The Enthalpy of Formation of Coordination Compounds of Trimethyltin Chloride

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Abstract: The enthalpies of formation and equilibrium constants for a number of 1:1 complexes of trimethyltin chloride have been measured in nonpolar solvents by calorimetric, infrared, and nmr procedures. It was found that trimethyltin chloride interacts more strongly with oxygen and nitrogen donors than with sulfur or phosphorus donors. The recently proposed double-scale enthalpy equation was applied to the trimethyltin chloride system and the values $C_A = 0.60$ and $E_A = 6.25$ were derived.

Recently, the following equation was proposed[2] for the evaluation of the enthalpy of formation of Lewis acid–base adducts

$$-\Delta H_c = C_A C_B + E_A E_B \qquad (1)$$

where ΔH_c represents the calculated enthalpy of formation (in kcal/mole) of a given adduct, C_A and E_A represent constants assigned to a given Lewis acid, and C_B and E_B represent constants assigned to a given Lewis base. These constants are determined empirically, and excellent agreement between the calculated and measured enthalpy of formation of the adduct (when measured in the gas phase or in an inert solvent) is observed. In connection with these studies, it was of interest to extend this treatment to a system in which the Lewis acid or base undergoes extensive changes in geometry upon coordination. The Lewis acid trimethyltin chloride was chosen for this study since only 1:1 adducts are observed for triorganotin halide–base complexes.

Upon adduct formation, trimethyltin chloride undergoes extensive rearrangement from a structure with local C_{3v} symmetry in the free acid to one approaching a trigonal bipyramidal structure in the adduct with the three methyl groups in the equatorial plane.[3] If the above relationship is valid for this system, the reorganization energy would have to be incorporated into the acid constants.

It is of interest to point out that the *C* and *E* constants encompass the qualitative concepts of type A and B[4] or of hard and soft[5] Lewis acids and bases. If the ratio *C*/*E* is comparatively large, the acid or base is classified as type B or soft. Conversely, if the ratio is comparatively small, the acid or base is classified as type *A* or hard. Equation 1 is in accord with the observation that combination of "like" acids and bases gives rise to the most effective interaction.

The evaluation of the *E* and *C* constants for trimethyltin chloride is of interest because there has been some speculation in the literature as to the nature of the acidity of organotin compounds. For example, a viscosity study[6] of the relative ability of a Lewis base, B, to cause depolymerization of a polymeric trialkyltin imidazole by the reaction

$$[\text{X–Sn(R}_3\text{)–]}_n + n\text{B} \longrightarrow n[\text{X–Sn(R}_3\text{)–B}] \qquad (2)$$

was interpreted to indicate that this Lewis acid exhibits definite type-B character. However, in a study[7] of the stability of R_2Sn^{2+} complexes, this ion was compared with class A acceptors. Clearly, these systems are very complex and quantitative enthalpy data on simple adducts are needed to classify these acids as type A or B so that qualitative predictions of their interactions with different donors can be made.

Experimental Section

A. Preparation and Purification of Chemicals. Fisher Spectranalyzed carbon tetrachloride was dried over Linde 4A molecular sieves and was used in the nmr, infrared, and calorimetric work. Spectrograde isooctane (2,2,4-trimethylpentane) and methylene chloride were similarly treated.

Eastman White Label N,N-dimethylacetamide (DMA) was purified as previously described.[8]

Pyridine, hexamethylphosphoramide (HMPA), and dimethyl sulfoxide (DMSO), were stored over Linde 4A molecular sieves for 2 days, refluxed at reduced pressure over fresh barium oxide for 4 hr, and fractionally distilled under reduced pressure through a 30-in. Vigreux column. The middle fractions were collected.

Reagent acetone was dried over anhydrous potassium carbonate, filtered, and purified[9] by use of the addition compound formed with sodium iodide ($NaI \cdot 3C_3H_6O$). Pure acetone was distilled from the complex through a 30-in. Vigreux column and the middle third collected, bp 56.2°. Linde 4A molecular sieves could not be used to dry acetone since decomposition occurred upon standing.

