄, and HCl or LiCl. The intensities were obtained by recording the A₁ mode of ClO₄⁻, the line attributed to the complex, and the A₁ ClO₄⁻ line again. The average of two such measurements was used. The instrument sensitivity was adjusted so that the 932-cm.⁻¹ ClO₄⁻ line gave a deflection about 0.8 full

scale resulting in integrated intensities of ca. 1000 cm.⁻¹ %. The scan rate was 0.05 cm.⁻¹/sec. and a single 10 cm. \times 10 cm.⁻¹ slit was used. The lines were integrated to obtain the relative intensities $I_{\text{Sn-Cl}}/I_{\text{ClO}_4}$.

Proton N.m.r. Spectra. Proton resonance measurements were made with either a Varian DP-60 spectrometer at 56.4 Mc./sec. or with a Varian A-60 spectrometer. Coupling constants were determined with the side-band technique and are believed accurate to ± 1 c.p.s. The solutions were prepared as for the Raman studies.

Results

E.m.f. Measurements. The equilibrium data for the chloro complexing of the dimethyltin(IV) ion are shown in Figure 1 as \bar{n} , the average number of chloride ions coordinated per (CH₃)₂Sn²⁺, as a function of log [Cl⁻]. A total of 47 points from 10 different runs were used in the final calculations of the chloro complexing constants. For the bromo complexing only three titrations were made, and five points in the range $\bar{n} \simeq 0.01$ ([Br⁻] > 100 mM) were used to estimate the equilibrium constant. For higher bromide concentrations, the reliability of the electrodes was uncertain. All of these data apply to a medium containing 3 M total ([ClO₄⁻] + [X⁻]) (X = Cl⁻ and Br⁻), 2.8 M Na⁺, and 0.2 M H⁺ at a temperature of 25°.

A point by point calculation for the stability constant of the monochloro complex was made using the data in Figure 1, and this gave the value $\log \beta_1 = 0.388 \pm 0.006$. The upper limit to the standard error was estimated from $[\sum(pK_i - pK_i)^2/(N - 1)]^{1/2}$. The solid line in Figure 1 was calculated with this value for the constant. Similar calculations for the bromide case gave $\log \beta_1 = -1.0$. An error analysis indicated that the upper limit to the value was certainly less than -0.5.

Since the data deviated from the theoretical 1:1 curve at the highest chloride concentrations, values of $\log \beta_1$ were calculated from the data obtained in titrations where the chloride ion concentration was approximately constant. These values of $\log \beta_1$ varied almost linearly with the chloride ion concentration. Extrapolation to zero chloride ion concentration gave the value $\log \beta_1 = 0.383$ for a 3 M perchlorate medium.

There are several possible causes of the deviations at higher chloride ion concentrations: a 2:1 complex might be formed, the glass electrode might respond to the substitution of Cl⁻ for ClO₄⁻ in the ionic medium, or the activity coefficients of the ions might undergo small changes as up to 200 mM Cl⁻ replaces ClO₄⁻ in the 3 M medium. Values of the cell E° calculated with varying [Cl⁻] in the absence of (CH₃)₂Sn²⁺ showed no detectable change ($\leq \pm 0.02$ mv.) with [Cl⁻] ≤ 20 mM. For 200 mM Cl⁻, the deviation was only ca. 0.6 mv. with the free chloride ion concentration appearing too low. Similar measurements with the Ag-AgBr-Br⁻ electrodes indicated that the effect was only about one-third as great. Measurements of the potentials of cells consisting of the glass electrodes vs. a hydrogen electrode were made for solutions with total ([ClO₄⁻] + [Cl]) = 3 M. The cell potentials remained

(14) A. S. Brown, *J. Am. Chem. Soc.*, **56**, 646 (1934).

