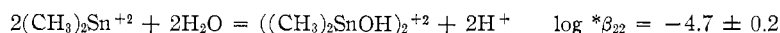
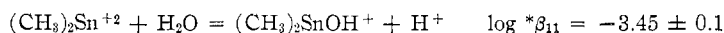


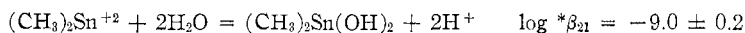
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINNESOTA**Studies on the Mono- and Polynuclear Hydroxo Complexes
of the Dimethyltin(IV) Ion in Aqueous Solution¹**BY R. STUART TOBIAS, IEVA OGRINS,² AND BRIAN A. NEVETT³

Received January 30, 1962

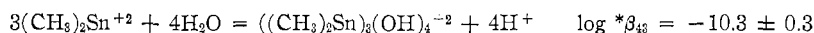
The hydroxo complexes of the aquodimethyltin(IV) ion have been studied in solutions with $[\text{ClO}_4^-] = 3.00 M$ by e.m.f. measurements of $[\text{H}^+]$. The conjugate bases formed by the proton transfer from aquo ion to solvent show a pronounced tendency to dimerize by rapid and completely reversible reactions. Throughout the entire range of the data, $1.0 \leq \text{pH} \leq 8.0$, the measurements could be explained only by assuming the formation of five complexes. For $\bar{n} \leq 0.7$, $[(\text{CH}_3)_2\text{SnOH}^+]$ and the dimer $[(\text{CH}_3)_2\text{SnOH}]_2^{+2}$ predominate, and the cumulative equilibrium constants for their formation are



A point of maximum polymerization is reached at pH 5.5. When the total $(\text{CH}_3)_2\text{Sn(IV)}$ concentration is 5 mM or less, no precipitation occurs, and the single complex $[(\text{CH}_3)_2\text{Sn}(\text{OH})_2]$ exists at pH 8. The cumulative equilibrium constant is



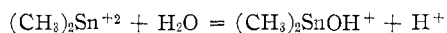
In the intermediate pH range, the presence of the complexes $[(\text{CH}_3)_2\text{Sn}_3(\text{OH})_4^{+2}]$ and $[(\text{CH}_3)_2\text{Sn}_2(\text{OH})_3^+]$ also is indicated, and the values for the equilibrium constants are



These data are compared to those for the hydroxo complexes of tin(II), and structures for the polymeric species are discussed with respect to information obtained from the preparative chemistry of alkyltin(IV) compounds with tin-oxygen bonds.

Introduction

It has been reported that the hydrolysis of the aquodimethyltin cation is rapid and reversible.⁴ By measuring the pH of aqueous solutions of dimethyltin dichloride and assuming that the acidity of the solutions was a result of the reaction



Rochow and Seyferth calculated the equilibrium constant for the formation of $(\text{CH}_3)_2\text{SnOH}^+$, ${}^*\beta_{11} = 8.05 \times 10^{-4}$ and 7.6×10^{-4} in 0.916 and 2.05 mM solutions, respectively, of $(\text{CH}_3)_2\text{SnCl}_2$. There was no evidence for the formation of polydimethylstannoxanes. Studies by Rochow, Seyferth, and Smith have shown that, in many ways, the dimethyltin(IV) ion behaves similarly to the

tin(II) ion.⁵ Since tin(II) has been shown to form polynuclear hydroxo complexes upon hydrolysis,⁶ it seemed likely that the dimethyltin(IV) ion also would form polymers in solution, in which case treatment of the hydrolysis data in terms of a single soluble hydroxo complex would not be correct. It also was possible that in the presence of Cl^- and in the dilute solutions studied by Rochow and Seyferth the dimethyltin(IV) would be distributed among mononuclear species only but that polymers could be formed in slightly more concentrated solutions. The fact that the oxide $(\text{CH}_3)_2\text{SnO}$, which precipitates from solution upon the addition of base, is rather insoluble in water and in organic solvents and hence usually is described as an infinite polymer $[(\text{CH}_3)_2\text{SnO}]_n$ ⁷ also tends to indicate that polymeric species probably exist in aqueous solution. The pro-

(1) This work was supported by the United States National Science Foundation under Grant NSF-14173.

(2) N. S. F. Undergraduate Research Participant.

(3) Research Fellow in Chemistry.

(4) E. G. Rochow and D. Seyferth, *J. Am. Chem. Soc.*, **75**, 2877 (1953).

(5) E. G. Rochow, D. Seyferth, and A. C. Smith, Jr., *ibid.*, **75**, 3099 (1953).

(6) R. S. Tobias, *Acta Chem. Scand.*, **12**, 198 (1958).

(7) G. E. Coates, "Organometallic Compounds," 2nd Ed., Methuen and Co., London, 1960, p. 189.

nounced tendency of the dimethyltin ion to form polydimethylstannoxanes is shown by the reaction of dimethyltin oxide and glacial acetic acid which yields a tetramethyl-1,3-diacetoxydistannoxane.⁸ While it has been suggested that the organotin acetates may involve bridging acetate groups,⁹ it seems unlikely that this is the case in $[\text{OAc}(\text{CH}_3)_2\text{Sn}]_2\text{O}$. Compounds also have been reported which have the composition $[\text{Br}(\text{C}_2\text{H}_5)_2\text{Sn}]_2\text{O}^{10}$ and $[\text{Cl}(\text{CH}_3)_2\text{Sn}]_2\text{O}$,¹¹ although recent evidence indicated that these have an interesting tetrameric structure with two different configurations about the tin atoms.¹²

Since it seemed likely that oxygen-bridged polymeric species containing the dimethyltin(IV) cation were present in aqueous solution, it was decided to study the hydrolysis of the aquo-ion over a wide range of concentrations in order to elucidate the species present in the solutions.

The study of the hydrolytic polymerization of the dialkyltin ions is also of interest from another standpoint. Assuming that the tin atom can have a maximum coordination number of six, the two alkyl groups decrease the coordination number for oxygen to a maximum of four and reduce the sites through which polymerization can occur. One general characteristic of the hydrolytic polymerization of multivalent aquo-ions is that the transition from aquo-ion to the hydrous oxide occurs over a very narrow pH range. It was hoped that the study of alkyl-substituted ions might increase the pH range throughout which soluble hydroxo complexes exist and limit the number of possible polymers which could be formed. In addition, since the aquoacidity of the tin(II) ion has been studied,⁶ a quantitative comparison of the stability of the hydroxo complexes of $(\text{CH}_3)_2\text{Sn}^{+2}$ and Sn^{+2} could be made.

