basis of these data, it is proposed that the species present in the mixed solvent is a platinum complex of DMSO. It is assumed that the coordination positions above and below the ligand plane are occupied by molecules of dimethyl sulfoxide in a manner similar to that in neat dimethyl sulfoxide and that the platinum species is similar in both systems.

Exchange Study.—The kinetic data for chloride ion exchange with the platinum complex in neat DMSO are zero order in chloride and are consistent with the mechanism proposed[3] in which the displacement of chloride from the complex is the rate-controlling step. However, if it is mainly the donor strength of the DMSO which facilitates chloride ion displacement,[3] then the complex $[Pt(py)_2Cl_2(DMSO)_2]$ should undergo reaction by a similar mechanism in the solvent $CDCl_3$. Examination of the data in Table II shows that in the mixed solvent the chloride-dependent path (possibly in addition to some chloride-independent mechanism) is occurring. This result is in direct contradiction to the above prediction based on the reported[3] role of the solvent in this reaction. It appears in this instance as though the ability of the medium to facilitate charge separation (*i.e.*, the solvating ability of the solvent) is a more important parameter than the magnitude of the metal ion–solvent interaction. In order to test this proposal further, the exchange was investigated in pyridine and sulfolane. The former is a strong donor but poor solvating solvent,[4] and the latter is a poor donor solvent[10] but a good solvating solvent.[4] Again, the solvating properties dominate, and the reaction mechanism is found to be zero order in chloride in sulfolane and very much dependent on chloride ion concentration in pyridine.

For the solvents used in this study, the donor strength is in the order[4] pyridine > DMSO > sulfolane >> $CDCl_3$ and the solvating ability is in the order[4] DMSO $\sim$ sulfolane >> pyridine > $CDCl_3$.

Although the exchanges described above have been found to correlate with the solvating ability of the solvent, it would be naïve to attempt to account for the mechanism of this reaction in a series of solvents solely on the basis of solvating ability. For very good solvating solvents,[4] safe predictions for this reaction can be made. For example, a chloride-independent path would be predicted in N-methylformamide and N-methylacetamide, but an *a priori* prediction of the experimentally observed[3] chloride-dependent path in N,N-dimethylformamide could not have been anticipated. For borderline solvents, one must consider, in addition to donor strengths, how the change in solvent affects the relative rates of the two processes, *i.e.*, the chloride-dependent and chloride-independent paths. In this connection, many unknown parameters are introduced when the solvent is varied (*e.g.*, entropies and enthalpies of activation of the two mechanistic routes will change, and variations in the free energies and enthalpies of solvation of the chloride ion will occur in the different solvents).

In spite of the lack of complete understanding, studies in nonaqueous solvents can show when solvating properties are important. This approach is considerably better than ignoring solvation completely as has so often been done on studies carried out in water. The importance of solvation has been clearly demonstrated in this study and should cast doubt on many of the conclusions drawn from studies where solvation is neglected.

Acknowledgment.—The partial support of this research by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-758 is gratefully acknowledged.

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(10) It might be argued that sulfolane is "biphilic".[3] However, the donor strength of sulfolane toward iodine is low[3] and iodine should make use of the biphilic character of the donor. A very large interaction of iodine with donors containing empty d orbitals, *e.g.*, $(C_2H_5)_2S$, is found to occur. It appears that an assignment of biphilic character to $(CH_3)_2SO$ and CH_3NO_2 is not warranted on the basis of the reported[3] data. This biphilic concept (and possibly other concepts derived from reaction rates and orders in polar solvents) disappears in this system when solvent effects are considered.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINNESOTA 55455

Hydrolysis of the Aquo Ions R_3Sn^+ and R_2Sn^{2+}: Steric Effects on the Dissociation of Aquo Acids[1]