N,N-Dimethylthioacetamide (DMTA) was prepared from DMA and P_2S_5 by the following procedure. DMA (0.8 mole) was slowly added to 0.18 mole of P_2S_5 and stirred at 125° for 20 min. The residue was dissolved by the addition of 30 ml of H_2O. The solution was then cooled to 0°, filtered, and washed with several 20-ml portions of H_2O. The orange solid was dissolved in 1000 ml of ether to which 20 g of Darco had been added, and the mixture was allowed to stand overnight. After filtering, the solution was reduced to a volume of 60 ml and filtered; the solid was recrystallized from acetone. This purification procedure was repeated until clean white crystals were collected. The product was sublimed at 60° at reduced pressure before use.

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[1] Abstracted in part from the Ph.D. Thesis of T. F. Bolles, University of Illinois, Urbana, Ill., 1966.

[2] R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).

[3] N. A. Matwiyoff and R. S. Drago, *Inorg. Chem.*, **3**, 337 (1964), and references therein.

[4] S. Ahrland, J. Chatt, and N. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

[5] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[6] J. G. A. Luijten, M. J. Janssen, and G. J. M. Van Der Kerk, *J. Organometal. Chem.* (Amsterdam), **1**, 286 (1964).

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

[8] T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 5015 (1965).

[9] A. I. Vogel, "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1958.

Anal. Calcd for C_4H_9NS: C, 46.56; H, 8.79; N, 13.57. Found: C, 46.89; H, 8.78; N, 13.14.

Trimethyltin chloride, obtained from Metal and Thermit Chemicals, was purified by sublimation at 25° under reduced pressure, mp 37.5° (lit.[10] mp 37.0°).

B. Infrared Spectra. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a Model 104 ClC variable temperature chamber as previously described.[8]

The spectrophotometer was purged with dry nitrogen for several hours prior to the recording of far-infrared spectra. Since these solutions were not thermostated, the spectra were recorded immediately after the samples were placed in the infrared beam. Although the temperature of the samples undoubtedly changed somewhat during this time, all spectra could be retraced without change. Matched 0.4-mm CsBr cells were used.

C. Nuclear Magnetic Resonance Spectra. The Sn^{119}–CH_3 coupling constant values were determined from nmr spectra obtained on a Varian Model A-60 high-resolution nuclear magnetic resonance spectrometer equipped with a Varian temperature regulator. Temperatures in the probe were measured with an iron–constantan thermocouple to ±0.5°. The spectra were traced three times and found to be reproducible to ±0.2 cps. The spectrometer sweep was calibrated with a standard $(CH_3)_4Sn$ sample before and after the measurements, and all coupling constant values are reported relative to $J_{^{119}Sn-CH_3} = 54.0$ cps for $(CH_3)_4Sn$.

D. Preparation of Solutions. Solutions of hygroscopic materials were prepared in a drybox in standardized volumetric flasks which had been rinsed with acetone, heated at 120° for several hours, and flushed with dry nitrogen prior to use. Corrections were made for volume changes due to changes in temperature.

E. Calorimetric Measurements. The calorimetric measurements were performed as previously described.[8]

Results

A. Equilibrium Constants and Enthalpy Measurements by Calorimetry. Equation 3, which has been derived[5] for the simultaneous determination of the enthalpy of formation and equilibrium constant for a 1:1 adduct, was solved by a procedure similar to that previously proposed.[8,11] In eq 3, A^0 and B^0 represent

$$K^{-1} = \frac{1000H^1}{V\Delta H^\circ} + \frac{A^0B^0V\Delta H^\circ}{1000H^1} - (A^0 + B^0) \quad (3)$$

the initial concentrations of the acid and base, V represents the total volume of the solution in milliliters, H^1 the experimentally measured enthalpy of reaction, and ΔH° the calculated molar enthalpy of formation of the complex. Equation 3 was used to obtain equilibrium constants and molar enthalpies of formation for the association of trimethyltin chloride with DMSO, DMA, HMPA, and acetone. The experimental data and the calculated K^{-1} and ΔH° values are included in Table I. In some cases, in order to minimize random errors in the measurement of H^1, several experiments were performed at the same concentrations and the average A^0, B^0, V, and H^1 are reported. Error limits were estimated by the sharpness of fit procedure[8] and are also included in Table I. It was necessary to observe the acetone–$(CH_3)_3SnCl$ equilibrium in isooctane since the equilibrium constant is larger in this solvent. The HMPA–$(CH_3)_3SnCl$ equilibrium was also studied in isooctane because HMPA was found to react with carbon tetrachloride.

