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The Solution Chemistry of Organotin Compounds. III. A Thermodynamic Study of the Molecular Interaction of Me_2SnCl_2 with Lewis Bases by Means of Nuclear Magnetic Resonance Spectroscopy

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Molecular interaction of Me_2SnCl_2 with Lewis bases has been investigated by measuring the concentration and temperature dependence of NMR coupling constant $^2J(^{119}Sn,H)$. It is found that 1:1 and 1(acid):2(base) complexes are formed concurrently in solution. Association constants and coupling constants in these complexes are determined at different temperatures, leading to the enthalpies ΔH° and entropies ΔS° for the relevant molecular interaction. The coupling constants are temperature independent and a merit of using this constant as a diagnostic tool has been proven. The E and C parameter treatment of ΔH°_{AB} has given reasonable E_A and C_A values for Me_2SnCl_2. Entropies ΔS° are also estimated in gas phase on the basis of molecular theory for the third-law entropy, and the contribution from solvation is shown important in the solution of $CHCl_2CHCl_2$.

Thermodynamic parameters are essential for the discussion of molecular interactions, being independent on the method of investigation and measuring conditions such as concentration and temperature unless there is a special reason to the contrary. Under this idea much effort has been devoted to determine these parameters as accurately as possible, and quite a lot of data have been collected for different interacting systems.[1] Hitherto, several useful equations have been established empirically from these data, especially from the enthalpies. That is, the E and C parameter treatment has been proposed by Drago[2] stating that $-\Delta H^\circ_{AB}=E_AE_B+C_AC_B$, while Gutman[3] proposed the donor number which is equal to $-\Delta H^\circ$ for the complex formation of bases with $SbCl_5$ in CH_2ClCH_2Cl. Such studies are important not only for the understanding of solution-chemical behavior of each compound treated but also for that of the nature of molecular interactions generally.

In this series of our study, organotin compounds which are of wide industrial and agricultural use are taken up as a model compound, and the molecular interaction is studied from the stand point of solution equilibria and thermodynamics. The authors have investigated the substituent effect in the complex formation of $MeSnCl_3$ with substituted pyridines, and derived and discussed the thermodynamic parameters in relation to the position of substituent in the Me_2SnCl_2 plus picoline systems.[4,5] In the present study acidic character of Me_2SnCl_2 is examined on the complex formation with typical Lewis bases, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), and γ-picoline *N*-oxide (PINO).[6] NMR coupling constant $^2J(^{119}Sn, H)$ is measured in an inert solvent $CHCl_2CHCl_2$, and enthalpies and entropies of the molecular interaction are determined from variable temperature experiments. The results are discussed in relation to the empirical treatment of the enthalpies and to the molecular theory of the third-law entropies.

Experimental

NMR coupling constant was measured with a Hitachi R-22 NMR spectrometer at 90 MHz. Variable temperature experiments were carried out in the conventional way. The sample temperature was measured by a copper-constantan thermocouple immersed in the solvent in a separate sample tube. Temperature variation was less than ±0.3 °C during the measurement of all samples at a given temperature. ^{119}Sn satellite position was measured by a YHP5315A frequency counter within an error of 0.05 Hz under internal mode of NMR lock.

All distillations and sample handling were done in dry boxes in order to prevent moisture contamination. $CHCl_2CHCl_2$ and DMSO were dried over CaH_2, and DMF, HMPA, and PINO were over BaO, and then they were distilled under reduced pressure after decantation. Me_2SnCl_2 (Tokyo Kasei Co.) was sublimed at about 60 °C. In the Job experiment, total concentration of acid and base was held constant at about 0.15 mol dm^{-3} and the molar ratio was varied. In the concentration and temperature dependence study, molarity of Me_2SnCl_2 was held constant at a value as low as possible, *ca.* 0.025 mol dm^{-3}.

Calculations were done on a NEAC S-900 and S-1000 computers at the Computer Center in Osaka University. The program CONDEP[5,7] was used for the equilibrium analysis. Linear equations were solved by a least squares method to obtain E_A and C_A parameters of Me_2SnCl_2, making use of a Library Program TLELSD transferred from the Computer Center in Tohoku University. ΔH° and ΔS° were obtained by a linear regression analysis of van't Hoff plot, together with their error limits.