BY R. STUART TOBIAS, HUMPHREY N. FARRER,
MARK B. HUGHES, AND BRIAN A. NEVETT

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Recently, there has been some interest in the solution chemistry of the dialkyltin(IV) and trialkyltin(IV) moieties from the standpoint of complexation reactions in aqueous solution,[2-8] complex formation in nonaqueous solution,[9] assignment of Raman spectra of these moieties in solutions,[10-12] and the interpretation of changes in the indirect tin-117 and tin-119 proton spin–spin coupling constants in aqueous solutions.[13-17]

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Of value for the interpretation of the spectroscopic measurements is a detailed knowledge of just what organotin species are present in the solutions and the nature of the interaction of these organometallic cations with water molecules in the first coordination sphere. The structures adopted by the di- and trialkyltin(IV) ions in aqueous solutions appear to be those which minimize the energy of the organometallic moiety. Thus the dialkyltin(IV) ions have linear C–Sn–C and the trialkyltin(IV) ions planar SnC_3 skeletons in aqueous solutions. Information pertaining to the structure and behavior of these ions in solution has been the subject of a recent review.[18]

These ions should have rather unusual effects on the structure of the solvent water. There should be particularly pronounced ordering of water molecules in the equatorial plane of the dialkyltin(IV) ions because of the strong electrostatic field near the tin atom. In addition, the hydrophobic nature of the alkyl groups will tend to force more hydrogen bonding in the solvent around the axial positions. Thus these ions should lead to rather extensive ordering of the water molecules in the solvent, and the effect should become more pronounced the larger the alkyl groups. An ion like di-*n*-butyltin(IV) should be rather like a normal nonane hydrocarbon molecule but with a +2 charge localized on the middle atom in the chain. The trialkyltin(IV) ions would be expected to exhibit a similar effect although to a lesser extent, since the ions are more compact and the electrostatic fields are much weaker.

Although it was suggested earlier that there were probably four water molecules in the first coordination sphere of $(CH_3)_2Sn^{2+}$ by analogy with the structure of the isoelectronic $Sn(OH)_6{}^{2-}$,[12] preliminary oxygen-17 nmr measurements indicate that the half-life for exchange of water in the first coordination sphere of $(CH_3)_2Sn^{2+}$ is less than 10^{-3} sec at 0°.[19] Thus it is likely that all of these organotin ions have labile aquo complexes, and the concept of the hydration number becomes less precise.

Hydrolyses of both the dimethyltin(IV)[20] and dimethyllead(IV)[21] ions have been examined carefully, and they follow essentially the same pattern with extensive dimerization of the simple monohydroxo complex. As the pH increases, this is followed by depolymerization to the simple dihydroxide. Recent studies on another organometallic cation, the methylmercury(II) ion, CH_3Hg^+, which might be expected to be somewhat similar to $(CH_3)_3Sn^+$, have shown that a binuclear complex $[CH_3Hg–OH–HgCH_3]^+$ is formed by hydrolysis.[22]

This communication reports measurements on the acidity of $(CH_3)_3Sn^+(aq)$, $(C_2H_5)_2Sn^{2+}(aq)$, and $(C_3H_7)_2Sn^{2+}(aq)$ and also summarizes the effects of changes in the R groups on the acidity of the ions R_3Sn^+, R = CH_3 and C_2H_5, and R_2Sn^{2+}, R = CH_3, C_2H_5, C_3H_7, and C_4H_9.

Experimental Section

Preparation of Solutions.—Tetramethyltin was prepared by the usual Grignard reaction and allowed to react with $SnCl_4$ to yield $(CH_3)_3SnCl$. This was hydrolyzed with 55% NaOH to produce $(CH_3)_3SnOH$,[23] and the product was collected, dried, and purified by vacuum sublimation. *Anal.* Calcd for $(CH_3)_3SnOH$: C, 20.0; H, 5.57. Found: C, 19.9; H, 5.21.