Experimental

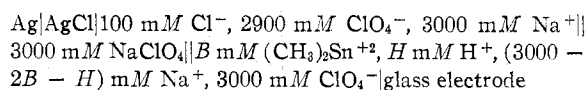
Preparation of Solutions.—Dimethyltin(IV) perchlorate solutions were prepared by dissolving weighed amounts of $(\text{CH}_3)_2\text{SnO}$ in excess standard 2 M perchloric acid so that the resulting solution was approximately 0.2 M in H^+ . The $(\text{CH}_3)_2\text{SnO}$ was prepared from $(\text{CH}_3)_2\text{SnCl}_2$ obtained from the Metal and Thermit Corporation, New York. The $(\text{CH}_3)_2\text{SnCl}_2$ was recrystallized from benzene and had

a melting point of 106°. The dichloride was dissolved in distilled water, and $(\text{CH}_3)_2\text{SnO}$ was precipitated from the solution with dilute NaOH solution. The precipitate was washed with large quantities of water until no Cl^- could be detected, washed with absolute ethanol, and dried at 110°. *Anal.* Calcd.: C, 14.58; H, 3.64; Sn, 72.04. Found: C, 14.23; H, 3.34; Sn, 72.44. Tin was determined by the method of Luijten and van der Kerk.¹³ The total perchlorate concentration of the stock solutions was determined by passing a definite volume of the solution through the hydrogen ion form of the cation-exchange resin Dowex 50W-X8. The eluate was titrated with standard NaOH, which gave the total perchlorate ion concentration, and the analytical excess of H^+ , denoted by H in the following discussion, was calculated from $H = [\text{ClO}_4^-] - 2[(\text{CH}_3)_2\text{Sn}^{+2}]$. The ultraviolet absorption spectra of the stock solutions of $(\text{CH}_3)_2\text{Sn}^{+2}$ were determined several times during the course of the study to ascertain if any cleavage of the Sn-C bond were occurring. These solutions were found to be virtually transparent to light with wave lengths longer than 2200 Å., while it has been reported that tin(IV) perchlorate solutions absorb rather strongly to 2900 Å. and have extinction coefficients of greater than 10^3 at 2400 Å.¹⁴ In addition, no change in the $[\text{H}^+]$ was detectable over a period of several months, and exactly the same formation curves ($\bar{n}(-\log [\text{H}^+])$) were obtained at different times. The value of the analytical hydrogen ion concentration obtained from the ion-exchange measurements agreed within 0.6% with the value calculated from the quantity of standard acid used to dissolve the $(\text{CH}_3)_2\text{SnO}$.

Crystals of $(\text{CH}_3)_2\text{Sn}(\text{ClO}_4)_2$, in the form of long needles, could only be obtained by storage of concentrated solutions in a vacuum desiccator over P_2O_{10} for several weeks. Because of the potentially explosive nature of the compound, no further studies were made.

Standard NaHCO_3 , NaOH, and HClO_4 were prepared from reagent grade chemicals. Sodium perchlorate was prepared by neutralization of reagent Na_2CO_3 with HClO_4 and was recrystallized three times from water. Both the stock $(\text{CH}_3)_2\text{Sn}(\text{ClO}_4)_2$ and NaClO_4 solutions gave negative tests for Cl^- . The NaClO_4 solutions were standardized by drying aliquots at 110° to a constant weight. Silver perchlorate solutions were prepared as described elsewhere.⁶ Nitrogen gas was purified by passing it over hot activated copper and then by washing with 10% H_2SO_4 , 10% NaOH, distilled water, and finally 3 M NaClO_4 .

Apparatus and Procedure.—The hydrogen ion concentration of the solutions was determined with the cell



A Beckman type 40498 glass electrode was used. The behavior of the glass electrode as a concentration probe was checked in the range $1.0 \leq \text{pH} \leq 4.0$ by measuring the cell e.m.f. during the titration of perchloric acid with sodium hydrogen carbonate and sodium hydroxide solutions. The e.m.f. was described by the equation $E_g = E^0 + 59.16 \log [\text{H}^+] - 0.0175 [\text{H}^+]$, e.m.f. values in

(13) J. G. A. Luijten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, Middlesex, England, 1955, p. 83.

(14) C. H. Brubaker, *J. Am. Chem. Soc.*, **76**, 4269 (1954).

(8) R. Okawara and E. G. Rochow, *J. Am. Chem. Soc.*, **82**, 3285 (1960).

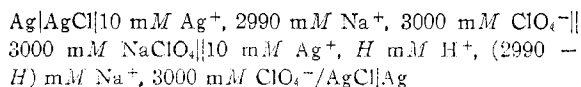
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mv., $[H^+]$ in mM. The cell design was similar to that described by Forsling, Hietanen, and Sillén,¹⁵ and the linear correction factor $0.0175 [H^+]$ is essentially that described for these cells by Biedermann and Sillén and co-workers.^{6,16-18} As usual, with this apparatus, the correction factor is attributable to the liquid junction potential, since the same correction factor was found to be applicable to the e.m.f. values of the cell



In addition, since it was found that measurements could be made to high pH values without precipitation from the $(\text{CH}_3)_2\text{Sn(IV)}$ solutions, the electrode behavior was checked with buffer solutions from pH 4 to 10, and the value of $dE/d \log [H^+]^+$ was found to be within 1% of the theoretical value within this range.

Cell potentials were read to 0.01 mv. using a Leeds and Northrup K-3 potentiometer with a Cary 31-V vibrating reed electrometer as the null point indicator. As a rule, the potentiometer was adjusted to balance all but about 0.1 mv. of the cell e.m.f., and this signal was applied to the vibrating reed electrometer. The output was recorded on a Varian G-11A potentiometer recorder which had a full scale deflection of 1 mv. The noise was of the order of $10 \mu\text{v.}$, and potentials constant to ± 0.01 mv. usually were obtained within a minute after mixing the solutions. Potentials were constant to within 0.1 mv. overnight. The cell was immersed in an oil bath thermostat maintained at $25 \pm 0.1^\circ$ by circulating water from an external thermostat through copper coils in the oil bath. The bath was stirred with an air motor, and the entire thermostat and a Weston standard cell were enclosed in a grounded aluminum cabinet serving as a Faraday cage. All of the apparatus was contained in a room thermostated at $25 \pm 2^\circ$. The potentiometer-electrometer circuit was standardized by replacing the experimental cell with the standard cell.

The titrations were carried out in a glass multinecked flask of 500 ml. capacity which was fitted with N_2 inlet and outlets, buret delivery tubes, glass electrode, and the salt bridge "j" tube. Each individual run was made with the total $(\text{CH}_3)_2\text{Sn}^{+2}$ concentration, B , held constant. In general, equal volumes of an acidic $(\text{CH}_3)_2\text{Sn}^{+2}$ solution of concentration $2B$ and a base solution were added to an acidic $(\text{CH}_3)_2\text{Sn}^{+2}$ solution with the concentration B . As the base, NaHCO_3 solutions usually were used to pH 5; and then NaOH solutions were employed at higher pH values. In some of the runs NaOH was used exclusively, and no difficulty was experienced with precipitate formation. The back titrations were carried out by adding the acidic $(\text{CH}_3)_2\text{Sn}^{+2}$ solution with concentration $2B$ and either NaClO_4 or HClO_4 solution. All solutions were prepared so that $[\text{ClO}_4^-]$ remained constant at 3 M. The equilibria were found to be reversible throughout the entire range of measurements, as is illustrated in Fig. 1. Measurements were discontinued at the first trace of a permanent precipi-

tate in the solutions with $B \geq 10 \text{ mM}$. No precipitate was formed with $B \leq 5 \text{ mM}$, even in the most alkaline solutions.