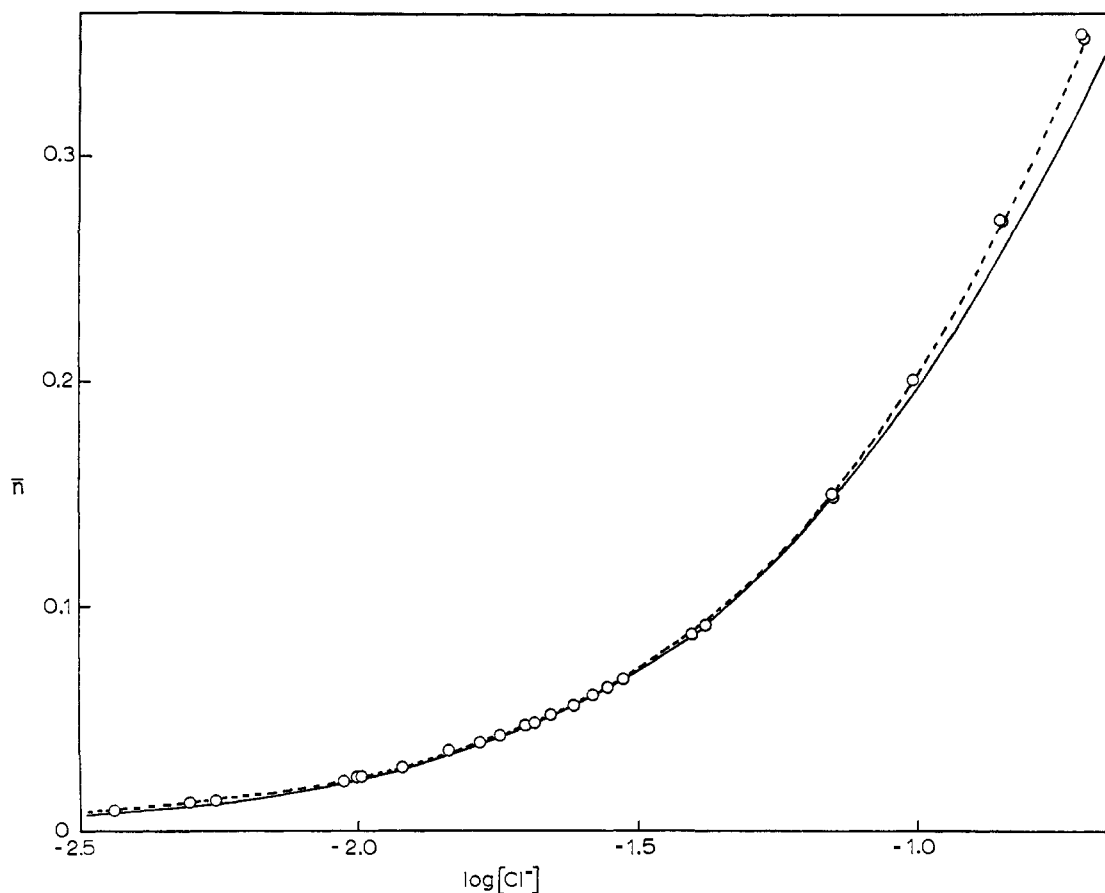


Figure 1. The average number of chloride ions bound per $(\text{CH}_3)_2\text{Sn}^{\text{IV}}$ at 25° . The solid line is calculated with $\log K_1 = 0.388$, and the broken line is calculated with $\log K_1 = 0.380$ and $\log K_2 = -0.52$. Only a portion of the experimental points are shown.

constant as the chloride ion concentration was changed, indicating that the deviation noted above was not caused by changes in the glass electrode asymmetry potential. In this system, it is not possible to determine if the deviation is caused by activity coefficient variations or by the formation of small quantities of a 2:1 complex, although the latter explanation seems the more likely.

In order to test just how much improvement in the fit could be obtained assuming that both a 1:1 and a 2:1 complex were formed, values for these constants were refined by a least-squares procedure using the program GAUSS Z.¹⁰ The trial values $\log \beta_1 = 0.383$ and an estimate $\log \beta_2 = -1$ were used. All of the data were given equal weights. The refined values were $\log \beta_1 = 0.380 \pm 0.001$, $\log \beta_2 = -0.14 \pm 0.01$, $\sigma_{\bar{n}} = 0.0012$. This gives for the second stepwise constant $\log K_2 = -0.52 \pm 0.01$. The broken line in Figure 1 was calculated with these values. Table I gives the calculated and observed \bar{n} values together with the values of the total dimethyltin(IV) concentration, M , and the log of the equilibrium ligand concentration, $\log L$.

Proton Nuclear Magnetic Resonance. It was noted several years ago that the tin proton spin-spin coupling constants of dimethyltin dichloride undergo a very large increase when the compound is dissolved in water.^{15,16} In order to determine if the coupling con-

stants undergo a corresponding decrease as chloro complexing occurs, values were determined for solutions of $(\text{CH}_3)_2\text{SnCl}_2$ as a function of concentration and also as a function of the total chloride ion concentration.