Table I. ΔH° and Equilibrium Constant Determination by Calorimetry at 26°

A^0, mole l.$^{-1}$	B^0, mole l.$^{-1}$	V, ml	$-H^1$, cal	K^{-1}_{cal}, mole l.$^{-1}$
$(CH_3)_3SnCl$–DMSO/CCl_4				
0.03198	0.2524	100.3	17.15	0.122
0.04686	0.2979	100.3	26.96	0.113
0.04339	0.4378	100.3	28.42	0.102
0.04061	0.5621	100.3	27.58	0.110
0.02427	0.7843	100.3	17.24	0.118
$K^{-1}_{cal} = 0.11 \pm 0.03$ mole l.$^{-1}$ $\Delta H^\circ_{cal} = -8.2 \pm 0.3$ kcal mole^{-1} at sharpness ≥ 20				
$(CH_3)_3SnCl$–DMA/CCl_4[a]				
0.03331	0.1208	100.4	6.79	0.326
0.03342	0.2571	100.4	11.50	0.319
0.03344	0.3579	100.4	13.90	0.311
0.03552	0.4980	100.4	17.03	0.314
0.03971	0.6409	100.4	20.65	0.326
$K^{-1}_{cal} = 0.32 \pm 0.03$ mole l.$^{-1}$ $\Delta H^\circ_{cal} = -7.9 \pm 0.3$ kcal mole^{-1} at sharpness ≥ 20				
$(CH_3)_3SnCl$–HMPA/Isooctane				
0.03330	0.02347	100.8	20.15	0.00243
0.03519	0.04414	100.8	29.53	0.00314
0.03210	0.04519	100.8	28.27	0.00261
0.02818	0.07131	100.7	27.33	0.00196
0.02986	0.09479	100.7	28.96	0.00292
$K^{-1}_{cal} = 0.0026 \pm 0.0004$ mole l.$^{-1}$ $\Delta H^\circ_{cal} = -10.1 \pm 0.3$ kcal mole^{-1} at sharpness ≥ 20				
$(CH_3)_3SnCl$–Acetone/Isooctane				
0.04037	0.5360	100.7	7.94	1.08
0.03203	0.5958	100.7	6.73	1.09
0.04091	0.6472	100.8	9.16	1.07
0.04010	0.8672	100.8	10.82	1.05
0.04106	1.1950	100.8	12.87	1.09
$K^{-1}_{cal} = 1.1 \pm 0.1$ moles l.$^{-1}$ $\Delta H^\circ_{cal} = -6.0 \pm 0.5$ kcal mole^{-1} at sharpness ≥ 20				

[a] Also see ref 8.

B. Equilibrium Constants by Infrared. When DMSO interacts with trimethyltin chloride, the S–O stretching frequency is lowered. Since trimethyltin chloride does not absorb at this frequency, the equation

$$K^{-1} = \frac{A^T - A_0}{\epsilon_C - \epsilon_B} - (C_B + C_A) + \frac{C_BC_A(\epsilon_C - \epsilon_B)}{A^T - A_0} \quad (4)$$

may be used to calculate the equilibrium constant.[12] In eq 4, C_B and C_A represent the initial concentrations of the base and acid, ϵ_C and ϵ_B are the molar absorptivities of the complex and base, A_0 is the absorbance which corresponds to that for the initial concentration of base, and A^T is the measured absorbance of a solution containing the acid, base, and complex. Equation 4 was solved by employing a procedure which is similar to that previously described for the calorimetric data.[8] Table II includes the experimental data the calculated K^{-1} for this system.

For the determination of the equilibrium constant for the pyridine–trimethyltin chloride system, the tin–

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(10) C. A. Kraus and C. C. Callis, *J. Am. Chem. Soc.*, **45**, 2628 (1923).

(11) K. Conrow, G. D. Johnson, and R. E. Bowen, *ibid.*, **86**, 1025 (1964).

(12) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).

