

the thiophosphoryl sulfur would be in the equatorial plane of the transition state. Since there is much less phosphorus π bonding to sulfur than to oxygen, it is reasonable to expect a much smaller contribution to stabilization of the transition state through π bonding in PSCl_3 . Since oxygen is more electronegative than sulfur, POCl_3 would be expected to exchange more slowly than PSCl_3 on the basis of the inductive argument presented above correlating the formal charge on phosphorus with the difficulty in obtaining the transition state.

It should be mentioned that in the previous discussion, we have been relating an enthalpy of activation

to an observed rate of exchange. It is assumed that the principal factor affecting the exchange order is the enthalpy for the formation of the transition state. We have obtained a crude value of approximately 14 kcal./mole for the enthalpy of activation for POCl_3 . We cannot distinguish unambiguously between the enthalpies of activation of the compounds studied because of experimental error introduced by the rapid exchange occurring at temperatures significantly higher than those reported herein.

Acknowledgment. The partial support of this research by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-578 is gratefully acknowledged.

A Calorimetric Procedure for Determining Free Energies, Enthalpies, and Entropies for the Formation of Acid-Base Adducts

Theodore F. Bolles¹ and Russell S. Drago

Contribution from the Wm. A. Noyes Laboratory, University of Illinois, Urbana, Illinois. Received May 27, 1965

In this article, a calorimetric method is presented which allows simultaneous measurement of both the equilibrium constant and enthalpy of adduct formation. Thermodynamic data obtained by this procedure for the adduct of $(\text{CH}_3)_3\text{SnCl}$ with $\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2$ in the solvent CCl_4 are reported. The equilibrium constant is found to agree within experimental error with the value obtained from an infrared study of this system.

Introduction

In a previous article,² we have reported an equation for the rigorous evaluation of an equilibrium constant from spectrophotometric data. Equation 1 was derived for a 1:1 complex ($\text{A} + \text{B} \rightleftharpoons \text{C}$) under conditions where the complex and free acid or base spectral curves overlapped and the molar absorptivity of the complex could not be measured directly. In eq. 1,

$$K^{-1} = \frac{A^0 - A^T}{\epsilon_B - \epsilon_C} - ([\text{A}]_0 + [\text{B}]_0) + \frac{[\text{A}]_0[\text{B}]_0(\epsilon_B - \epsilon_C)}{A^0 - A^T} \quad (1)$$

ϵ_B denotes the molar absorptivity of the free base or acid, $[\text{A}]_0$ and $[\text{B}]_0$ are the initial concentrations of the acid and base, respectively, A^0 is the absorption of a solution of concentration $[\text{A}]_0$ or $[\text{B}]_0$, ϵ_C is the molar absorptivity of the complex, A^T is the total absorbance, and K^{-1} is the reciprocal of the formation equilibrium

constant. Simultaneous equations for several sets of experimental data are solved to produce values for the two unknowns K^{-1} and ϵ_C .

If instead of measuring spectrophotometric absorbance the heat evolved on combination of an acid and a base is measured, this quantity can be used in place of A^T to calculate an equilibrium constant. The analog of ϵ_C in the enthalpy experiment is ΔH° , the molar enthalpy of formation of the adduct. Consequently, both K and ΔH° can be evaluated simultaneously by this technique. The necessary equations are derived and the best experimental conditions for obtaining the data are discussed.

Experimental Section

Materials. Eastman White Label N,N-dimethylacetamide was stored over Linde 4A molecular sieves for 2 days, refluxed at reduced pressure over calcium hydride for 2 hr., and fractionally distilled through a 30-in. Vigreux column. The middle fraction was collected, b.p. 42–42.5° (20 mm.).

Trimethyltin chloride, obtained from Metal and Thermit Chemicals, was sublimed at 25° under reduced pressure, m.p. 37.5°.

Fisher Spectranalyzed carbon tetrachloride was dried over Linde 4A sieves and was used in both the infrared and calorimetric work.