Results

Stoichiometry of the complexes formed in solution was first tested by the Job plot. An example is shown in Fig. 1 for the PINO system typically. The curve reaches its maximum at a molar ratio larger than 0.5 and contribution of an 1(acid):2(base) complex is suggested besides the 1:1 complex. In the other systems the plots show maximum at the molar ratio 0.5, and only the 1:1 is supported from this experiment. The NMR parameter $^2J(^{119}Sn, H)$ reflects well the order and degree of coordination around Sn atom and is less subject to the other subsidiary solvent effect. An example of the concentration and temperature dependence is shown in Fig. 2 for the system of DMSO. In the Me_2SnCl_2 plus DMSO system, concentration dependence of $^2J(^{119}Sn,$

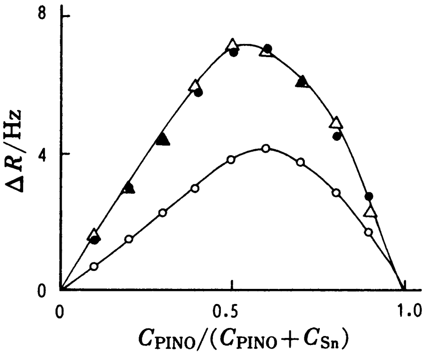

Fig. 1. Job plots for the system of Me_2SnCl_2 plus PINO at 34.1 °C. In the abscissa plotted are the molar ratio times variation in the NMR parameter, *e.g.*, $R_{acid}\cdot\Delta J$ for $^2J(^{119}Sn,H)$ where $\Delta J = J_{obsd} - J_{free}$. $\delta_H(SnCH_3)$ decreases on addition of the base and $R_{acid}\cdot(-\Delta\delta)$ is plotted.
R_{acid}=molar ratio of the acid. NMR parameters observed are: ●; $^2J(^{119}Sn,H)$, ○; $\delta_H(SnCH_3)$, △; $\delta_H(PINO,CH_3)$.
Total molarity of the acid and base is 0.18 mol dm^{-3} in $CHCl_2CHCl_2$.

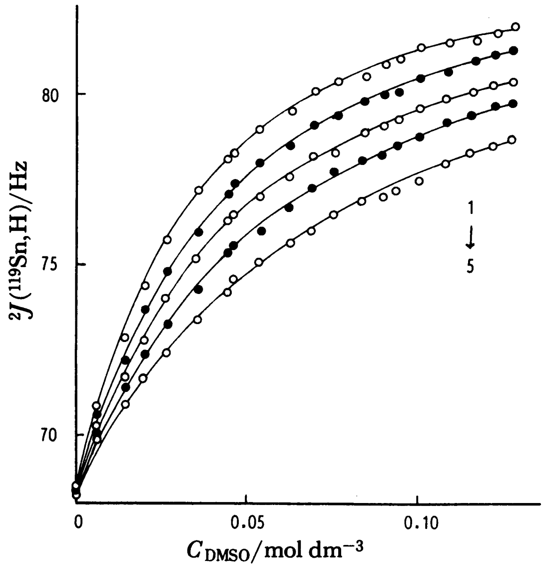

Fig. 2. Concentration and temperature dependence of $^2J(^{119}Sn,H)$ in the Me_2SnCl_2 plus DMSO system in $CHCl_2CHCl_2$.
Molarity of Me_2SnCl_2=0.025 mol dm^{-3}. Measurement temperatures are 34.1, 43.3, 51.4, 59.4, and 68.7 °C for curves 1 to 5.

H) is reproduced well within the experimental error by assuming only the 1:1 complex. This fact, together with the result of Job plot, indicates negligible contribution from 1:2 complex in solution treated here. In Table 1 analysis of the concentration dependence assuming only the 1:1 complex is compared with that assuming both 1:1 and 1:2 complexes. Standard deviation σ between the observed and the simulated coupling constants decreases only very slightly even if 1:2 complex is incorporated and one more adjustable parameter K_2 is introduced. K_2 is, if incorporated, very small and its temperature dependence is scattered, indicating negligible contribution of the 1:2 complex. Calculations are also compared for the 1:1 complex formation in Table 1 using the total and the lower half of the concentration range of DMSO. The parameters are almost unchanged in these two calculations, supporting the model assumed. The results from the lower half of the concentration range are adopted below, because ten data points are usually sufficient for the simulation of two parameters, K_1 and J_{AB}, and because contribution of the 1:2 complex becomes much smaller with lowering the concentration of DMSO if it presents at all. Calculation of this DMSO system is summarized in Table 2. The error in each parameter is an estimation from the program or reproducibility in repeated experiments whichever is larger. When dissolved in neat DMSO, Me_2SnCl_2 is expected to form the 1:2 complex predominantly as evidenced by the *J* value of 112.4 Hz which is much larger than those of the free tin compound (68 Hz) and of the 1:1 complex (84 Hz). However, experiments with higher concentration of DMSO complex in $CHCl_2CHCl_2$ were prevented by the insufficient solubility.