Table II. Equilibrium Constant Determinations by Infrared at 27°

A^0, mole l.$^{-1}$	B^0, mole l.$^{-1}$	$(A^0 - A^T)$, mole l.$^{-1}$	$K^{-1}{}_{\mathrm{ir}}$, moles l.$^{-1}$
$(CH_3)_3SnCl$-DMSO/CCl_4 at 1175 cm^{-1}			
0.0446	0.07209	0.109	0.12
0.1536	0.07091	0.258	0.13
0.3322	0.06950	0.370	0.13
0.5169	0.06785	0.406	0.12
$K^{-1}{}_{\mathrm{ir}} = 0.12 \pm 0.01$ mole l.$^{-1}$ $(\epsilon - \epsilon_c) = 385 \pm 20$ at sharpness ≥ 20			
$(CH_3)_3SnCl$-DMA/CCl_4 at 1665 cm^{-1}			
0.5466	0.06901	0.381	0.26
0.2387	0.07212	0.267	0.26
0.1425	0.07287	0.192	0.26
$K^{-1}{}_{\mathrm{ir}} = 0.26 \pm 0.03$ mole l.$^{-1}$ $(\epsilon - \epsilon_c) = 842 \pm 20$ at sharpness ≥ 20			
$(CH_3)_3SnCl$-Pyridine/CCl_4 at 338 cm^{-1}			
0.04931	0.4793	0.151	0.54
0.04870	0.6432	0.181	0.55
0.04824	0.7874	0.199	0.53
0.04752	0.9264	0.208	0.54
$K^{-1}{}_{\mathrm{ir}} = 0.54 \pm 0.04$ mole l.$^{-1}$ $(\epsilon - \epsilon_c) = 186 \pm 20$ at sharpness ≥ 20			

chlorine band, which occurs in the far-infrared, was observed. Upon complexation, the tin–chlorine stretching frequency is lowered and eq 4 again applies. The tin–chlorine stretching frequency for the free acid decreases slightly as the concentration of the pyridine increases. Since the complex does not absorb in this region, this shift can be attributed to a change in dielectric constant and refractive index of the mixed solvent compared to CCl_4. Table II includes the data for the calculation of K^{-1} for the pyridine–trimethyltin chloride system. The data previously reported[8] for the DMA–$(CH_3)_3SnCl$ equilibrium are also included in Table II for comparison.

C. Equilibrium Constants by Nmr. In the case of rapid exchange, the observed coupling constant, $J_{^{119}Sn-CH_3}$, is described by

$$J_{\mathrm{obsd}}(A^0) = J_f(A^0 - C) + J_c(C) \qquad (5)$$

In eq 5, J_{obsd}, J_f, and J_c represent the observed coupling constant, the coupling constant of the free acid, and the coupling constant of the complex, respectively, and A^0 and C represent the initial acid concentration and the equilibrium concentration of the complex. The expression for the equilibrium constant combined with eq 5 leads to the equation

$$K^{-1} = \frac{(J_{\mathrm{obsd}} - J_f)A^0}{(J_c - J_f)} + \frac{B^0(J_c - J_f)}{(J_{\mathrm{obsd}} - J_f)} - (A^0 + B^0) \qquad (6)$$

Equation 6 is of the same form as eq 3 and 4 and was solved for the unknowns J_c and K^{-1} using the same procedure. The data for the calculation of the equilibrium constant for the trimethyltin chloride systems with DMA, DMSO, and DMTA are given in Table III. Since the equilibrium constant for the DMTA–$(CH_3)_3SnCl$ equilibrium in CCl_4 is quite small at 34°, J_c and K^{-1} were evaluated in methylene chloride at −70°. At this temperature, the equilibrium constant is large enough to allow an accurate evaluation of both K^{-1} and J_c. This value of J_c evaluated in CH_2Cl_2 should be identical with J_c in CCl_4 since the coupling constant is relatively solvent independent.

Table III. J_c and Equilibrium Constant Determination for $(CH_3)_3$-SnCl–Base Systems by Nmr

A^0, mole l.$^{-1}$	B^0, mole l.$^{-1}$	$(J_{\mathrm{obsd}} - J_f)A^0$, cps mole l.$^{-1}$	$K^{-1}{}_{\mathrm{nmr}}$, mole l.$^{-1}$	$(J_c - J_f)$, cps
$(CH_3)_3SnCl$-DMSO/CCl_4 (34°)				
0.04708	0.9358	0.4708	0.17	11.8 ± 0.4
0.04695	0.6499	0.4413	0.16	
0.04654	0.4785	0.4142	0.15	
0.04657	0.2966	0.3353	0.17	
$K^{-1}{}_{\mathrm{nmr}} = 0.16 \pm 0.03$ mole l.$^{-1}$ at sharpness ≥ 20 $J_c = 69.0$ cps				
$(CH_3)_3SnCl$-DMA/CCl_4 (34°)				
0.04707	0.6868	0.3624	0.32	11.5 ± 0.1
0.04655	0.4800	0.3119	0.33	
0.04617	0.3534	0.2678	0.33	
0.04674	0.2187	0.2057	0.32	
$K^{-1}{}_{\mathrm{nmr}} = 0.32 \pm 0.01$ mole l.$^{-1}$ at sharpness ≥ 20 $J_c = 68.7$ cps				
$(CH_3)_3SnCl$-DMTA/CH_2Cl_2 (−70°)				
0.1087	1.490	0.6098	0.67	8.5 ± 0.2
0.1058	1.041	0.5401	0.66	
0.1059	0.6812	0.4316	0.69	
0.1055	0.3934	0.3233	0.66	
$K^{-1}{}_{\mathrm{nmr}} = 0.67 \pm 0.04$ mole l.$^{-1}$ at sharpness ≥ 20 $J_c = 65.8$ cps				