Spectra. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a CIC variable temperature chamber (Model 104). The temperature of the solutions was measured to $\pm 1^\circ$ with a thermometer positioned adjacent to the infrared cell. Preliminary experiments using a copper-

(1) Abstracted in part from the Ph.D. thesis of T. F. Bolles, University of Illinois, Urbana, Ill.

(2) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

constantan thermocouple positioned directly in the sample solution gave excellent agreement with the thermometer reading after equilibration. The spectra were recorded 15 min. after thermal equilibrium had been established in the cell chamber and could be retraced without change 15 min. later. Since the reference cell was not thermostated, it was necessary to remove it from the infrared beam between measurements in order to maintain a reproducible base line.

The solutions were prepared in a drybox and corrections were made for the volume changes due to temperature changes.

Calorimetry. The calorimeter was essentially that designed by Professor E. Arnett.³ A 200-ml. silvered dewar flask was fitted with a Teflon top and a vibromixer stirrer, which extended through the top. The stirrer was driven by a Model E-1 vibro-mixer. The trimethyltin chloride sample tube, a resistance heater for use in calibration, and a thermistor, Sargent Model S-81620, were suspended from the calorimeter top. Temperature changes in the calorimeter were detected by the thermistor in conjunction with a Sargent SR recorder. The sensitivity of this detector circuit was such that 6 cal. of heat added to the system would produce a pen deflection of approximately 100 mm. The calorimeter was calibrated by measuring the heat of neutralization of NaOH with HCl, which agreed within 1% of the reported value.

The N,N-dimethylacetamide solutions and trimethyltin chloride samples were prepared in a drybox. After the calorimeter had been purged with dry nitrogen, the solution was transferred to the dewar without exposure to the atmosphere. The sample of trimethyltin chloride, which was enclosed in a stoppered glass tube, was suspended in the calorimeter well below the level of the solution. After thermal equilibrium was established, the calorimeter was calibrated by passing a measured amount of current through the resistor and noting the recorder deflection. The sample tube was then broken to release the trimethyltin chloride and the recorder deflection again noted. After the reaction was complete, the system was again calibrated. Using the average of these calibrations and correcting for the heat of solution of the acid, the heat of reaction was computed.

Treatment of the Data and Results

Calorimetric Determination of Equilibrium Constants. For the case $A + B \rightleftharpoons C$, the equilibrium constant, K , for a 1:1 equilibrium between a Lewis acid and a Lewis base can be represented by the equation

$$K = \frac{[C]}{[A][B]} \quad (2)$$

in which [C] represents the equilibrium concentration of the complex, [A] the equilibrium concentration of the acid, and [B] the equilibrium concentration of the base. If the initial concentration of the acid is A_0 and the base B_0 , eq. 2 can be written

$$K = \frac{[C]}{(A_0 - [C])(B_0 - [C])} \quad (3)$$

(3) E. M. Arnett, W. G. Benitude, J. J. Burke, and P. M. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

If ΔH° is the heat of formation of 1 mole of complex, then the concentration of the complex may be written

$$[C] = \frac{1000\Delta H'}{\nu \Delta H^\circ} \quad (4)$$

where ν is the volume in milliliters of the solution and $\Delta H'$ is the measured heat of formation for an unknown amount of the complex. Combining eq. 3 and 4 gives

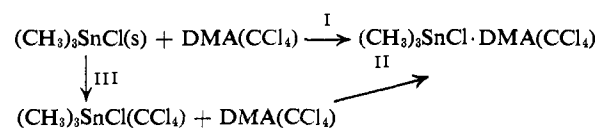
$$K = \frac{1000\Delta H'}{(\nu)\Delta H^\circ} \left[A_0 - \frac{1000\Delta H'}{\Delta H^\circ(\nu)} \right] \left[B_0 - \frac{1000\Delta H'}{(\nu)\Delta H^\circ} \right] \quad (5)$$