Data for the concentration dependence of the coupling constants of aqueous $(\text{CH}_3)_2\text{SnCl}_2$ are given in Table II together with values for other dimethyltin compounds. Figure 2 shows the variation of coupling constants with the total chloride ion concentration in solutions with $[(\text{CH}_3)_2\text{Sn}^{+2}] = 1.5 M$ and $[\text{H}^+] = 6.8 M = ([\text{Cl}^-] + [\text{ClO}_4^-])$. In these solutions, the water activity should remain fairly constant. A solution was prepared with $\text{Cl}^- = \text{ca. } 2 M$ for this series but $(\text{CH}_3)_2\text{SnCl}_2$ precipitated.

Raman Spectra. Figure 3 gives the relative Raman intensities of the tin-chlorine stretching vibration at 325 cm.^{-1} for solutions $1 M$ in $(\text{CH}_3)_2\text{Sn}^{+2}$ with varying total chloride ion concentrations. There was no evidence for any shift or broadening of the already broad line with increasing chloride ion concentration. Solutions were prepared using both HCl and LiCl to control the chloride concentration; however, $(\text{CH}_3)_2\text{SnCl}_2$ was precipitated from the solutions when the concentration of LiCl exceeded about $3.4 M$, while at lower concentrations the 325-cm.^{-1} line was very weak. The determinations of the integrated intensities were not highly precise, because the broad tin-chlorine stretching line overlaps the broad, intense line at 175 cm.^{-1} to some extent. The Raman spectrum of a concentrated chloride solution has been given previously, illustrating the broad nature of this band.⁷

(15) J. J. Burke and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 326 (1961).

(16) J. R. Holmes and H. D. Kaesz, *ibid.*, **83**, 3903 (1961).

Table I. Observed and Calculated \bar{n} Values

M	$\text{Log } L$	\bar{n}_{calcd}	\bar{n}_{obsd}
0.020146	-2.2573	0.0131	0.0132
0.020398	-1.9919	0.0240	0.0241
0.050606	-2.2999	0.0119	0.0123
0.050656	-2.0024	0.0234	0.0243
0.050671	-1.8377	0.0340	0.0353
0.101460	-2.4336	0.0088	0.0092
0.101460	-2.0251	0.0223	0.0222
0.101460	-1.9214	0.0281	0.0283
0.101460	-1.8435	0.0335	0.0341
0.101460	-1.7808	0.0386	0.0393
0.019856	-1.4045	0.0883	0.0877
0.036219	-1.3989	0.0894	0.0884
0.053167	-1.3935	0.0904	0.0891
0.075318	-1.3871	0.0917	0.0903
0.100376	-1.3802	0.0930	0.0912
0.023642	-1.7436	0.0419	0.0423
0.033458	-1.7006	0.0461	0.0464
0.046347	-1.6520	0.0514	0.0514
0.057379	-1.6158	0.0557	0.0554
0.069858	-1.5801	0.0602	0.0601
0.080287	-1.5531	0.0639	0.0634
0.092685	-1.5255	0.0679	0.0675
0.020078	-0.7001	0.3554	0.3510
0.035228	-0.7011	0.3548	0.3527
0.050346	-0.7023	0.3541	0.3548
0.072822	-0.7038	0.3532	0.3548
0.101312	-0.7057	0.3520	0.3545
0.020235	-0.8490	0.2721	0.2705
0.035378	-0.8497	0.2717	0.2721
0.050536	-0.8503	0.2714	0.2727
0.071506	-0.8512	0.2710	0.2727
0.102040	-0.8520	0.2706	0.2715
0.020393	-1.0082	0.2006	0.2007
0.035819	-1.0087	0.2004	0.2006
0.051192	-1.0094	0.2001	0.2012
0.072363	-1.0101	0.1999	0.2011
0.103120	-1.0108	0.1996	0.2002
0.020567	-1.1535	0.1498	0.1474
0.035979	-1.1541	0.1496	0.1487
0.051382	-1.1550	0.1493	0.1498
0.072690	-1.1557	0.1491	0.1494
0.103690	-1.1568	0.1488	0.1495
0.020804	-1.6857	0.0477	0.0474
0.036529	-1.6866	0.0476	0.0480
0.052190	-1.6872	0.0475	0.0481
0.073724	-1.6876	0.0475	0.0478
0.105010	-1.6881	0.0474	0.0476