Tetraethyltin prepared by the Grignard reaction was allowed to react with an equimolar amount of $SnCl_4$ to yield diethyltin dichloride, which was recrystallized from petroleum ether. *Anal.* Calcd for $(C_2H_5)_2SnCl_2$: C, 19.4; H, 4.07. Found: C, 19.6; H, 3.94. The oxide was precipitated from an aqueous solution of the chloride with dilute ammonia, washed free of chloride, and dried. *Anal.* Calcd for $(C_2H_5)_2SnO$: C, 24.9; H, 5.23; Sn, 61.6. Found: C, 23.7; H, 4.76; Sn, 57.9. This oxide does not burn well, and it was difficult to analyze.

Di-*n*-propyltin dichloride obtained from M and T Chemicals was dissolved in ether and hydrolyzed with aqueous KOH. The precipitate was collected on a filter, washed free of chloride ion, and dried. *Anal.* Calcd for $(C_3H_7)_2SnO$: C, 32.3; H, 7.24. Found: C, 32.7; H, 6.63.

Di-*n*-butyltin dichloride obtained from M and T Chemicals was recrystallized from benzene, and the oxide was precipitated by the addition of concentrated aqueous ammonia to a solution of the chloride in absolute ethanol. The product was washed free of chloride and dried. *Anal.* Calcd for $(C_4H_9)_2SnO$: C, 38.6; H, 7.29. Found: C, 38.8; H, 7.06.

Solutions of the organotin perchlorates were prepared by dissolving the appropriate oxide or hydroxide in standard perchloric acid. Generally, the total perchlorate concentrations of the solutions were checked by exchanging the organotin cations for hydrogen ion and titrating the liberated acid. The calculated analytical hydrogen ion concentrations were found to agree within 1% of the values calculated from the quantities of standard acid used to prepare the solutions.

The general experimental procedure was essentially the same as that employed for similar studies in this laboratory.[21]

Because of the low solubility of the hydroxo complex of the di-*n*-butyltin ion, the ionic medium 0.5 *M* $(Na)ClO_4$ was used; all other measurements were made with 3 *M* $(Na)ClO_4$.

Determination of the Species Present and Their Equilibrium Constants.—In the case of the hydrolysis of $(CH_3)_3Sn^+$, the values of $\bar{n}$, the average number of protons transferred per organotin ion, plotted *vs.* pH for different total trimethyltin(IV) concentrations all fell on a single curve within the anticipated experimental error. A trial value of log $^*K_{11}$[24] was obtained from the pH value corresponding to $\bar{n} = 0.5$. A least-squares refinement with equal weights[21] for all 236 data sets was carried out using the Fortran-60 program GAUSS Z[25] and the University of Minnesota's CDC-1604 computer. The refined value of the constant is given in Table I, and the observed and calculated $\bar{n}$ values from the last least-squares cycle are listed in Table II.[26] The final value of the residual $R = \Sigma|\bar{n}_{obsd} - \bar{n}_{calcd}|/\Sigma|\bar{n}_{obsd}|$ was 1.72%.

As is generally the case with data obtained by a titration technique, the observed and calculated $\bar{n}$ values exhibit small syste-

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TABLE I

ACID DISSOCIATION CONSTANTS FOR SEVERAL ALKYLTIN(IV) AQUO IONS IN 3 M NaClO$_4$ AT 25°

Ion	log $^*K_{11}$[a]	log K_d[b]	$\sigma_{\bar{n}}$[c]
$(CH_3)_3Sn^+$	-6.599 ± 0.002	...	± 0.015
$(C_2H_5)_3Sn^+$[d]	-6.808 ± 0.005	...	± 0.019
$(CH_3)_2Sn^{2+}$[e]	-3.54 ± 0.01	$+2.48 \pm 0.02$	± 0.035
$(C_2H_5)_2Sn^{2+}$	-3.40 ± 0.01	$+2.43 \pm 0.01$	± 0.014
$(C_3H_7)_2Sn^{2+}$	-2.92 ± 0.01	$+2.27 \pm 0.01$	± 0.017