Equation 5 may be rewritten in the following form.

$$K^{-1} = \frac{1000\Delta H'}{(\nu)\Delta H^\circ} + \frac{A_0 B_0}{\Delta H'} \frac{\nu}{1000\Delta H^\circ} - (A_0 + B_0) \quad (6)$$

Equation 6 is analogous to eq. 1 and may be solved by measuring $\Delta H'$ at different acid and/or base concentrations. Using arbitrary values of ΔH° , measured values of $\Delta H'$, and the known initial acid and base concentrations, a series of solutions to eq. 6 can be obtained. For each experimentally measured $\Delta H'$, a straight line is often obtained when K^{-1} is plotted vs. ΔH° over narrow ranges of ΔH° . The intersection of the lines should ideally occur at one point which represents the unique solution to eq. 6 for the values of K^{-1} and ΔH° . Usually, however, the lines cross at points which define a series of triangles, the total area of which is an indication of the precision of the experiments.

The relationship between the way the calorimetric experiment was carried out (step I) and the enthalpy of adduct formation in CCl_4 from the reagents in the solvent CCl_4 (step II) can be illustrated with the following Born-Haber type cycle.



The heat of adduct formation in CCl_4 from the reagents in CCl_4 , $\Delta H'$ (step II), is obtained by subtracting the heat of solution of $(\text{CH}_3)_3\text{SnCl(s)}$ in CCl_4 (ΔH_{III}) from the observed heat (step I), *i.e.*

$$\Delta H' = \Delta H_{\text{obsd}} - \Delta H_{\text{III}} \quad (7)$$

Values measured for ΔH_{III} are contained in Table I. Table II gives experimental data for the determination of the equilibrium constant for the reaction of $(\text{CH}_3)_3\text{SnCl}$ with DMA in carbon tetrachloride. Calculated values of K^{-1} for arbitrary values of ΔH° are also reported. The graphical solution to eq. 6 is illustrated in Figure 1. The equilibrium constant was determined by computing the average ΔH° and $\Sigma(\Delta H^\circ_{\text{exptl}} - \Delta H^\circ_{\text{av}})^2$ at a series of values for K^{-1} . The best value for K^{-1} was taken where the sum of the squares of the deviations of the experimental data from their average was the smallest. At $27 \pm 1^\circ$, this gives $K^{-1} = 0.29 \pm 0.03$ and $\Delta H^\circ = -7.7 \pm 0.3$ kcal./mole.

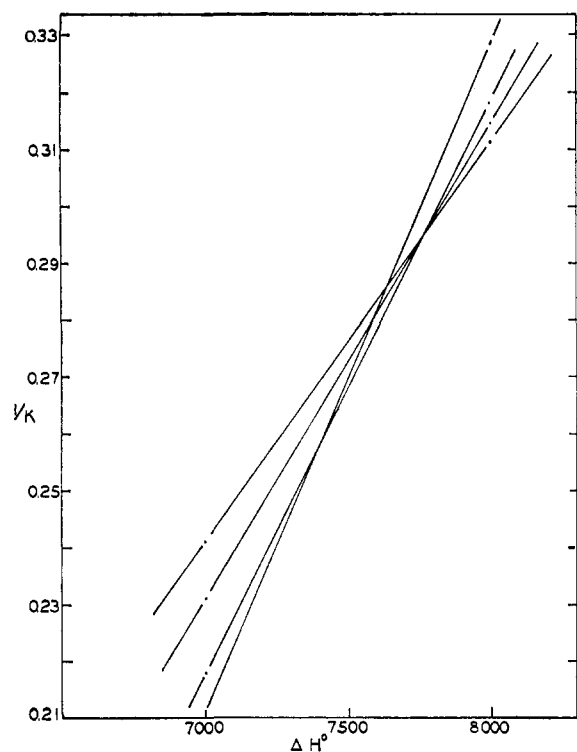


Figure 1. K^{-1} vs. ΔH° plot for the DMA- $(\text{CH}_3)_3\text{SnCl}$ system.