Table II. Tin Proton Spin-Spin Coupling Constants at 28°

Compound	Concn., M	Solvent	J	J
			$^{117}\text{Sn}-\text{C}-\text{H}$, c.p.s.	$^{119}\text{Sn}-\text{C}-\text{H}$, c.p.s.
$(\text{CH}_3)_2\text{Sn}(\text{NO}_3)_2$	2	1 M HNO_3	104	109
$(\text{CH}_3)_2\text{Sn}(\text{ClO}_4)_2$	2	1 M HClO_4	102	106
$(\text{CH}_3)_2\text{SnCl}_2$	1.0	H_2O	102	106
	2.9	H_2O	99.0	103.5
	3.0	H_2O	98.5	102.8
	4.1	H_2O	97.4	102.1
	5.7	H_2O	94.2	98.6
	6.2	H_2O	94.3	98.4
	0.6	11.5 M HCl	89.0	93.5
	(satd.)			
	14%	CCl_4	66.6	69.7

The hydrogen ion concentration of the solutions used in the intensity measurements varied from 1 M in the LiCl solution to 6 M in the most concentrated chloride solution. Although there has been some uncertainty as to the magnitude of the dissociation constant of

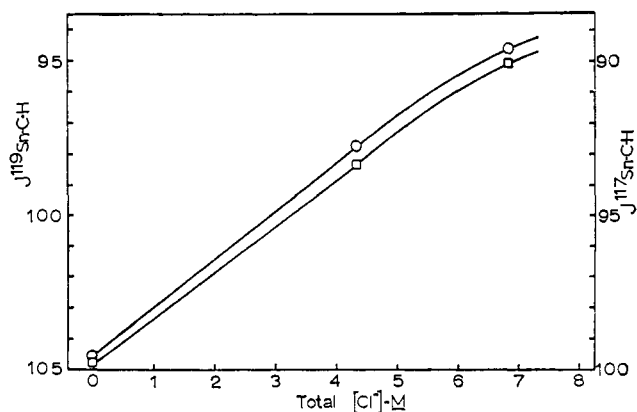


Figure 2. Tin proton spin-spin coupling constants of $(\text{CH}_3)_2\text{Sn}^{\text{IV}}$ as a function of chloride ion concentration in solutions with $([\text{Cl}^-] + [\text{ClO}_4^-]) = 6.8 M$ at 28°: \circ , ^{119}Sn ; \square , ^{117}Sn .

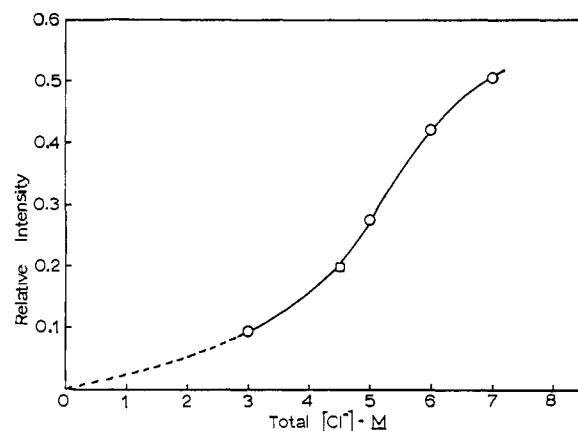


Figure 3. Relative Raman intensities of the $\text{Sn}-\text{Cl}$ stretching vibration as a function of chloride ion concentration at 25°: \circ , HCl ; \square , LiCl .

perchloric acid, recent measurements have shown that the intensities of the A_1 perchlorate line are identical in NaClO_4 and HClO_4 solutions up to 8 M ,¹⁷ at least, so the perchlorate intensity should serve as a reliable standard in these solutions.

The Raman spectrum of a solution 0.67 M in $(\text{CH}_3)_2\text{SnBr}_2$ and 5.3 M in HBr was recorded to see if any evidence for bromo complexing could be obtained. This was essentially a saturated solution, for the bromide is considerably less soluble than the chloride. The results are given in Table III together with values for $(\text{CH}_3)_2\text{Sn}^{+2}(\text{aq})$ from measurements on nitrate solutions⁷ and for *ca.* 1 M $(\text{CH}_3)_2\text{SnCl}_2$ in 9 M HCl .⁷ The lines in the spectrum of the bromide solutions at 210 cm^{-1} , and below, all overlap extensively making the frequency assignments uncertain. The assignments for this type of complex have been discussed earlier.⁷

Discussion

The e.m.f. data show that the dimethyltin(IV) ion forms a 1:1 chloro complex, and the data fall closely about the theoretical formation curve for such a complex. Data are tabulated in Table IV for the interaction of $(\text{CH}_3)_2\text{Sn}^{+2}$, Sn^{+2} , and Cd^{+2} with chloride and

(17) K. Keinzinger and R. E. Weston, *J. Chem. Phys.*, **42**, 272 (1965).