Treatment of Data

Since the entire set of data consists of 772 items, the values of the primary data \bar{n}_i , the average number of OH^- bound per $(\text{CH}_3)_2\text{Sn}^{+2}$, and $\log [H^+]_i$ have been deposited with the American Documentation Institute.¹⁹ Figure 1 gives the data $\bar{n}(-\log [H^+])$ with the total dimethyltin concentration as a parameter as calculated from the e.m.f. data. Only $1/4$ of the data items selected at random are shown for clarity. These data show that at least one polynuclear hydroxo complex is formed, since if only mononuclear complexes were formed, \bar{n} would be independent of the total $(\text{CH}_3)_2\text{Sn}^{+2}$ concentration, B . When the total $(\text{CH}_3)_2\text{Sn}^{+2}$ concentration was $\leq 5 \text{ mM}$, no precipitate was observed at any point along the formation curve to $\bar{n} = 2.0$. With the higher concentrations of $(\text{CH}_3)_2\text{Sn}^{+2}$, traces of a precipitate were observed at about $\bar{n} = 1.4$, and the measurements were discontinued. The system exhibits a "cross over" point at an \bar{n} of about 1.43 and $-\log [H^+] = 5.5$. The existence of this "isohydric or pseudo-isohydric point" indicates that the degree of polymerization of the system is a maximum at this pH and that the further addition of OH^- converts the polymeric species to monomeric or at least to polymeric species with lower degrees of polymerization and with higher ligand-metal ratios.²⁰

In the ensuing discussion, the following symbols will be used: B = total stoichiometric concentration of $(\text{CH}_3)_2\text{Sn}^{+2}$, b = equilibrium concentration of the aquo $(\text{CH}_3)_2\text{Sn}^{+2}$ ion, H = total equilibrium concentration of H^+ computed with the assumption that no hydroxo-complexes are formed with $(\text{CH}_3)_2\text{Sn}^{+2}$, and $h = [H^+]$. The notation is essentially that of Sillén and co-workers, and a glossary of these symbols may be generally found in their publications, e.g., reference 6. The more familiar \bar{n} is, however, used in place of Z for the average ligand number, and the nomenclature of the Chemical Society Tables²¹ is followed for the equilibrium constants.

The first step in the analysis of the data was to construct projection maps, $\log B(-\log h)_{\bar{n}}$, of the three-dimensional $\bar{n}(-\log h)_B$ surface by cutting the experimental curves at constant \bar{n} values. This is shown in Fig. 2. It immediately is apparent that the simplified *core + links* sets of complexes; $M((\text{OH})_tM)_n$, $t = \text{constant}$, $n = 1, 2, \dots$; suggested by Sillén^{22,23} are not applicable even in the range $0.1 \leq \bar{n} \leq 1.3$. For the *core + links* complexes

(19) Material supplementary to this article has been deposited as Document Number 7130 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting \$2.50 for photoprints or \$1.75 for 35-mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(20) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961, p. 372.

(21) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants of Metal-ion Complexes with Solubility Products of Inorganic Substances, Part II, Inorganic Ligands," Special Publication No. 7, The Chemical Society, London, 1958, p. xi.

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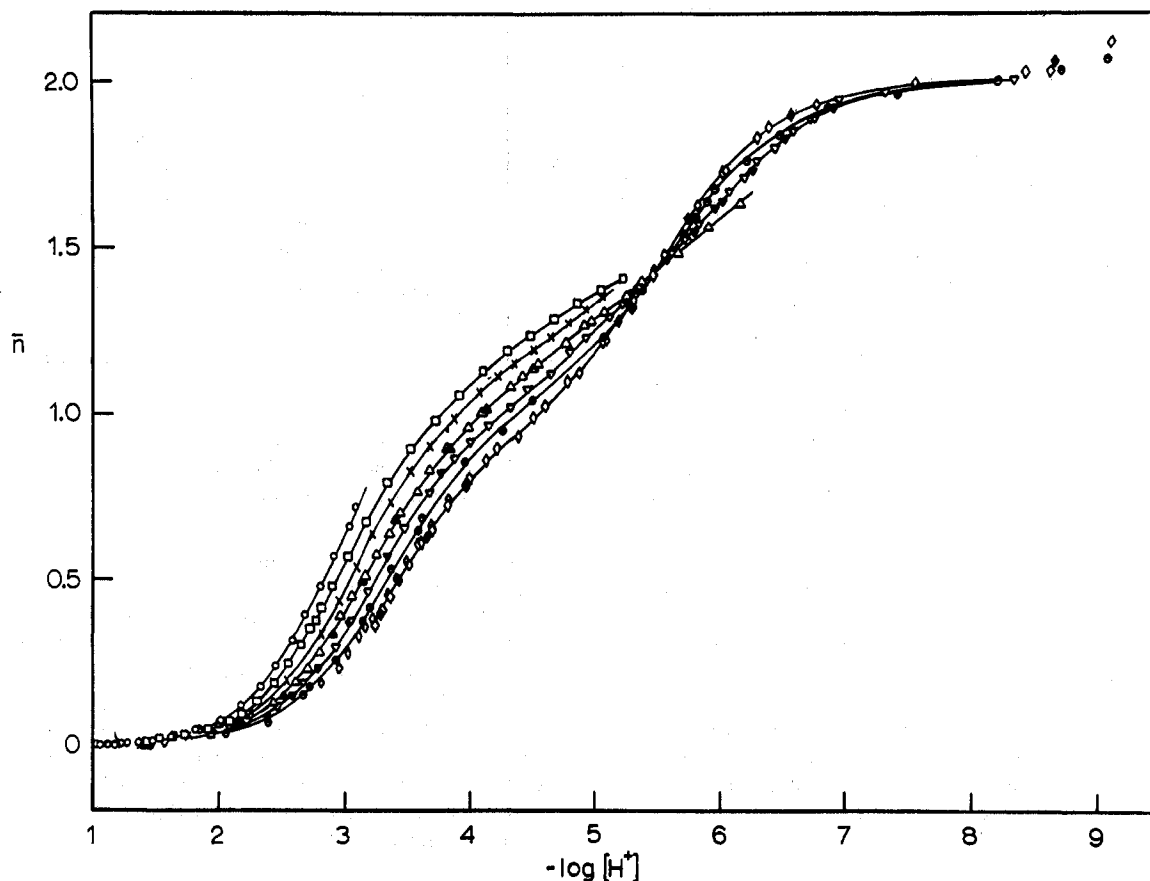


Fig. 1.—Average number of OH^- bound per dimethyltin(IV), \bar{n} , as a function of $-\log [\text{H}^+]$ for the following values of the total $[(\text{CH}_3)_2\text{Sn}^{+2}]$: O, 80 mM; \square , 40 mM; X, 20 mM; Δ , 10 mM; ∇ , 5 mM; \bullet , 2.5 mM; and \diamond , 1 mM. Smooth curves have been drawn through the experimental data. Filled symbols and \bullet represent points from back titrations.

to be a good approximation, it is necessary that the lines $\log B(-\log h)^{-\bar{n}}$ all be parallel, in which case the slope is equal to t . The tendency of $-\log h$ to become independent of B for a given \bar{n} at low B values indicates that an appreciable fraction of the $(\text{CH}_3)_2\text{Sn}^{+2}$ is in the form of mononuclear hydroxo-complexes, presumably $(\text{CH}_3)_2\text{SnOH}^+$, for the most part. Even the limiting slopes at high B values vary from 3.3 to 1.8 in the range $0.1 \leq \bar{n} \leq 1.3$. In order to obtain an estimate of the size of the polynuclear complexes formed, a t value of 2 was assumed, and the curves for $B = 20$ and 40 mM were compared with our library of normalized curves calculated after Sillén.²² This comparison indicated that the complexes probably contained no more than $3(\text{CH}_3)_2\text{Sn}^{+2}$, and the lower portion of the formation curve was approximately fitted by the curve for a single complex with two metal atoms. All of the continuous polymerization hypotheses placed too much emphasis on large complexes.