Table 1. Analysis of concentration dependence of $^2J(^{119}Sn,H)$ in the system of Me_2SnCl_2 plus DMSO in $CHCl_2CHCl_2$ at 34 °C

	Model	K/dm^3 mol^{-1}	J_{AB}/Hz	σ/Hz
I$^{a)}$	A+B=AB AB+B=AB_2	K_1=64±2 K_2=0.14±0.02	83.5±0.1	0.083
II	A+B=AB	58.5±1.8	84.0±0.1	0.089
III$^{b)}$	A+B=AB	64.9±1.8	83.6±0.1	0.087

a) J_{AB_2} is set to 112.4 Hz. b) Lower half of the concentration range of DMSO is used for calculation.

Method of analysis of the Me_2SnCl_2 plus DMF system is similar to that of the DMSO system. When 1:2 complex was taken into account, K_2 value estimated was very small, sometimes even negative at higher temperatures. Therefore, only 1:1 complex is assumed. Calculation is also summarized in Table 2. It is worth noting that J_{AB} calculated is constant throughout the temperature range studied in common with above DMSO system. It is usual that chemical shift of complex exhibits quite large temperature dependence: this value needs be determined at each temperature and is not easily compared when derived at different temperatures or by different investigators. The temperature independency found in this study for the coupling constant indicates an intrinsic merit of using this constant as an observable.

Although 1:2 complex is not suggested from the Job plot in the Me_2SnCl_2 plus HMPA system, its formation is inevitable for the interpretation of the concentration dependence. Systematic errors appear between the observed and the recalculated *J* values, varying systematically with the concentration of HMPA. These errors are improved satisfactorily by incorporating the 1:2 complex, and the K_2 values change consistently

TABLE 2. ANALYSIS OF CONCENTRATION AND TEMPERATURE DEPENDENCE OF $^2J(^{119}Sn,H)$ FOR THE Me_2SnCl_2 PLUS BASE SYSTEMS IN $CHCl_2CHCl_2$

Base	t/°C	K_1/dm^3 mol^{-1}	K_2/dm^3 mol^{-1}	$J_{AB}$$^{a)}$/Hz	σ/Hz
DMF	34.1	30.9±1.5		83.7±0.2	0.17
	45.2	21.6±0.7		83.2±0.2	0.11
	51.8	17.9±0.7		83.1±0.2	0.14
	60.8	11.3±0.5		83.8±0.3	0.17
	69.5	10.1±0.3		82.4±0.2	0.10
DMSO	34.1	64.9±1.8		83.6±0.1	0.09
	43.3	50.5±1.7		83.1±0.2	0.11
	51.4	34.7±1.1		83.5±0.2	0.11
	59.4	27.3±0.9		83.1±0.2	0.11
	68.7	20.4±0.7		82.8±0.2	0.11
HMPA	34.1	2450±188	0.64±0.03	86.7±0.1	0.11
	43.1	1590±58	0.53±0.02	86.8±0.1	0.10
	53.1	1058±123	0.40±0.01	86.8±0.1	0.08
	61.0	762±2	0.23±0.01	87.0±0.1	0.07
PINO	34.1	1526±700	11.5±0.4	82.4±0.2	0.17
	43.2	503±77	7.3±0.3	83.5±0.2	0.14
	51.3	501±124	5.6±0.3	83.2±0.3	0.22
	59.8	287±41	3.7±0.3	83.9±0.2	0.20
	69.5	168±13	2.1±0.2	84.5±0.2	0.16

a) J_{AB2} is set equal to the J value in neat base: 104.5(DMF), 112.4(DMSO), 121.6(HMPA), and 106.2(PINO) Hz.

with the measurement temperature. The 4-parameter calculation including J_{AB_2} in adjustable parameters, however, proved unreliable because reproducibility of the two parameters K_2 and J_{AB_2} breaks down on repeated experiments. A small amount of 1:2 complex formed in solution seems responsible for this difficulty. This resembles to the Me_2SnCl_2 plus pyridine system,[7] but differs from the case in reference[4] where four parameters are simulated successfully in calculation. For this reason, calculation was done with the three adjustable parameters, fixing J_{AB_2} at a value in neat base.