Infrared Determination of Equilibrium Constants. The equilibrium between DMA and $(\text{CH}_3)_3\text{SnCl}$ can be studied by infrared spectroscopy because the carbonyl stretching frequency of DMA shifts to lower energy upon complexation (Figure 2). Since trimethyltin

Table I. ΔH_{soln} of Solid $(\text{CH}_3)_3\text{SnCl}$ in CCl_4

$(\text{CH}_3)_3\text{SnCl}$ added, mole	Concn., M	$+\Delta H_{\text{soln}}$, kcal. mole^{-1}
0.002285	0.06464	4.68
0.002605	0.04757	4.62
0.003213	0.03213	4.66
0.003179	0.03179	4.68
0.002154	0.02154	4.73
0.001191	0.01191	4.74
0.001164	0.01164	4.62
		Av. = +4.68

Table II. Calorimetric Results

B_0 , moles l.^{-1}	A_0 , moles l.^{-1}	$\Delta H'$, cal.	ΔH° , cal. mole^{-1}	$1/K$
0.6409	0.03971	20.65	7000	0.2113
			8000	0.3289
0.4980	0.03552	17.03	7000	0.2179
			8000	0.3188
0.3579	0.03344	13.90	7000	0.2313
			8000	0.3149
0.2485	0.03366	11.55	7000	0.2412
			8000	0.3116

chloride does not absorb in this region, eq. 1 can be employed to solve the spectrophotometric data for K^{-1} . It is evident from Figure 2 that the DMA absorption band with no acid present (line 1) does not pass through

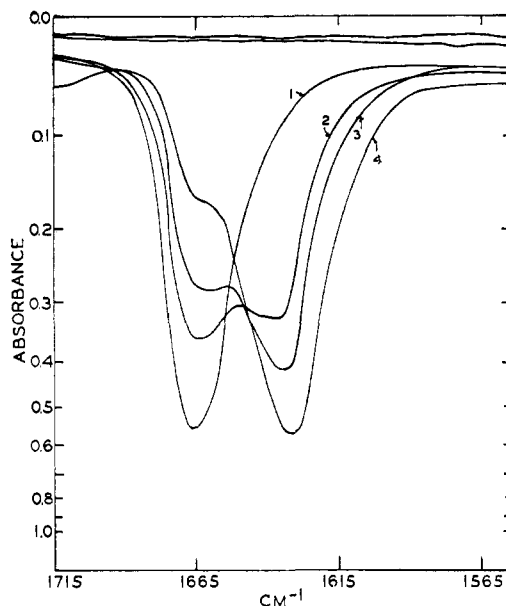


Figure 2. Infrared spectra for the DMA- $(\text{CH}_3)_3\text{SnCl}$ system: (1) 0.07464 M DMA; (2) 0.07287 M DMA, 0.1425 M $(\text{CH}_3)_3\text{SnCl}$; (3) 0.07212 M DMA, 0.2387 M $(\text{CH}_3)_3\text{SnCl}$; (4) 0.06901 M DMA, 0.5466 M $(\text{CH}_3)_3\text{SnCl}$.