In order to gain more information on the size of the complexes, calculations were made of the average number of ligands, \bar{p} , and of dimethyltin ions, \bar{q} , in the complexes, as first suggested by Sillén.^{24,25} The defining equations are

$$\bar{p} = \frac{B\bar{n}}{BR - b} = \frac{\sum_p \sum_q p [((\text{CH}_3)_2\text{Sn})_q(\text{OH})_p^{(2q-p)+}]}{\sum_p \sum_q [((\text{CH}_3)_2\text{Sn})_q(\text{OH})_p^{(2q-p)+}]} \quad (1)$$

$$\bar{q} = \frac{B - b}{BR - b} = \frac{\sum_p \sum_q q [((\text{CH}_3)_2\text{Sn})_q(\text{OH})_p^{(2q-p)+}]}{\sum_p \sum_q [((\text{CH}_3)_2\text{Sn})_q(\text{OH})_p^{(2q-p)+}]} \quad (2)$$

The reciprocal average degree of polymerization, R , is calculated from the equation

$$R = \frac{b + \sum_p \sum_q [((\text{CH}_3)_2\text{Sn})_q(\text{OH})_p^{(2q-p)+}]}{b + \sum_p \sum_q q [((\text{CH}_3)_2\text{Sn})_q(\text{OH})_p^{(2q-p)+}]} = 1 - \int_{\log h = \infty}^{-\log h} \left(\frac{\partial \bar{n}}{\partial \log B} \right)_h d(-\log h)_B \quad (3)$$

The derivatives $(\partial \bar{n} / \partial \log B)_h$ were obtained by graphical differentiation of the $n(-\log h)_B$ data, and the integrals also were obtained graphically. Since the equilibrium concentration of the aquo- $(\text{CH}_3)_2\text{Sn}^{+2}$ ion also was needed for the determination of \bar{p} and \bar{q} and this was not experimentally determined, the values were calculated from the equation

$$\log b = \log B + (R - 1)/2.303 - \int_{\log h = \infty}^{-\log h} \bar{n} d(-\log h)_B \quad (4)$$

(24) L. G. Sillén, private communication.

(25) F. J. C. Rossotti and H. Rossotti, ref. 20, p. 348.

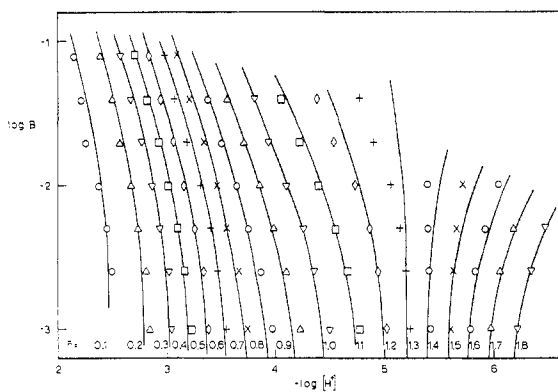


Fig. 2.—Surface fitting of the experimental data using the best set of constants obtained by the "trial method" for the five parameter case: $\log^* \beta_{11} = -3.45$, $\log^* \beta_{21} = -9.0$, $\log^* \beta_{22} = -4.7$, $\log^* \beta_{32} = -9.8$, $\log^* \beta_{43} = -10.3$.

Again, the integrals were obtained graphically. The results of these calculations are given as $\bar{p}(-\log h)_B$ in Fig. 3 and $\bar{q}(-\log h)_B$ in Fig. 4 for $B = 5, 10$, and 20 mM $(\text{CH}_3)_2\text{Sn}(\text{IV})$. Since \bar{q} attains a maximum value of about 2 and \bar{p} a maximum of 3, the polynuclear complexes $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_2^{+2}$ and $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_3^+$ are suggested.

A normalized projection map²⁶ was calculated for the two complexes $(\text{CH}_3)_2\text{SnOH}^+$ and $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_2^{+2}$ in an effort to fit the data at low \bar{n} values. The defining equations for this map, $\log B$ ($\log u$) \bar{n} are

$$B = v + uv + 2u^2v^2 \quad (5)$$

$$B\bar{n} = uv + 2u^2v^2 \quad (6)$$

The scaled concentrations B , v , and u are given by the relations: $B = {}^*\beta_{22}{}^*\beta_{11}^{-2}B$, $v = {}^*\beta_{22}{}^*\beta_{11}^{-2}b$, and $u = {}^*\beta_{11}h^{-1}$, and the map (11, 22) is calculated by elimination of v from eq. 5 and 6. In this two parameter case, the displacements along the two coordinates give the equilibrium constants when a comparison is made with the experimental data $\log B$ ($-\log h$) \bar{n} , since $\log u - (-\log h) = \log^* \beta_{11}$ and $\log B - \log B = \log^* \beta_{22} - 2 \log^* \beta_{11}$.

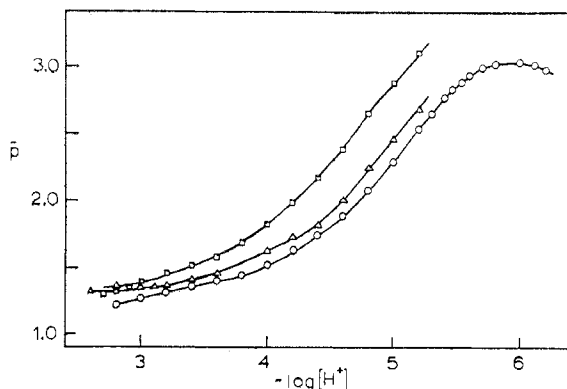


Fig. 3.—The average number of OH^- bound per complex, \bar{p} , as a function of $-\log [\text{H}^+]$ for the following values of B : \circ , 5 mM; Δ , 10 mM; \square , 20 mM.

(26) For a general discussion of the use of projection maps to simplify surface fitting, see F. J. C. Rossotti and H. Rossotti, ref. 20, pp. 374, 381.

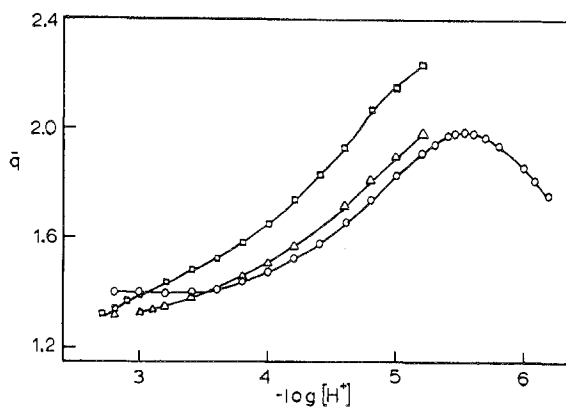


Fig. 4.—The average number of $(\text{CH}_3)_2\text{Sn}^{+2}$ bound per complex, \bar{q} , as a function of $-\log [\text{H}^+]$. The symbols refer to the same concentrations as in Fig. 3.

An excellent fit to the experimental data was obtained in the range $0 \leq \bar{n} \leq 0.7$, and the values of the constants obtained, $\log^* \beta_{11} = -3.45$ and $\log^* \beta_{22} = -4.54$, were used to compute the curves given in Fig. 5. For \bar{n} values greater than 0.7, complexes with higher ligand:metal ratios must be included.