It is also possible to determine J_c directly. Since coupling constants are relatively unaffected by nonspecific solvent effects, the coupling constants for the Lewis base adducts of trimethyltin chloride may be measured directly in the liquid base if all the trimethyltin chloride is complexed. Table IV includes the values observed for J_c. In order to test for complete complexation of the acid, each system was observed at a series of successively lower temperatures until a further decrease in temperature produced no change in the J_c value observed. The temperatures corresponding to complete complexation are also included in Table IV.

Table IV. $J_{^{119}Sn-CH_3}$ for B·$(CH_3)_3SnCl$ Adducts

Donor (B)	[Acid],[a] mole l.$^{-1}$	[Donor],[a] moles l.$^{-1}$	Temp, C°	$J_{^{119}Sn-CH_3}$, cps
HMPA	0.49	5.4	35	71.8
DMSO	0.47	13.3	35	69.2
DMA	0.53	10.1	35	68.8
Pyridine	0.51	12.3	35	67.0
Acetone	0.52	12.7	−20	66.1
$CH_3C{\equiv}N$	0.45	17.9	−20	64.2
(CCl_4)	0.51	...	−20	57.6

[a] Calculated at 26°.

D. Equilibrium Constant and Enthalpy Determinations from Combined Data. Using the previously evaluated values of J_c, it is possible to determine equilibrium constants by nmr directly from eq 6. In turn, ΔH° can be evaluated from thermochemical data by use of the K^{-1} (after temperature corrections have been made) determined by nmr (or infrared) and eq 3. Data for the evaluation of K^{-1} by nmr for several Lewis base–trimethyltin chloride systems are included in Table V. The evaluation of ΔH° from the values of K^{-1} and the corresponding thermochemical data is included in Table VI. The equilibrium constants were corrected to 26° by guessing a value for ΔH° to calculate an approximate K^{-1} at 26° and using this K^{-1} to evaluate ΔH° from the thermochemical data. Using this enthalpy as a better approximation of ΔH°, the equilibrium constant was recalculated until the trial ΔH° agreed with that evaluated from the thermochemical data.

Table V. Evaluation of K^{-1} at 34° by Nmr Using Measured Values of J_c

A^0, mole l.$^{-1}$	B^0, mole l.$^{-1}$	$(J_{obsd} - J_f)A^0$, cps mole l.$^{-1}$	K^{-1}, moles l.$^{-1}$
	$(CH_3)_3SnCl$–Acetone/CCl_4 $(J_c - J_f) = 8.9$ cps		
0.04772	0.8492	0.08590	3.31
0.04705	0.5988	0.07058	2.91
0.04721	0.4281	0.05193	2.99
0.04683	0.2624	0.03278	3.03
	$K^{-1}{}_{34°} = 3.1$ moles l.$^{-1}$ $K^{-1}{}_{26°} = 2.4$ moles l.$^{-1}$		
	$(CH_3)_3SnCl$–$CH_3C{\equiv}N$/CCl_4 $(J_c - J_f) = 7.0$ cps		
0.04729	1.1633	0.1135	2.20
0.04685	0.8151	0.08433	2.32
	$K^{-1}{}_{34°} = 2.3$ moles l.$^{-1}$ $K^{-1}{}_{26°} = 1.8$ moles l.$^{-1}$		
	$(CH_3)_3SnCl$–DMTA/CCl_4 $(J_c - J_f) = 8.5$ cps		
0.04816	0.7909	0.08669	2.90
0.04690	0.5584	0.07035	2.56
0.04733	0.3961	0.05206	2.62
	$K^{-1}{}_{34°} = 2.7$ moles l.$^{-1}$ $K^{-1}{}_{26°} = 2.1$ moles l.$^{-1}$		

Table VII includes a summary of the equilibrium constants, the coupling constants, and enthalpy of formation of the complexes.