[a] Equilibrium constant for $M^{z+}(aq) + H_2O \rightleftarrows MOH^{z-1}(aq) + H_3O^+$. [b] Equilibrium constant for $2M(OH)^+(aq) \rightleftarrows [M(OH)_2M]^{2+}(aq)$. [c] Variance to the fit. [d] Data from ref 26. [e] Values taken from five-parameter fit for $0 \leq \bar{n} \leq 2^{27}$; the somewhat larger variance to the fit, $\sigma\bar{n}$, results from the very wide pH range fitted, 1–9.

matic differences. In effect, these systematic errors should be randomized by the measurements at different concentrations if they are caused by analytical errors. For the two highest concentrations studied, the observed $\bar{n}$ values are slightly greater than the calculated values for $\bar{n}$ less than *ca.* 0.5, while the opposite is true above $\bar{n}$ = *ca.* 0.5. This could be caused by the formation of traces of a binuclear complex $[(CH_3)_3Sn(OH)Sn(CH_3)_3]^+$. The maximum difference was only 0.04 unit in $\bar{n}$, and for most points the difference was half this or less; so no effort was made to obtain an additional constant from the data.

For the hydrolysis of $(C_2H_5)_2Sn^{2+}$, trial values for the constants $^*K_{11}$ and $^*\beta_{22}$ were evaluated by graphical procedures[21] and refined by least squares using 440 data sets. The maximum value of $\bar{n}$ attained before precipitation was *ca.* 0.9. The inclusion of a term for the formation of $(C_2H_5)_2Sn(OH)_2$ gave no improvement to the fit. No other combination of species could be found which would fit the experimental data at all satisfactorily. The refined constants are listed in Table I and the observed and calculated values of $\bar{n}$ in Table III.[26] The least-squares refinement converged to the same values for the constants even when quite different starting values were employed, giving an R of 4.10%.

The analysis of the $(C_3H_7)_2Sn^{2+}$ data was carried out in the same manner as for the other dipositive ions using 296 data sets except the constants for the hydrolysis of $(C_2H_5)_2Sn^{2+}$ were used as the initial values for the least-squares refinement. The final set of constants is listed in Table I, and the observed and calculated $\bar{n}$ values are listed in Table IV.[26] The value of R was 5.03%. Again, there was no indication that the neutral hydroxide was a significant product in the pH range examined.

The experimental data for the $(C_3H_7)_2Sn^{2+}$ hydrolysis are believed to incorporate somewhat larger experimental errors than the other data because of the stronger acidity of this ion. It was necessary to make many measurements in the range from pH 1 to 2 where small errors in the cell liquid–liquid junction potential cause rather large errors in the hydrogen ion concentration. The cell $E°$ values were obtained from acid–base titrations in the absence of $(C_3H_7)_2Sn^{2+}$, and there was some indication of small changes in $E°$ as the di-*n*-propyltin ion was added. This change appeared to be approximately linear in $[(C_3H_7)_2Sn^{IV}]$ and amounted at most to 1.5 mv in a 100 mM solution.

An attempt was made to obtain the acidity constants for $(C_4H_9)_2Sn^{2+}$, but the very low solubility of the conjugate base made it impossible to obtain accurate values. Data obtained with 5 and 10 mM total $(C_4H_9)_2Sn^{IV}$ in 0.5 M (Na)ClO$_4$ medium were compared with data for the hydrolysis of $(C_2H_5)_2Sn^{IV}$ in the same medium, and they indicated that the dissociation constant for the butyl compound was *ca.* 0.5 pK unit larger or about the same as that of the di-*n*-propyltin ion. Precipitation occurred at $\bar{n} \simeq 0.2$.

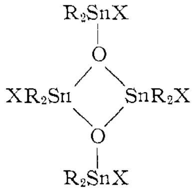
Results and Discussion

Values for the refined constants for the acid dissociation and condensation reactions of the aquo ions $(CH_3)_3Sn^+$, $(C_2H_5)_3Sn^+$,[27] $(CH_3)_2Sn^{2+}$,[27] $(C_2H_5)_2Sn^{2+}$, and $(C_3H_7)_2Sn^{2+}$ are tabulated in Table I.