Since the maximum values of \bar{p} and \bar{q} indicate that $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_3^+$ probably is formed, a projection map was computed for the set of complexes $(\text{CH}_3)_2\text{SnOH}^+$, $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_2^{+2}$, and $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_3^+$ (11, 22, 32) from the defining equations

$$B = v + uv + 2\alpha u^2v^2 + 2u^3v^2 \quad (7)$$

$$B\bar{n} = uv + 2\alpha u^2v^2 + 3u^3v^2 \quad (8)$$

As before, $u = {}^*\beta_{11}h^{-1}$, and now $B = {}^*\beta_{32}{}^*\beta_{11}^{-3}B$, $v = {}^*\beta_{32}{}^*\beta_{11}^{-3}b$, and $\alpha = {}^*\beta_{22}{}^*\beta_{11}{}^*\beta_{32}^{-1}$. In this three parameter case, approximate values of the constants must be known in order to obtain trial values of the parameter α . The values of ${}^*\beta_{11}$ and ${}^*\beta_{22}$ given above from the best fit of the two parameter map (11, 22) were used, and the approximate value of ${}^*\beta_{32}$ was obtained from the equations for \bar{p} and \bar{q} . Assuming that for $0 \leq \bar{n} \leq 1.3$, only these three complexes are important

$$\bar{p} = \frac{{}^*\beta_{11} + 2{}^*\beta_{22}h^{-1}b + 3{}^*\beta_{32}h^{-2}b}{{}^*\beta_{11} + {}^*\beta_{22}h^{-1}b + {}^*\beta_{32}h^{-2}b} \quad (9)$$

$$\bar{q} = \frac{{}^*\beta_{11} + 2{}^*\beta_{22}h^{-1}b + 2{}^*\beta_{32}h^{-2}b}{{}^*\beta_{11} + {}^*\beta_{22}h^{-1}b + {}^*\beta_{32}h^{-2}b} \quad (10)$$

Letting $R = {}^*\beta_{22}{}^*\beta_{11}^{-1}$ and $R' = {}^*\beta_{32}{}^*\beta_{11}^{-1}$, these equations become upon division of the numerator and denominator by ${}^*\beta_{11}$

$$\bar{p} = \frac{1 + 2Rh^{-1}b + 3R'h^{-2}b}{1 + Rh^{-1}b + R'h^{-2}b} \quad (11)$$

$$\bar{q} = \frac{1 + 2Rh^{-1}b + 2R'h^{-2}b}{1 + Rh^{-1}b + R'h^{-2}b} \quad (12)$$

Equations 11 and 12 were solved simultaneously for R and R' and hence for ${}^*\beta_{22}$ and ${}^*\beta_{32}$ using the earlier value of ${}^*\beta_{11}$. The (11, 22, 32) maps were calculated for the values of $\alpha = 4, 12$, and 40, and these indicated that the mononuclear complex $(\text{CH}_3)_2\text{Sn}(\text{OH})_2$ also would have to be considered.

Maps then were calculated for the four parameter case

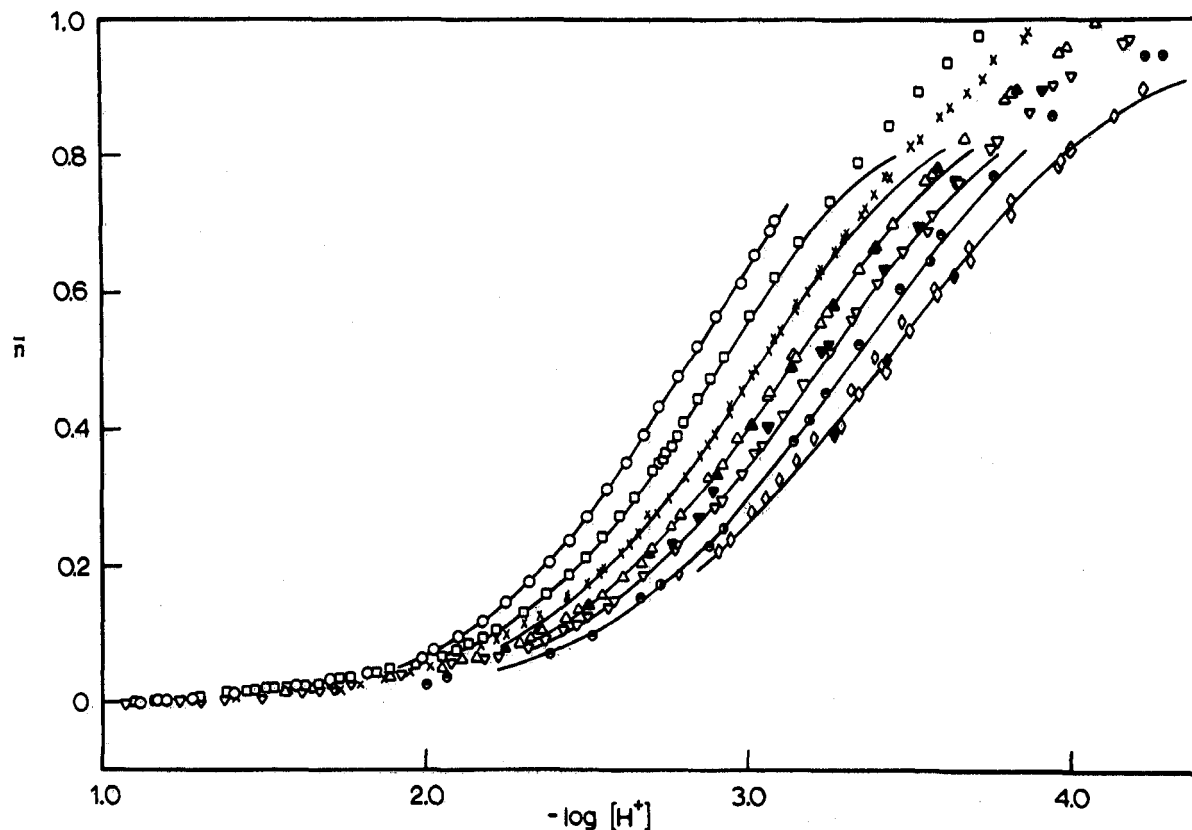


Fig. 5.—The average number of OH^- bound per dimethyltin(IV) for $0 \leq \bar{n} \leq 0.7$. The symbols refer to the same concentrations as in Fig. 1. The curves are calculated with $\log \beta_{11} = -3.45$, $\log \beta_{21} = -4.54$.

with the complexes $(\text{CH}_3)_2\text{SnOH}^+$, $(\text{CH}_3)_2\text{Sn}(\text{OH})_2$, $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_2^{+2}$, and $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_3^+$ (11, 21, 22, 32) using the defining equations

$$B = v + \alpha uv + u^2v + 2\beta u^2v^2 + 2u^3v^2 \quad (13)$$

$$B\bar{n} = \alpha uv + 2u^2v + 2\beta u^2v^2 + 3u^3v^2 \quad (14)$$

Now $u = \beta_{21}^{1/2}h^{-1}$, $B = \beta_{32}\beta_{21}^{-3/2}B$, $v = \beta_{32}\beta_{21}^{-3/2}b$, $\beta = \beta_{22}\beta_{21}^{1/2}\beta_{32}^{-1}$, and $\alpha = \beta_{11}\beta_{21}^{-1/2}$. For this calculation, β_{21} also must be estimated so that trial values of α and β can be obtained. For this purpose it was assumed, to a first approximation, that only one polynuclear complex was important at the cross-over point, $\bar{n}^* = 1.43$, $-\log h = 5.5$, in which case $\bar{n}^* = \bar{n}_{\text{mono.}}^{20}$. From the trial value of β_{11} and the following relation, β_{21} could be estimated.