Table VI. Evaluation of ΔH° from Measured Values of K^{-1} at 26°

A^0, mole l.$^{-1}$	B^0, mole l.$^{-1}$	V, ml	$-H^1$, cal	$-\Delta H^\circ$, kcal mole^{-1}
	$(CH_3)_3SnCl$–Acetone/CCl_4 $K^{-1}{}_{nmr} = 2.4$ moles l.$^{-1}$			
0.03139	0.5757	100.3	3.51	5.8
0.02857	0.6855	100.3	3.59	5.7
0.03098	0.7654	100.3	4.18	5.6
0.03107	0.9726	100.3	5.20	5.8
	$\Delta H^\circ = -5.7$ kcal mole^{-1}			
	$(CH_3)_3SnCl$–$CH_3C{\equiv}N$/CCl_4 $K^{-1}{}_{nmr} = 1.8$ moles l.$^{-1}$			
0.02332	0.3182	100.0	1.70	4.89
0.01609	0.5919	100.0	1.91	4.83
0.01955	0.6492	100.0	2.52	4.93
0.01315	0.8472	100.0	2.01	4.80
0.01365	0.9390	100.0	2.19	4.71
	$\Delta H^\circ = -4.8$ kcal mole^{-1}			
	$(CH_3)_3SnCl$–Pyridine/CCl_4 $K^{-1}{}_{ir} = 0.54$ mole l.$^{-1}$			
0.01819	0.1986	100.3	3.06	6.35
0.01545	0.2826	100.2	3.47	6.61
0.01595	0.3235	100.2	3.72	6.29
0.01950	0.3440	100.3	4.79	6.38
0.01517	0.4139	100.2	4.38	6.70
0.01503	0.4939	100.2	4.79	6.71
	$\Delta H^\circ = -6.5$ kcal mole^{-1}			
	$(CH_3)_3SnCl$–DMTA/CCl_4 $K^{-1}{}_{nmr} = 2.1$ moles l.$^{-1}$			
0.02028	0.3017	100.3	1.52	5.74
0.01369	0.4491	100.3	1.28	5.68
0.01869	0.4879	100.3	2.08	6.36
	$\Delta H^\circ = -5.9$ kcal/mole			

Discussion

From Table VII, it is evident that the equilibrium constants determined by the various methods are internally consistent. The evaluation of ΔH° from calorimetric measurements by use of the equilibrium constants (and J_c values) calculated by the various procedures is validated by the good agreement between the ΔH° and K^{-1} values evaluated for the DMA and DMSO systems by use of all of these procedures. The value of ΔH° for the HMPA–$(CH_3)_3SnCl$ adduct evaluated in isooctane can be compared to enthalpies evaluated in CCl_4 as evidenced by the similarity of ΔH° for the $(CH_3)_2CO$–$(CH_3)_3SnCl$ adduct in both solvents.[13]

The enthalpies of formation of these adducts are of the same order of magnitude as that previously estimated for the dissociation energy of the Sn–O bond of a pentacoordinate distannoxane.[14] Also, the linear enthalpy-entropy relationship observed for a large number of charge-transfer type complexes[15] appears to exist qualitatively in these systems even though the bases are quite dissimilar.

In all cases, the data indicate the formation of only 1:1 adducts. This is not surprising in view of the reported instability of adducts of the form $[B_2(CH_3)_3Sn]^+Cl^-$[16] and the lack of conductivity in base–$(CH_3)_3SnCl$ systems.[17]

***E* and *C* Correlation.** If there is a linear relationship between the rehybridization energy of the acid upon adduct formation and the measured enthalpy of adduct formation, this system may be described by the proposed

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[13] For a discussion of the effect of solvent on measurements of this type, see R. S. Drago, T. F. Bolles, and R. J. Niedzielski, submitted for publication.

[14] W. J. Considine, J. A. Baum, and R. C. Jones, *J. Organometal. Chem.* (Amsterdam), **3**, 308 (1965).

[15] See, for example, W. B. Person, *J. Am. Chem. Soc.*, **84**, 536 (1962).