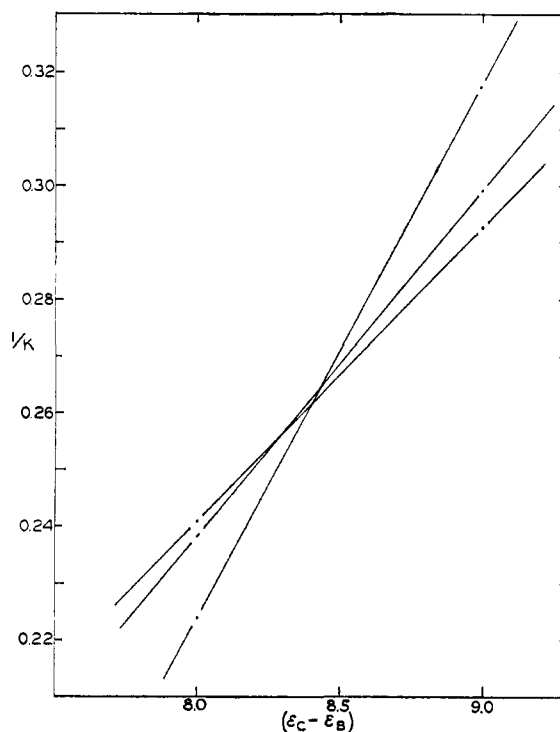


Figure 3. K^{-1} vs. $\epsilon_C - \epsilon_B$ plot for the DMA- $(\text{CH}_3)_3\text{SnCl}$ system.

the isosbestic point. This is due to a small shift ($\approx 5 \text{ cm.}^{-1}$) of the free DMA $\text{C}=\text{O}$ absorption to lower energy in the solvent mixture $(\text{CH}_3)_3\text{SnCl}-\text{CCl}_4$. This shift can be attributed to a change in the dielectric constant and refractive index of the mixed solvent compared to CCl_4 .

As previously reported, eq. 1 may be solved graphically. The experimental data are given in Table III and the graphical solution is shown in Figure 3. An evaluation similar to that previously described for the

Table III. Infrared Equilibrium Constant at 1665 Cm.^{-1}

A_0 , moles l.^{-1}	B_0 , moles l.^{-1}	$A_0 - A^T$	$(\epsilon_C - \epsilon_B)$	$1/K$
0.5466	0.06901	0.381	8.00	0.2240
			9.00	0.3177
0.2387	0.07212	0.267	8.00	0.2384
			9.00	0.2991
0.1425	0.07287	0.192	8.00	0.2413
			9.00	0.2927

calorimetric data gives, at $27 \pm 1^\circ$, a K^{-1} value of 0.26 ± 0.03 .

Discussion

The Calorimetric Procedure for K and ΔH° . The excellent agreement between the infrared and calorimetric equilibrium constants has established the feasibility of the calorimetric procedure outlined in the Experimental Section. This procedure has several pronounced advantages. First, the method evaluates ΔH° and K simultaneously at one temperature. Secondly, the seriously limiting requirement of a spectrophotometric procedure that an absorption band exist which changes upon complexation is eliminated, yet this method is also suitable for reactions with a relatively small K and ΔH° (*i.e.*, of the order of magnitude reported here).

In a critical examination of the errors involved in the determination of K for weak complexes, it has been shown that, for the best values of K , the donor concentration must be greater than $0.1K^{-1}$ in the most concentrated solution.⁴ While these conditions are fulfilled, an indication of the reliability of the calculated equilibrium constant is necessary. To this end, we have employed a test involving the sharpness of the fit.^{5,6}

For the calorimetric determination of the equilibrium constant, this sharpness has a value of 27.5, which compares favorably to the suggested minimum of about 20 for a reliably determined K . The infrared data give a sharpness of 20.

The usual procedure employed to solve for K^{-1} using a graphical method is to evaluate the value of K^{-1} at all the crossing points and compute the average. However, this method leaves much to be desired. For example, if two measurements were made under approximately the same experimental conditions, the slopes of the plots of K^{-1} vs. ΔH° may be nearly identical, and quite small errors would cause a large variation in their crossing point, giving a large variation in K^{-1} . Also, if many more measurements were observed at one concentration point than the others, the data may tend to be biased. For these reasons, we feel that the following procedure should be employed to determine K^{-1} and ΔH° (or ϵ) from plots of the type illustrated in Figures 1 and 3.