$$\bar{n}_{\text{mono}} = \frac{\beta_{11}h^{-1} + 2\beta_{21}h^{-2}}{1 + \beta_{11}^{-1} + \beta_{21}\beta^{-21}} \quad (15)$$

The value $\log \beta_{21} = -9.14$ was obtained. Maps were computed with the following sets of α and β : 12, 2; 12, 0.5; 12, 0; 1, 0.5; 20, 0.5; 10, 5. A good fit to the experimental data was obtained for $0 \leq \bar{n} \leq 0.8$ and $1.5 \leq \bar{n} \leq 2.0$, and this is shown in Fig. 6. It also is apparent that complexes higher than dimers are being formed in the range of ligand concentrations corresponding to the interval $0.8 \leq \bar{n} \leq 1.5$. From the best fit of this map, the values $\log \beta_{11} = -3.50$, $\log \beta_{21} = -9.00$, $\log \beta_{22} = -4.60$, and $\log \beta_{32} = -9.8$ were obtained.

Two procedures were followed to ascertain just what larger species were formed. The first was to calculate

the function \bar{n}_c and B_c where the contribution to B and \bar{n} from monomeric species has been calculated with the values of β_{11} and β_{21} given above and subtracted out according to the equations

$$B_c = B - \beta_{11}h^{-1}b - \beta_{21}h^{-2}b \quad (16)$$

$$B_c\bar{n}_c = B\bar{n} - \beta_{11}h^{-1}b - 2\beta_{21}h^{-2}b \quad (17)$$

The functions $\bar{n}_c(-\log h)_{B_c}$ were compared to the normalized equations given by Sillén for the *core + links*

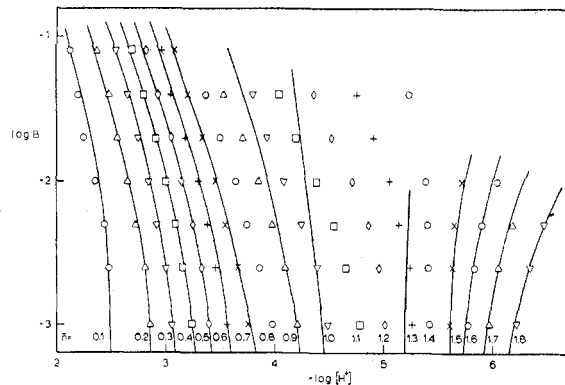


Fig. 6.—Surface fitting of the experimental data using the best set of constants for mononuclear and dinuclear complexes obtained by the "trial method": $\log \beta_{11} = -3.50$, $\log \beta_{21} = -9.00$, $\log \beta_{22} = -4.60$, and $\log \beta_{32} = -9.8$.

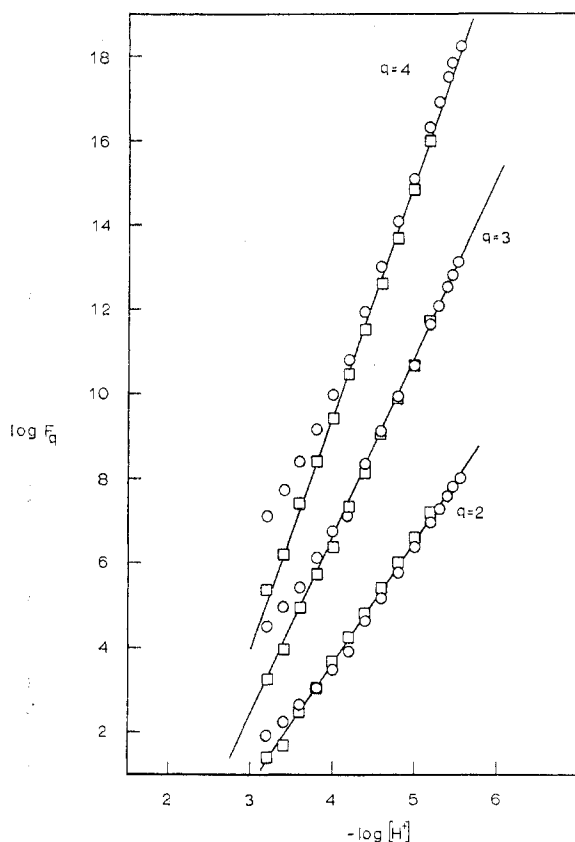


Fig. 7.—Determination of the higher complexes: $\log F_2$, $\log F_3$, and $\log F_4$ (eq. 18) vs. $-\log [H^+]$. The straight line for $[(CH_3)_2Sn]_3(OH)_4^{+2}$ is calculated using $\log \beta_{43} = -10.2$; \circ , 5 mM and \square , 20 mM.

polynuclear complexes.²² The only curve which fitted the experimental data at all was the one for the single complex $M[(OH)_tM]_N$ with $t = 1$ and $N = 1$, i.e., $[(CH_3)_2Sn]_2(OH)_2^{+2}$, which gave a good fit for $0 \leq \bar{n} \leq 0.8$ with $\log \beta_{22} = -4.58$. Comparison with the theoretical curves at higher \bar{n} values indicated that complexes having more than about three metal atoms were not important.

The second approach was to examine the variation with respect to h of the function

$$F_q = (B\bar{n} - \beta_{11}h^{-1}b - 2\beta_{21}h^{-2}b - 2\beta_{32}h^{-2}b^2 - 3\beta_{32}h^{-3}b^2)b^q = p\beta_{pq}h^{-p} \quad (18)$$

The trial values of the equilibrium constants obtained from the (11, 21, 22, 32) map were used to calculate F_q for $q = 2, 3$, and 4. These data are plotted in Fig. 7 as $\log F_q$ ($-\log h$) for $B = 5$ and 20 mM. The best straight line for both B values is obtained with $q = 3$, and the slope of the plot gives $p = 4.2$, indicating that the one additional complex $[(CH_3)_2Sn]_3(OH)_4^{+2}$ is important up to the cross-over \bar{n} . The intercept of the plot of F_3 ($-\log h$) gives $\log \beta_{43} = -10.2$.

In order to fit the experimental data in the range $0 \leq \bar{n} \leq 1.3$, the projection maps were calculated for the four parameter case with the set of complexes $(CH_3)_2SnOH^+$, $(CH_3)_2Sn(OH)_2$, $[(CH_3)_2Sn]_2(OH)_2^{+2}$, $[(CH_3)_2Sn]_3(OH)_4^{+2}$ (11, 21, 22, 43). The defining equations in this case are

$$B = v + \alpha uv + u^2v + 2\beta u^2v^2 + 3u^4v^3 \quad (19)$$

$$B\bar{n} = \alpha uv + 2u^2v + 2\beta u^2v^2 + 4u^4v^3 \quad (20)$$

Here $B = \beta_{43}^{1/2}\beta_{21}^{-1}B$, $v = \beta_{32}^{1/2}\beta_{21}^{-1}b$, $u = \beta_{21}^{1/2}h^{-1}$, $\alpha = \beta_{11}\beta_{21}^{-1/2}$, and $\beta = \beta_{22}\beta_{43}^{-1/2}$. Since trial values of all four equilibrium constants are now known, tentative values of α and β can be calculated. In this case calculation of $\log B$ ($-\log u$) involves the solution of an equation quadratic in v for each point on the map; and since this requires rather lengthy calculations, the computation was programmed for the Univac ERA 1103 digital computer at the University of Minnesota. Calculations of the projection maps were carried out for the following sets of α and β , respectively: 8, 3.63; 10, 3.63; 12.3, 3.63; 80, 3.63; 12.3, 1; 12.3, 2; 12.3, 3; 10, 5. A fairly good fit was obtained with the set $\alpha = 12.3$, $\beta = 3$.