[16] H. C. Clark, R. J. O'Brien, and A. L. Pickard, *J. Organometal. Chem.* (Amsterdam), **4**, 43 (1965).

[17] A. B. Thomas and E. G. Rochow, *J. Inorg. Nucl. Chem.* **4**, 205 (1957); *J. Am. Chem. Soc.*, **79**, 1843 (1957).

Table VII. Summary of $\Delta H°$ and K^{-1} (at 26°) as Evaluated by the Different Methods

Donor	Solvent	K^{-1}, l. mole^{-1}			K^{-1}_{nmr} (measured J_c)	J_c, cps		$-\Delta H°$, kcal mole^{-1}	
		Cal	Infrared	Nmr		Equilibrium	Direct	Calcd	Combn
HMPA	Isooctane	0.0026					71.6	−10.1	
DMSO	CCl_4	0.11	0.12	0.11	0.11	69.0	69.2	−8.2	−8.2
DMA	CCl_4	0.32	0.26	0.25	0.25	68.7	68.8	−7.9	−7.7
Pyridine	CCl_4		0.54				67.0		−6.5
Acetone	Isooctane	1.1					66.1	−6.0	
Acetone	CCl_4				2.4		66.1		−5.7
DMTA	CCl_4				2.1	65.8[a]			−5.9
$CH_3C{\equiv}N$	CCl_4				1.8		64.2		−4.8

[a] Determined in CH_2Cl_2 at −70°.

double-scale enthalpy equation for Lewis acid–base systems (eq 1). The constants E_A and E_B are believed to be associated with the electrostatic interaction between acid, A, and base, B, and C_A and C_B with the covalent interaction. Substitution into eq 1 gives the enthalpy of interaction, ΔH_c, which should agree with the measured enthalpy of formation. If the correlation is to work for this system, the rehybridization energy of the acid must be included in the E_A and C_A constants. The constants were evaluated for trimethyltin chloride from the reported base constants,[2] the experimental enthalpies of formation, and eq 1. The method of least squares was employed to determine the best fit. The E_A and C_A constants for $(CH_3)_3SnCl$ and the ΔH_c values calculated by eq 1 are included in Table VIII. The small C_A/E_A ratio calculated for trimethyltin chloride indicates that this acid is a type-A Lewis acid.

To better elucidate the nature of the acidity of trimethyltin chloride, an attempt was made to evaluate the enthalpy of interaction of $(C_6H_5)_3P$, $(C_4H_9)_3P$, and $(C_2H_5)_2S$ with trimethyltin chloride, but the enthalpy changes and/or equilibrium constants were too small to be measured by these techniques. This result is consistent with that expected from the small C_A/E_A ratio, and clearly indicates that trimethyltin chloride interacts more strongly with nitrogen or oxygen donors than with phosphorus or sulfur donors and may be classified as a type-A or relatively hard Lewis acid.

Of the six donors studied, only the enthalpy predicted for the pyridine adduct does not agree with the measured enthalpy within the experimental error limits. The deviation of the enthalpy of formation of the pyridine adduct from the E and C relationship may be due to a steric interaction between the 2,6-pyridine protons and the tin methyl groups. If this is the case, the experimentally measured enthalpy of formation would be expected to be less than ΔH_c, as observed. The proposal that steric effects are operative in trimethyltin chloride adducts is consistent with the observation that no measurable heat of reaction is detected when 0.0025 mole of $(CH_3)_3SnCl$ is added to a 0.53 *M* 2,6-lutidine solution in CCl_4. Although similar steric effects have been intimated[18] to rationalize subtle differences between solvates of Bu_2SnCl_2 with diethoxyethane and dimethoxyethane, more quantitative studies are needed before definite conclusions can be drawn.

Table VIII

Acid	*C*	*E*
$(CH_3)_3SnCl$	0.60	6.25

Base	*C*	*E*	$-\Delta H_c$, kcal mole^{-1}	$-\Delta H_{\mathrm{obsd}}$, kcal mole^{-1}
DMSO	3.42	0.969	8.1	8.2
DMA	3.00	1.00	8.0	7.9
Pyridine	6.92	0.88	9.6	6.5
Acetone	3.22	0.61	5.7	5.7, 6.0
DMTA	9.06	0.064	5.8	5.9
$CH_3C{\equiv}N$	1.77	0.533	4.4	4.8

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