Table III. Raman Spectra of the Dimethyltin(IV) Aquo Ion and of the Chloro and Bromo Complexes

$\bar{\nu}$, cm. ⁻¹			
(CH ₃) ₂ Sn ⁺²	Cl ⁻ soln.	Br ⁻ soln.	Assignment ^a
3020	3020	3021 m, bd, dp	CH ₃ stretch (antisym.)
2933	2930	2928 ms, sh, p	CH ₃ stretch (sym.)
1226	1204	1204 m, sh, p	CH ₃ deform. (sym.)
...	577	573 w, mbd, dp	SnC ₂ stretch (antisym.)
529	518	519 vs, sh, p	SnC ₂ stretch (sym.)
...	325	210 w, bd, p?	Sn-X stretch
180	175	175 shoulder	Skeletal
		126 s, vbd	deformations

^a See ref. 7.

Table IV. A Comparison of (CH₃)₂Sn⁺², Sn(II), and Cd(II) in 3 M Perchlorate Solution

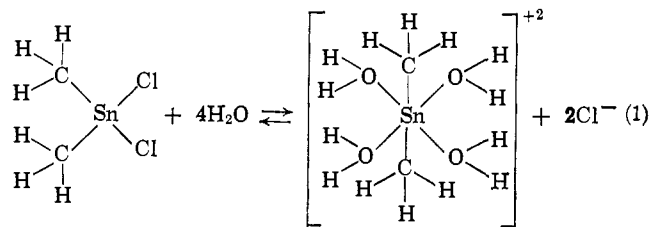
Cation	Log β_1		Log * β_{11} hydrolysis
	Chloride	Bromide	
(CH ₃) ₂ Sn ⁺²	0.383	-1.0	-3.45 ^a
Sn ⁺²	1.180 ^b	0.73 ^c	-3.9 ^d
Cd ⁺²	1.59 ^e	1.76 ^e	-10.1 ^f

^a See ref. 13. ^b R. S. Tobias and Z. Z. Hugus, Jr., *J. Phys. Chem.*, **65**, 2165 (1961). ^c C. E. Vanderzee, *J. Am. Chem. Soc.*, **74**, 4806 (1952). ^d R. S. Tobias, *Acta Chem. Scand.*, **12**, 198 (1958). ^e I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941). ^f G. Biedermann and L. Ciavatta, *Acta Chem. Scand.*, **16**, 2221 (1962).

bromide ions as well as values of the hydrolysis constants * β_{11} for the formation of M(OH)⁺ for a measure of the interaction of the cations with water molecules in the first coordination sphere.

From an examination of the data in Table IV, it is seen that the dimethyltin ion has the least tendency to coordinate halide ions of these three dipositive ions, that it is a typical "A" type ion,¹⁸ and that of the three it has the strongest effect on the acidity of the water molecules in the first coordination sphere. The high affinity of the dimethyltin(IV) ion for water molecules is certainly an important factor in accounting for the high solubility in water of the dimethyltin dihalides.

The solution process involves a pronounced rehybridization of the tin atom, and this dissolution may be described by



Four water molecules are probably coordinated in the first hydration sphere of the tin atom,¹⁹ although, as yet, there has been no direct determination of the hydration number of this ion.

Since the tin methyl proton spin-spin coupling constants increase by more than 35 c.p.s. in going from the tetrahedral dimethyltin dichloride to the aquo cation,

(18) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev. (London)*, **12**, 265 (1958).

(19) R. S. Tobias and C. E. Freidline, *Inorg. Chem.*, **4**, 215 (1965).

it might be expected that a large decrease in the coupling constants would be observed as the monochloro complex was formed. It does not seem likely that appreciable concentrations of tetrahedral dimethyltin dichloride would exist in the solutions, since one would expect a very low water solubility for this uncharged molecule. Indeed, dimethyltin dichloride can be precipitated from aqueous solutions containing (CH₃)₂Sn⁺²(aq) by the addition of large amounts of a soluble chloride. Kriegsmann and Pischtschan noted that (CH₃)₃SnCl is precipitated effectively by the addition of a soluble chloride to solutions containing (CH₃)₃Sn⁺(aq), and they could find no evidence for the existence of the neutral molecule in aqueous solutions using Raman spectroscopy.²⁰

The tin proton coupling constants do show a decrease either as the stoichiometric concentration of dimethyltin dichloride is increased or as excess chloride ion is added at a constant concentration of the dimethyltin ion; however, the decrease is also only about 10 c.p.s. in going from 0 to 7 M Cl⁻ with 1.5 M (CH₃)₂Sn⁺². Essentially limiting values appear to be attained for saturated solutions of (CH₃)₂SnCl₂ in concentrated HCl. This gives the values $J_{\text{H-Sn-C-H}} = 89.0$ c.p.s. and $J_{\text{H-Sn-C-H}} = 93.5$ c.p.s. van der Berghe and van der Kelen have observed essentially the same limiting values in their study of (CH₃)₂SnCl₂ in HCl solutions.²¹

It is especially interesting that the coupling constants for 1 M aqueous (CH₃)₂SnCl₂ are the same as for the perchlorate solutions. Using the value given above for the first chloro complexing constant, calculations indicate that about 75% of the dimethyltin ion would be in the form of the monochloro complex in this solution.