Finally, in order to fit the data in the vicinity of the isohydric point, the complex $[(CH_3)_2Sn]_2(OH)_3^+$ was included and projection maps calculated for this five parameter case. The defining equations for this map (11, 21, 22, 32, 43) are

$$B = v + \alpha uv + u^2v + 2\beta u^2v^2 + 2\gamma u^3v^2 + 3u^4v^3 \quad (21)$$

$$B\bar{n} = \alpha uv + 2u^2v + 2\beta u^2v^2 + 3\gamma u^3v^2 + 4u^4v^3 \quad (22)$$

All of the comparable variables in this map are the same as in the four parameter (11, 21, 22, 43) map, and in addition $\gamma = \beta_{32}\beta_{21}^{-1/2}\beta_{43}^{-1/2}$. Trial values of γ were obtained using the value of β_{32} obtained from the best fit with the (11, 21, 32) map. This computation also was programmed for the Univac 1103 computer, and maps were calculated for the following sets of α , β , and γ : 10, 2.5, 0.6; 10, 2.7, 0.6; 10, 3.5, 0.6; 10, 5, 0.6; 10, 2.7, 0.8; 10, 2.7, 1.0; 8, 2.5, 0.6; 12, 2.5, 0.6; 12, 2.5, 1.0; 20, 3.6, 0.6. Variations of as little as 20% in the α , β , and γ parameters have a pronounced effect on the shape of the normalized projection maps. The best over-all fit was obtained with the parameters $\alpha = 12$, $\beta = 2.5$, and $\gamma = 0.6$, giving the following values for the equilibrium constants: $\log \beta_{11} = -3.4 \pm 0.1$, $\log \beta_{21} = -8.9 \pm 0.1$, $\log \beta_{22} = -4.8 \pm 0.2$, $\log \beta_{32} = -9.8 \pm 0.3$, and $\log \beta_{43} = -10.3 \pm 0.2$. The curves in Fig. 2 were drawn using these constants. The errors given were estimated from a comparison of the fits obtained with the theoretical, normalized projection maps together with the effect of the small variations in α , β , γ on the fit.

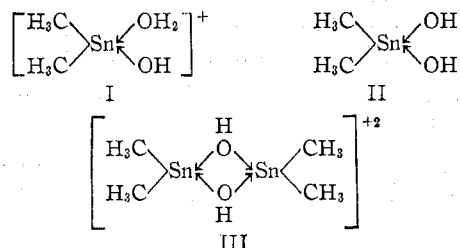
The deviations of the experimental data from the calculated curves at high total $(CH_3)_2Sn^{+2}$ concentrations in the region of the cross-over point indicate that small concentrations of higher complexes probably exist at hydrogen ion concentrations just slightly larger than that at which precipitation occurs.

Since the experimental data at lower \bar{n} values are to be weighted more heavily in an analysis of the data, the following "best" set of constants and their estimated errors was obtained from a consideration of all of the calculations: $\log \beta_{11} = -3.45 \pm 0.1$, $\log \beta_{22} = -4.7 \pm 0.2$, $\log \beta_{21} = -9.0 \pm 0.2$, $\log \beta_{32} = -9.8 \pm 0.3$, $\log \beta_{43} = -10.3 \pm 0.3$.

Discussion

The analysis of the data by the various "surface fitting" procedures described in the previous section indicates that the hydrolysis of $(CH_3)_2Sn^{+2}$

to give $(\text{CH}_3)_2\text{SnOH}^+$ is accompanied by condensation of the monohydroxo complex to give appreciable concentrations of the dimer $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_2^{+2}$. These two complexes are essentially the only species besides the aquo-cation which are present at pH values < 3 even with the total $(\text{CH}_3)_2\text{Sn(IV)}$ concentration as high as 80 mM. As the pH is raised, more than one proton, on the average, is transferred per $(\text{CH}_3)_2\text{Sn}^{+2}$ aquo-ion, and the assumption that $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_3^+$ and $[(\text{CH}_3)_2\text{Sn}]_3(\text{OH})_4^{+2}$ are produced allows the experimental data to be reproduced rather well. When the total $(\text{CH}_3)_2\text{Sn(IV)}$ concentration is ≥ 10 mM, precipitation occurs at about pH 5.5. Very low concentrations of even larger complexes appear to exist in the more concentrated solutions at pH values slightly less than 5.5. Finally, for the more dilute solutions the degree of polymerization of the complexes reaches a maximum at pH 5.5, and the addition of more base to the system causes the Sn-OH-Sn linkages to be broken so that the only soluble species at pH 8 is $(\text{CH}_3)_2\text{Sn(OH)}_2$. The stoichiometry of the complexes together with the observation that no more than two protons were transferred per $(\text{CH}_3)_2\text{Sn}^{+2}$ aquo-ion in the range $1 \leq \text{pH} \leq 8$ indicates that in aqueous solution $(\text{CH}_3)_2\text{SnOH}^+$, $(\text{CH}_3)_2\text{Sn(OH)}_2$, and $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_2^{+2}$ have the structures I to III, respectively.



The principal question to be asked concerning equilibrium constants obtained by a trial method such as is described in the preceding section is whether another set of parameters will reproduce the experimental data as well. In this case there seems to be little question about the existence of the complexes $(\text{CH}_3)_2\text{SnOH}^+$ and $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_2^{+2}$ or the values for their formation constants; no other complexes will reproduce the experimental data when $0 \leq \bar{n} \leq 0.7$. This includes combinations with $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_3^+$ as well as larger polynuclear complexes, and in no case is the agreement with the experimental data even close. The existence of $(\text{CH}_3)_2\text{Sn(OH)}_2$ at large \bar{n} values also seems to be without question, and $^*\beta_{21}$ must

be essentially correct, for changes in the larger polynuclear complexes assumed to exist in the intermediate \bar{n} range do not have an appreciable effect on $^*\beta_{21}$. This is a result of the fact that mononuclear complexes predominate in the most dilute solutions studied, 2.5 and 1 mM. In the intermediate range, $0.8 \leq \bar{n} \leq 1.5$, higher complexes certainly exist, and the inclusion of $[(\text{CH}_3)_2\text{Sn}]_2(\text{OH})_3^+$ and $[(\text{CH}_3)_2\text{Sn}]_3(\text{OH})_4^{+2}$ substantially improves the fit. It is probable that even higher polynuclear complexes exist over about 0.5 pH unit before precipitation occurs from the more concentrated $(\text{CH}_3)_2\text{Sn(IV)}$ solutions. It is hoped that studies on the structure of the solid phases isolated from these solutions will clarify this question.