Janssen and Luijten have studied the acidity of several triorganotin(IV) compounds in a solvent consisting of 44% ethanol by weight in water.[28] Considering the difference in the solvent system, it is essentially fortuitous that they obtained nearly the same values for $(CH_3)_3SnCl$ and $(C_2H_5)_3SnCl$, log $^*K_{11}$ = 6.56 ± 0.05 and 6.85 ± 0.05, respectively, as found in this work. Since the SnC$_3$ moiety appears to be planar in these ions with the tin valence orbitals probably 5s5p^2 hybrids to a first approximation,[18] the tin orbital electronegativity would be expected to be rather high for these cations. Thus the decrease in acidity as ethyl groups replace methyl groups probably reflects the greater electron-releasing (inductive) effect of the ethyl group as suggested by Janssen and Luijten. Further comparisons with the trialkyl species studied by Janssen and Luijten could not be made, since the conjugate base of $(C_3H_7)_3Sn^+$, that is, the uncharged hydroxide, is virtually insoluble in the aqueous perchlorate medium.

The hydrolysis of the trimethyltin ion was studied particularly carefully in order to determine whether any singly bridged dimers analogous to those observed with CH_3Hg^+ [22] were formed. Some association might be expected since the hydroxide itself has been reported to be somewhat associated in organic solvents.[29] While two bridging hydroxo groups are found frequently with coordination compounds, single OH bridges are observed rarely. No appreciable concentrations of such a dimer were found to exist in the range of concentrations studied, refuting a suggestion made earlier[30] and in agreement with the results of Janssen and Luijten with the mixed solvent system.

In the case of the dialkyltin cations, the hydrolysis reactions appear to be similar and also similar to those of the R_2Pb^{2+} and R_2Tl^+ ions.[21] The simple mononuclear conjugate base $R_2Sn(OH)^+$ has a pronounced tendency to dimerize, and monomer and dimer are the only significant hydrolysis products up to $\bar{n}$ values of almost 1. A variety of organotin compounds which are presumed to have the general structure I or II have been synthesized, and these have been described in a review by Poller.[31] The tin atoms in the binuclear ions in solution are probably also bridged by two oxygen atoms.



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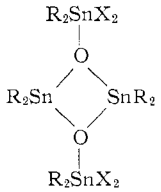