The Raman spectra show negligible evidence for association in 1 M (CH₃)₂SnCl₂, and it is only at higher chloride ion concentrations that the Sn-Cl stretching line appears. Since the relative intensity did not reach a limiting value at the highest chloride concentrations that could be studied, no calculations of an equilibrium constant could be made. Considering the large changes in the water activity of these solutions, it is unlikely that such calculations would even be meaningful. If one assumes that the Raman intensities are the result of the formation of a monochloro complex, the formation constant would be at least an order of magnitude smaller than that calculated from the e.m.f. data. Using the value determined here for the monochloro complex, 84% of the dimethyltin ion should be in the form of (CH₃)₂SnCl⁺ in the solution with 3 M Cl⁻, the lowest concentration for which any Sn-Cl stretching intensity could be measured.

It is apparent that the interaction of (CH₃)₂Sn⁺² with Cl⁻ as determined from the measurements of chloride ion activity with the electrochemical cell is different from that measured by Raman or proton n.m.r. spectroscopy. The most likely explanation of this effect is that it is difficult to displace water molecules from the first coordination sphere of (CH₃)₂Sn⁺², and an outer-sphere complex is formed first. With this kind of a complex, no tin-chlorine bond stretching vibration would appear. The chloride should have little effect on the nuclear spin coupling, and the spin-spin cou-

(20) M. Kriegsmann and S. Pischtschan, *Z. anorg. allgem. Chem.*, **308**, 212 (1961).

(21) E. V. van der Berghe and G. P. van der Kelen, *Ber. Bunsenges. Physik. Chem.*, **68**, 652 (1964).

pling constants should show little change. With outer-sphere complexing, it is quite conceivable that higher complexes could be formed in solution, *i.e.*, an outer-sphere $(\text{CH}_3)_2\text{SnCl}_2$ might be appreciably soluble while an inner-sphere $(\text{CH}_3)_2\text{SnCl}_2$ would not be expected to be so.

If the solutions are made highly concentrated in hydrochloric acid or an alkali metal chloride, an inner-sphere complex is formed as indicated by the appearance of the Sn-Cl bond stretching vibration. It has been inferred from the Raman spectra of these solutions that the C-Sn-C skeletal angle decreases from 180° as a chloride ion is coordinated, although this cannot be proved on the basis of symmetry arguments alone.⁷ Since the bonds from tin to the oxygen of the coordinated water molecules are very polar while those to carbon and chlorine are considerably less so, it would be expected that the C-Sn-C angle in the aquo ion would be 180° as observed, and that that in the monochloro complex it would decrease toward 120° . It would also be expected that the tin coordination number would decrease as good electron donors such as chloride are substituted in place of water. Thus the appearance of the inner-sphere complex in the concentrated electrolyte solutions may be due not only to the high chloride ion concentration but to the high concentration of cations which tie up the solvent water. In the 4.5 M LiCl solution, for example, up to 30% of the water may be bound in the first coordination sphere of the lithium ion, and addition of more LiCl to the solution precipitates $(\text{CH}_3)_2\text{SnCl}_2$.

Since the tin methyl proton spin-spin coupling constants decrease by more than 35 c.p.s. on going from the aquo ion to the dichloride, a decrease would be expected upon formation of the inner-sphere complex. Any change in hybridization at the tin atom would be expected to lead to a change in the coupling constants, for the Fermi contact term appears to dominate the coupling.^{11,22} The coupling constants determined in this work and that of van der Berghe and van der Kelen²¹ show that only very small decreases occur for other than high concentrations of chloride ion. This too supports the outer-inner-sphere model for the complexing. No broadening of the methyl proton signal was observed in any of the solutions containing chloride ion. Using the chemical shift data of van der Berghe and van der Kelen for solutions of $(\text{CH}_3)_2\text{SnCl}_2$ in water and in concentrated HCl, the upper limit to the half-life for exchange can be estimated to be *ca.* 5×10^{-3} sec.