It is clear from the Job plot that 1:2 complex is formed in solution for the Me_2SnCl_2 plus PINO system (Fig. 1). The 4-parameter calculation including J_{AB_2} was tested, but it gave rather scattered value of J_{AB_2}(104.6—108.3 Hz) at different temperatures and the van't Hoff plot of K_1 and K_2 deviated much from a linear line. Therefore, 3-parameter calculation was adopted for this case.

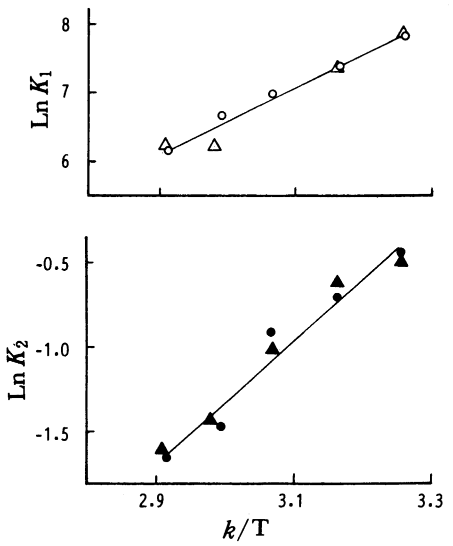

Fig. 3. van't Hoff plots for the Me_2SnCl_2 plus HMPA system from duplicate experiments. ○ and ●; run 1. △ and △; run 2.

TABLE 3. ENTHALPIES AND ENTROPIES FOR THE COMPLEX FORMATION OF Me_2SnCl_2 WITH BASES IN $CHCl_2CHCl_2$

Base	$-\Delta H^\circ_{AB}$	$-\Delta S^\circ_{AB}$	$-\Delta H^\circ_{AB_2}$$^{a)}$	$-\Delta S^\circ_{AB_2}$$^{a)}$
	kJ mol^{-1}	J K^{-1}mol^{-1}	kJ mol^{-1}	J K^{-1}mol^{-1}
DMF	30.5±1.5	70.4±4.3		
DMSO	31.8±2.6	69.3±8.1		
HMPA	40.8±1.7	67.8±5.2	70.2±3.2	166.9±9.7
PINO	45.3±5.2	87.7±15.8	85.0±6.9	195.8±20.9

a) $\Delta H^\circ_{AB_2}$ and $\Delta S^\circ_{AB_2}$ for the complex formation of AB_2 from A and 2B.

Discussion

Thermodynamic parameters of the complex formation are derived from van't Hoff plot of K_1 and K_2 obtained above (Fig. 3 and Table 3). Enthalpy-entropy compensation relation holds approximately (Fig. 4). A linear relation is also seen between ΔH°_{AB} and ΔJ_{AB} except for PINO (Fig. 5), as is often observed in a similar case.[8] This line will go through the origin in the Figure because ΔH° should be zero when $\Delta J=0$. NMR coupling constants are usually interrelated with the s-character of chemical bonds. Under this concept the break down of the ΔH—ΔJ proportionality for PINO will be interpreted as due to the different type of the complex suggested from IR study.[9] The E and C parameter treatment of ΔH°_{AB} proposed by Drago and Wayland[2] gives values of $E_A=13.30$ and $C_A=5.48$ for Me_2SnCl_2 with the $r.m.s.$ deviation of 1.0 kJ mol^{-1}. These values are comparable to those for Me_3Al(E_A=12.9, C_A=1.43) and for Me_3Ga(E_A=13.3, C_A=0.881), but definitely larger than those for Me_3SnCl(E_A=5.76, C_A=

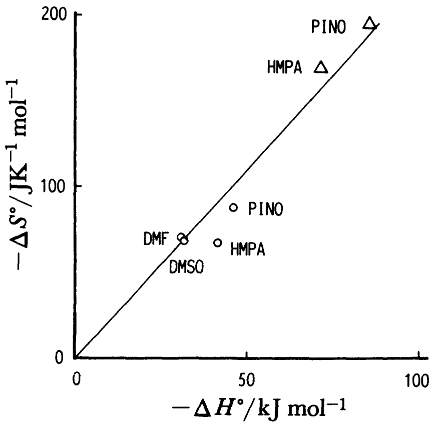

Fig. 4. Plots for enthalpy-entropy compensation relation.
O denotes data point for 1:1 complex and Δ that for 1:2 complex.