(1) The equilibrium constant should be evaluated by a procedure analogous to that previously described.^{5,6} In this method, an average ΔH° is com-

puted for a series of values for K^{-1} . The best value for K^{-1} is then taken as that point where the sum of the squares of the deviations of the experimental data from their average is the smallest. (Programs have been reported which employ this technique⁶.) This procedure would tend to ignore data points from closely parallel lines.

(2) Experimental conditions should be chosen so the plots of K^{-1} vs. ΔH° give lines which differ in slope as much as possible.

(3) At each concentration chosen, only one line should be drawn. Actually, it would be optimal to perform several measurements at each chosen concentration and use their average for the K^{-1} vs. ΔH° plot.

(4) A sharpness of the fit or similar test should be employed to evaluate the reliability of the measured K^{-1} .

(5) The reliability of the least accurate measurements should be evaluated. For example, in the calorimetric determination of K^{-1} , the most concentrated solutions (where large amounts of complex are formed and $\Delta H'$ is large) give lines which are nearly vertical, while the least concentrated give horizontal lines. For greatest accuracy, as great a difference in slope as possible is needed. However, as the lines become more horizontal, less complex is formed, and the measurement of $\Delta H'$ becomes less reliable, giving rise to a large error in this line. However, it is possible that a single measurement under these adverse conditions may give data which, when plotted, give lines that intersect closely with the other lines by chance. If these data were included, a sharpness of fit test would suggest that the measurement of K^{-1} is far better than it actually is. Thus, the least accurate determinations acceptable for a K^{-1} vs. ΔH° plot are those which are reproducible within a chosen error limit. While these procedures do not include a test for systematic errors, they do give an indication of random errors and the reliability of K .

In the calculation of the equilibrium constant, the assumption has been made that any changes in the activity coefficients of the species involved cancel. This assumption is supported by the narrow range of intersections in the K^{-1} vs. ϵ or K^{-1} vs. ΔH° plots (Figures 1 and 3). It has previously been shown that even though the activity coefficient of DMA in CCl_4 varies, the equilibrium constant for DMA- I_2 does not. A constant ratio for $\gamma_{\text{complex}}/\gamma_{\text{DMA}}$ was proposed.⁷ Further support for this proposal is provided by the similarity in the equilibrium constants measured in excess base by the calorimetric procedure and in excess acid by the spectrophotometric procedure.

Nature of the Species in Solution. In an earlier article⁸ it was reported that $(\text{CH}_3)_3\text{SnCl}$ forms 1:1 addition compounds in solution with a whole series of Lewis bases. The results of infrared and n.m.r. studies were interpreted in terms of a five-coordinate adduct with a trigonal bipyramidal structure. The chlorine and donor molecule occupy apical positions and the three methyl groups equatorial positions. A similar structure was reported for the solid compound $\text{C}_5\text{H}_5\text{N} \cdot (\text{CH}_3)_3\text{SnCl}$ from the results of a single crystal

(4) W. B. Person, *J. Am. Chem. Soc.*, **87**, 167 (1965).

(5) E. Coburn and W. C. Grunwald, Jr., *ibid.*, **80**, 1322 (1958).

(6) K. Conrow, G. Johnson, and R. E. Bown, *ibid.*, **86**, 1025 (1964).

(7) R. S. Drago, R. L. Carlson, N. J. Rose, and D. Wenz, *ibid.*, **83**, 3572 (1961).

(8) N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 237 (1964).

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.

Acknowledgment. The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

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

Humphrey N. Farrer,² Mary Mercy McGrady,³ and R. Stuart Tobias

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received May 21, 1965

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: $\log \beta_1 = 0.380 \pm 0.001$ and $\log \beta_2 = -0.14 \pm 0.01$. 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 $\log \beta_1 < -0.5$. 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.

(1) Supported, in part, by the National Science Foundation under Grant GP-653 and by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-691-65.

(2) Research Fellow in Chemistry.

(3) N.S.F. Predoctoral Fellow.

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-