There is another model for the complexing which also could account for the experimental observations. The chloride ion might penetrate the first coordination sphere forming a complex by a hard-sphere coulombic interaction without leading to a decrease in the cation coordination number. It has been suggested that the Sn-Cl bond stretching vibration occurs at less than 250 cm^{-1} in the octahedral $(\text{CH}_3)_2\text{SnCl}_4^{-2}$ ion,²³ and it is possible that either the intensity or the frequency of the Sn-Cl stretching vibration in a complex like $(\text{CH}_3)_2\text{SnCl}(\text{OH}_2)_3^+$ might be too low to be observed. However, it is difficult to see how the chloride could displace water from the first coordination sphere without

the establishment of a rather strong bond. The transition from the "ionic" to the "covalent" tin-chlorine bond would result from the decrease in water activity in the concentrated solutions much as the transition from outer- to inner-sphere complex, so it is not possible to distinguish between these models on the basis of the experiments.

The Raman spectra of the bromide solutions indicate that weak inner-sphere complexing does occur in concentrated bromide solutions. The antisymmetrical SnC_2 stretch becomes Raman allowed and appears at 573 cm^{-1} . The skeletal bending modes which are Raman forbidden in the aquo ion are also quite intense in the bromide solutions. The Sn-Br stretching vibration is tentatively assigned to the line at 210 cm^{-1} , although all of the lines at 210, 175, and 126 cm^{-1} are very broad and overlap badly. The totally symmetrical stretching mode for SnBr_3^- occurs at 200 cm^{-1} ²⁴ and that for SnBr_6^{-2} occurs at 185 cm^{-1} .²⁵ For comparison, the corresponding Sn-Cl vibrations appear at 325, 272,²⁴ and 337^{25} cm^{-1} .

In the Raman spectra, the symmetrical methyl deformation is lowered by 22 cm^{-1} in both the concentrated chloride and bromide solutions. A similar decrease of 26 cm^{-1} was noted upon hydroxo complexing.¹⁹ Originally it seemed that replacement of water by a better electron donor would weaken the tin-carbon bonds, and since conservation of momentum requires that the symmetrical methyl deformation couple to some extent with the symmetrical tin-carbon stretch, this would shift the symmetrical methyl deformation. However, only one line was observed for any of the solutions in the $1200\text{--}1225\text{-cm}^{-1}$ region with widths at half-height ranging from 15 cm^{-1} for $(\text{CH}_3)_2\text{Sn}(\text{NO}_3)_2$ to 20 cm^{-1} for solutions with 11 M Cl^- and 24 cm^{-1} for solutions with 5.3 M Br^- . Since it is difficult to envisage a process by which the ligands could exchange with a half-life in the order of 10^{-13} sec., it appears that these shifts are due to a nonspecific electrolyte effect.

Kriegsmann and Pischtschan²⁰ have observed comparable shifts in the Raman frequencies of $(\text{CH}_3)_3\text{Sn}^+$ in concentrated HCl and HBr solutions where apparently no complexing occurs. van der Berghe and van der Kelen²¹ suggested that their solutions had decomposed and that the measurements actually were on solutions of $(\text{CH}_3)_2\text{Sn}^{+2}$. This does not seem likely, since Kriegsmann and Pischtschan observed no tin-chlorine stretching line, and the values for the antisymmetrical Sn-C_3 vibration were 553 cm^{-1} for both the HCl and HBr solutions. These are 24 and 20 cm^{-1} lower than the values reported here for $(\text{CH}_3)_2\text{Sn}^{+2}$ solutions, and this is certainly outside the range of experimental error.

Many years ago, Kraus compared the methyltin halides to the strong acids,²⁶ and many similarities can be noted in this work. In addition the chemistry of aquodimethyltin dichloride and dibromide solutions is rather more complicated than that of oxonium chloride and bromide because of the ability of the dimethyltin cation skeleton to undergo changes in structure and bonding in solution.

(22) H. Dreeskamp, *Z. Naturforsch.*, **19a**, 139 (1964).

(23) I. R. Beattie and G. P. McQuillan, *J. Chem. Soc.*, 1519 (1963).

(24) L. A. Woodward and M. J. Taylor, *ibid.*, 407 (1962).

(25) L. A. Woodward and L. E. Anderson, *ibid.*, 1284 (1957).

(26) C. A. Kraus, *Rec. trav. chim.*, **42**, 588 (1923).