No evidence was found for the existence of cationic 6- or 8-membered rings, such as might be anticipated by analogy with the hydrolysis product of $(\text{CH}_3)_2\text{Ga}^+$,^{27,28} or for neutral hexamethyltristannoxane or octamethyltetrastannoxanes. The rapidity and reversibility of the polymerization reactions indicate that polynuclear complexes containing tin-oxygen linkages are quite labile. This also has been observed in preparative work where the compound $(\text{CH}_3)_2\text{SnCl}_2\text{-O-SiCl(CH}_3)_2$ decomposed upon purification to regenerate the starting materials $(\text{CH}_3)_2\text{SnO}$ and $(\text{CH}_3)_2\text{SiCl}_2$.¹¹

The value of $\log ^*\beta_{11} = -3.1$ given by Rochow and Seyferth⁴ is only slightly too large, since in the dilute solutions studied by them the fraction of $(\text{CH}_3)_2\text{Sn(IV)}$ distributed in complexes other than $(\text{CH}_3)_2\text{SnOH}^+$ was not large. It is interesting to compare the constants for $(\text{CH}_3)_2\text{Sn}^{+2}$ and Sn^{+2} in the light of Rochow, Seyferth, and Smith's⁵ observations on the similarity of these ions. The value of $^*\beta_{11}$ reported for Sn^{+2} (-3.9 ± 0.15)⁶ is not greatly different from that for $(\text{CH}_3)_2\text{Sn}^{+2}$ (-3.45 ± 0.1). These values can be converted to the following stability constants for the monohydroxo complexes using $\log K_w = -14.22$ ²⁹ for the 3 M NaClO_4 medium: $\log \beta_{11} (\text{CH}_3)_2\text{Sn}^{+2} = 10.8$, $\log \beta_{11} \text{Sn}^{+2} = 10.3$. Indeed the surprising thing about Sn^{+2} is that it forms such strong hydroxo complexes, since the shielding effect of the lone pair of 5s electrons might be expected to reduce appreciably the strength of the metal-ligand bond. Since the two pairs of electrons be-

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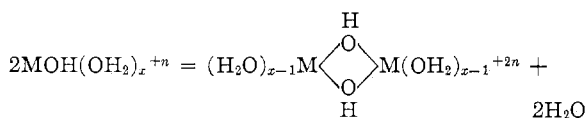
yond the d^{10} configuration of tin(IV) in $(\text{CH}_3)_2\text{Sn}^{+2}$ are localized in the σ bonds to C, this ion would be expected to be a good electron acceptor. If distortions of Sn^{+2} from spherical symmetry are important in explaining the solution behavior of divalent tin as suggested earlier,³⁰ the strength of the metal-oxygen bond in SnOH^+ should approach that of the corresponding bond in $(\text{CH}_3)_2\text{SnOH}^+$. Distortions of this type have long been recognized in SnO .³¹

Lawrence and Prue have measured the stability constant for $(\text{CH}_3)_2\text{TlOH}$ and compared it to the corresponding constant for TlOH ; the values for $\log \beta_{11}$ are: $(\text{CH}_3)_2\text{Tl}^+$, 1.04; Tl^+ , 0.51.³² The quantity $\Delta = \log \beta_{11} (\text{CH}_3)_2\text{M}^{n+} - \log \beta_{11} \text{M}^{n+}$, which is the log of the equilibrium constant for the reaction $(\text{CH}_3)_2\text{M}(\text{OH}_2)_x^{n+} + \text{MOH}(\text{OH}_2)_{y-1}^{(n-1)} = (\text{CH}_3)_2\text{MOH}(\text{OH}_2)_{x-1}^{(n-1)+} + \text{M}(\text{OH}_2)_y^{n+}$ is 0.5 for both Tl and for Sn. It is to be expected that the presence of the "inert pair" of 5s electrons in Sn^{+2} and 6s electrons in Tl^+ would lead to a slight reduction in the metal-ligand bond strength compared to the dimethyl ions with the same net charge.

Table I gives the first and second acid dissociation constants for the aquo- $(\text{CH}_3)_2\text{Sn}^{+2}$ ion, $*K_1 = *\beta_{11}$ and $*K_2 = *\beta_{21} *K_1^{-1}$, as well as the ratio of the first and second dissociation constants, R . The value $\log R = 2.0$ is much smaller than the value of about 5 found for the common oxy acids but larger than the values observed for simple aquo-metal ions. The definite step in the formation curve at an \bar{n} value of 2.0 indicates that two rather strong bonds to oxygen are formed, and $(\text{CH}_3)_2\text{Sn}(\text{OH})_2$ probably involves a tetra-

hedral arrangement of the 2C and 2O atoms about tin.

It is also of interest to examine the equilibrium constants for the dimerization reactions



where $K_d = *\beta_{22} *\beta_{11}^{-2}$, and values are given for Sn^{+2} and $(\text{CH}_3)_2\text{Sn}^{+2}$ as well as for other aquo-ions where these have been determined. For Sc(III), In(III), Sn(II), and Fe(III) the value of K_d decreases as $*K_1$ increases. Thus a strong metal-oxygen bond in the monohydroxo complex appears to reduce the donor character of the hydroxo oxygen and hence the tendency to form the di- μ -hydroxo bridges. The same effect is observed in a comparison of Sn^{+2} to $(\text{CH}_3)_2\text{Sn}^{+2}$ where the larger $*K_1$ is found for the dimethyl ion, which has the smaller K_d .

The most pronounced difference between Sn^{+2} and $(\text{CH}_3)_2\text{Sn}^{+2}$ is the comparative reluctance of the dimethyltin ion to coordinate a second hydroxo group either by a simple protolysis process to yield the mononuclear dihydroxo complex or by a substitution reaction to form the dinuclear di- μ -hydroxo complex. Part of this can be attributed to a statistical factor because of the smaller number of water molecules coordinated to the dimethyltin ion, but the major effect must be a lessening of the tin-oxygen bond strength. This reluctance to form polynuclear complexes makes it possible to study the hydrolysis of the dimethyltin ion over a much wider range of hydrogen ion concentration than usually is possible with simple aquo-ions. In the case of Sn^{+2} , a precipitate was obtained at a pH of about 3 and $\bar{n} = 1$, even with the most dilute solutions. With the total $[(\text{CH}_3)_2\text{Sn}^{+2}] \leq 5 \text{ mM}$, no precipitation occurred to the highest pH value studied, 9, and even with the more concentrated solutions, measurements could be made to $\bar{n} = 1.4$. While the hydrolysis of Sn^{+2} results mainly in the formation of a trimer, $\text{Sn}_3(\text{OH})_4^{+2}$, with $\log *\beta_{43} = -6.77^6$; $(\text{CH}_3)_2\text{Sn}^{+2}$ has a much less pronounced tendency to form polynuclear complexes beyond the dimer, and $\log *\beta_{43} = -10.3$.

Acknowledgment.—The authors would like to express their appreciation to Professor Z Z. Hugas, Jr., who programmed the projection map calculations for the Univac computer.

TABLE I

EQUILIBRIUM CONSTANTS FOR CATIONS WITH MONO- AND DINUCLEAR HYDROLYSIS PRODUCTS

Ion	$\log *K_1$	$\log *K_2$	$\log R$	$\log K_d$
Sc ⁺³ ^a	-5.1	-5.1	0	4.0
In ⁺³ ^a	-4.4	-3.9	-0.5	3.6
Sn ⁺² ^{a,6}	-3.9	3.4
Fe ⁺³ ^a	-3.05	-3.26	0.21	3.2
Tl ⁺³ ^c	-1.14	-1.49	0.35	.. ^b
$(\text{CH}_3)_2\text{Sn}^{+2}$	-3.45	-5.5	2.05	2.2

^a Values taken from L. G. Sillén, *Quart. Rev. (London)*, **13**, 146 (1959). ^b No polymers formed.

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