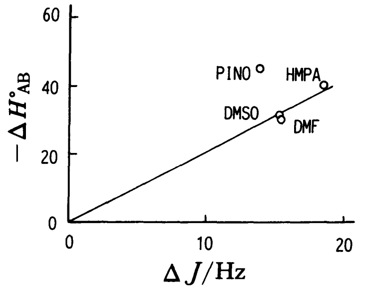

Fig. 5. Plots of ΔH-ΔJ proportionality relation for the 1:1 complex formation. $\Delta J = J_{AB} - J_A$, $J_A = 68.3$ Hz for the free acid molecule.

0.0296[2] or $E_A=6.25$, $C_A=0.60$[10]), indicating enhanced acidity of Me_2SnCl_2.

On the contrary to enthalpies, entropy data have been overlooked frequently in the discussion of thermodynamic aspects of interacting systems. However, important informations are included in entropies, especially concerning the molecular (internal) motions and solvation of molecules. The entropy change on complex formation of A+B=AB can be equalized to the difference in the thermodynamic third-law entropies of the components, *i.e.*, $\Delta S^\circ_{AB,calcd} = S^\circ_{AB} - (S^\circ_A + S^\circ_B)$, the latters being calculated from molecular theory of thermodynamic functions.[11] This $\Delta S^\circ_{AB,calcd}$ is considered to correspond to the gas-phase value of ΔS°. Experimental entropies are compared with thus calculated ones in Table 4 where translational and rotational parts of entropy are used for calculation and the vibrational one is not included considering almost similar contributions from the starting compounds and the product.

The observed entropies are seen to be about 1/3 of the expected (calculated) values. Where does such a discrepancy come from? Some new chemical bonds are formed on complex formation, but contributions to the vibrational entropy from such bonds are very small (in the order of a few $\mathrm{JK^{-1}\,mol^{-1}}$). Some internal motion will become restricted on complex formation, but such contribution is also small. In contrast, solvation by $CHCl_2CHCl_2$ is expected nontrivial. Its protons are known to have an acidic character, forming weak hydrogen bonding with base, and also it possesses polarity to solvate by means of electrostatic attraction. If, as a model calculation, $CHCl_2CHCl_2$ is assumed to solvate to a base molecule and the reaction proceeds in such a way as $A+BS \rightarrow AB+S$, $\Delta S^\circ_{AB,calcd}$ is reduced in great deal in absolute value and $-16\ \mathrm{JK^{-1}\,mol^{-1}}$ is obtained for the DMSO system. That is, the experimental value may be said correspond to the solvation number of 0.7. Similar number of 0.6—0.7 are reached for other systems studied here. Such calculation is only a model calculation, but it may be said soundly that the solvation as above contribute more (twice, roughly) to the entropy changes in $CHCl_2CHCl_2$ than the net entropy change in gas phase. It is well known that entropy changes in aqueous solutions become positive for ionic reactions such as protonation of bases, metal complex formation, or ion-pair formation, because of the release of water molecules on reaction. In the present case solvation does not take such a drastic role and the entropies remain negative, although the solvation takes a major part of the entropies observed.

TABLE 4. COMPARISON OF THE CALCULATED ENTROPIES (IN GAS PHASE) WITH THE EXPERIMENTAL ONES (IN SOLUTION)[a]

	Reaction: A+B=AB		$AB+B=AB_2$	
Base	$-\Delta S^\circ_{calcd}$	$-\Delta S^\circ_{obsd}$	$-\Delta S^\circ_{calcd}$	$-\Delta S^\circ_{obsd}$
DMF	238	70.4		
DMSO	242	69.3		
HMPA	257	67.8	283	99.1
PINO	244	87.7	324	108.1

a) In units of $\mathrm{J\,K^{-1}\,mol^{-1}}$.

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