The free uncomplexed linear dimethyltin(IV) ion which probably exists rarely, if ever, in chemical systems can be regarded as a very strongly polarizing but virtually nonpolarizable ion. In Pearson's classification of "hard" and "soft" acids,²⁷ it is to be regarded as a very hard acid. It interacts very strongly with hydroxide ion, water, and fluoride ion but much less strongly with more polarizable bases.^{9,10} Under anhydrous conditions complexes can be prepared easily with ligands which are good proton bases. With these hard bases, the coordination number of tin appears generally to be 6, e.g., in the aquo ion,⁷ the hydroxo complex,²⁴ and a variety of β -diketo complexes.¹¹ Aqueous solutions of the dimethyltin(IV) ion appear to be the most extensively hydrolyzed of all of the systems containing divalent ions which have been studied. This reflects the strong polarization of the water molecules in the first coordination sphere of this cation.

Complexation of the dimethyltin(IV) ion with a soft base, as expected, leads to the formation of considerably less polar bonds as indicated by the appearance of intense tin-ligand stretching vibrations in the Raman spectra of the complexes. There is a tendency for the coordination number to decrease to four when soft bases are bound, and this can be rationalized on the basis of Pauling's electroneutrality principle. Thus dimethyltin dichloride involves bonds from tin to the soft methide ion as well as the soft chloride ion, and this should lead to a rather high charge density on the tin atom. Back bonding does not seem to occur to any extent in these complexes, so there is no mechanism to reduce the high charge density at the tin atom. In

(27) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

general, these complexes with soft base ligands are of low thermodynamic stability as has been noted earlier.^{9,10}

The dimethyltin(IV) ion does form a complex, $(\text{CH}_3)_2\text{Sn}^+$, with the very soft base methide ion which is generally regarded as highly stable. In this case the stability is due to the high activation energy for the displacement of the soft methide by a hard base, and the "complex" must be synthesized in the absence of hard bases.

Because of the very high polarizing ability of the dimethyltin(IV) ion, it would be expected that it would give rise to a high electrical field at the near neighbor ligands in complexes with hard bases. It has been observed in compounds containing the lower charged $(\text{CH}_3)_2\text{Sn}^+$ that degenerate vibrations of symmetrical anions like ClO_4^- ,²⁸ BF_4^- ,²⁹ AsF_6^- ,³⁰ and SbF_6^- ³⁰ are often split in crystals. These splittings probably result from the combined effect of the high polarizing power of the cation and low anion site symmetries in the crystals with, perhaps, some degree of covalent character to the tin-ligand bond.

The behavior of the dimethyltin(IV) ion is that of a very small ion of high charge. The two pairs of σ -bonding electrons have little effect in screening the coordinated ligands, e.g., water molecules, from the $4d^{10}$ tin core. Experimentally, it is observed that the tin(II) ion is similar in many respects, and the hard acid nature of Sn(II) was attributed earlier to distortion of the ion from spherical symmetry in the presence of ligands.³¹

(28) R. Okawara, B. J. Hathaway, and D. E. Webster, *Proc. Chem. Soc.*, 13 (1963).

(29) B. J. Hathaway and D. E. Webster, *ibid.*, 14 (1963).

(30) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 1020 (1963).

(31) See footnote *b* in Table IV.

The Kinetics of the Reaction between Thallium(III) and Vanadium(III)¹

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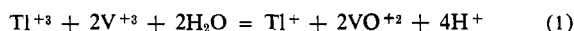
The kinetics of the reaction $\text{Tl(III)} + 2\text{V(III)} = \text{Tl(I)} + 2\text{V(IV)}$ have been studied in acid perchlorate solutions from 0.30 to 1.90 M in HClO_4 over a temperature range from 0.5 to 25.1° at $\mu = 2.0$ M. The reaction is first order with respect to both V(III) and Tl(III). The data do not allow the hydrogen ion dependence to be specified exactly, but the dependence is predominantly inverse first power in H^+ . Values of ΔH^ and ΔS^* for the major path are 13.9 ± 0.8 kcal./mole and 4.1 ± 2.4 e.u. A mechanism involving a two-electron step is not compatible with the data.*

(1) (a) Work done under the auspices of the U. S. Atomic Energy Commission; (b) presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

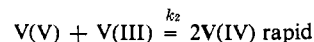
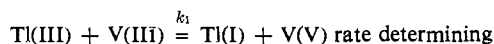
(2) On leave from Colorado State University, Fort Collins, Colo.

Introduction

The reaction between Tl(III) and V(III) is described by eq. 1. Plausible mechanisms involving either one-



electron or two-electron steps can be written for the reaction. A two-electron mechanism is shown below.



Since k_2 is known from previous work,³ a kinetic study

(3) N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **68**, 612 (1964).