II

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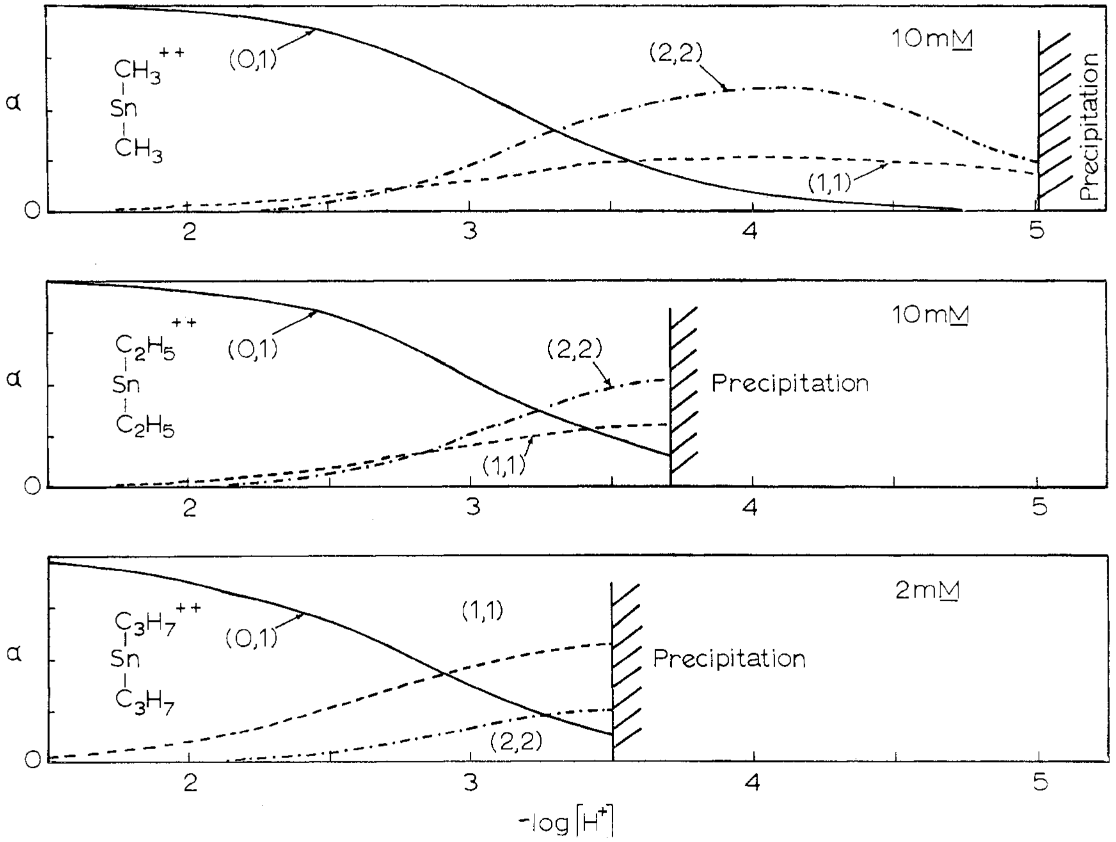

Figure 1.—Distribution of the organotin(IV) moieties among the different species as a function of pH; α is the fraction of the total organotin moiety in the indicated species. The numbers in parentheses indicate the number of hydroxo groups and organometallic moieties, respectively.

The increase in the acidity in the series $(CH_3)_2Sn^{2+}$, $(C_2H_5)_2Sn^{2+}$, and $(C_3H_7)_2Sn^{2+}$ is the opposite of the trend observed with the trimethyl- and triethyltin ions and opposite to what would be expected on the basis of simple inductive effects. A similar increase in acidity with increasing alkyl chain length was observed to occur with the trialkyltin chlorides in going from ethyl to *n*-propyl to *n*-butyl in the mixed ethanol–water solvent.[27] Similar trends with alkylammonium ions have been studied carefully and attributed to decreased solvation of the acid with increasing size of the alkyl group.[32] This effect would be expected to be even more pronounced with the strongly solvated, dipositive dialkyltin ions. As would be anticipated the di-*n*-butyltin ion appears to be at least as strong an acid as the di-*n*-propyltin ion, although its dissociation constants could not be measured accurately.

Figure 1 illustrates the distribution of tin among the various hydrolysis products for the R_2Sn^{2+} ions listed in Table I. All diagrams are appropriate for 10 m*M* organotin ion except for the di-*n*-propyltin system, which is for 2 m*M*. At the higher concentrations, precipitation of hydrolysis products occurs at rather low pH with this ion.

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York

Infrared Spectra of Group IV *gem*-Diamines and Their Cyclic Derivatives

By C. H. Yoder and J. J. Zuckerman

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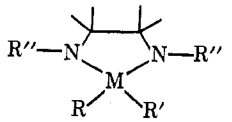
One of the advantages of studying homologous series of compounds is that variations in a property can be assigned to a structural or electronic change in the series. The infrared spectrum is such a property to the extent that absorptions are characteristic of independently vibrating groups. We report in this communication the results of our examination of three series of fourth group amines: *gem*-diamines, RR′M-[NR″]$_2$, where M = carbon, silicon, germanium, and tin and the various R's can be H, CH_3, C_2H_5; monocyclic imidazolidines



where M = carbon, silicon, and germanium and the various R's can be H, CH_3, and C_6H_5; and spiro-[imidazolidines]

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