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The Solution Chemistry of Organotin Compounds. Part 2.[1] Equilibrium and Thermodynamic Studies of Complex Formation between Dimethyltin Dichloride and Picolines

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The donor–acceptor complexes formed between Me_2SnCl_2 and 2-, 3-, and 4-picolines have been investigated by analysing the concentration and temperature dependence of ^1H, ^{13}C, and ^{119}Sn n.m.r. parameters. Detailed explanations of the data are based on the chemical equilibria which occur. It is concluded that two types of complex, 1 : 1 and 1 : 2 Me_2SnCl_2–picoline, coexist in solution. The equilibrium constants (K_1 and K_2) and the complex formation shifts (Δ_{AB} and Δ_{AB2}) were determined at several temperatures, and the thermodynamic parameters ($\Delta H°_{AB}$, $\Delta H°_{AB2}$, $\Delta S°_{AB}$, and $\Delta S°_{AB2}$) derived. Entropy terms are shown to be responsible for the small free energy change in case of 2-picoline. Enthalpy terms are discussed in relation to the basicity of picolines. Me_2SnCl_2 was found to be partly hydrolysed by moisture producing 1,3-dichloro-1,1,3,3-tetramethyldistannoxane, and all sample preparations were done in dry boxes to prevent this. ^1H and ^{119}Sn n.m.r. data of this distannoxane are also assigned.

Recently, complex formation between organotin compounds and Lewis bases has been investigated to help understand the effect of solvents on the kinetics and mechanism of the reaction of these compounds.[2] Complex formation of this sort plays an important role in the optical instability of chiral organotin compounds.[3] In earlier papers,[1,4] we reported a method of analysis of complicated equilibria in solution, and applied it to a few organotin compounds to elucidate the features of the solution chemistry of tin compounds. As a result of those studies, a 1 : 1 complex was shown to exist in solution for Me_2SnCl_2–pyridine and $MeSnCl_3$–4-substituted pyridines, and n.m.r. parameters were measured for these complexes.

In this report, an equilibrium study as above is applied to the system of Me_2SnCl_2–2-, 3-, and 4-picolines, and thermodynamic parameters are derived from variable temperature experiments. These results are discussed in relation to the position of methyl substitution on the pyridine ring.

Experimental

All distillations and sample handling were done in dry boxes. Me_2SnCl_2 was sublimed under reduced pressure. Picolines were distilled over BaO. Nitrobenzene was dried over BaO and distilled under reduced pressure.

^1H N.m.r. spectra were observed with a Hitachi R-22 spectrometer at 90 MHz. Variable temperature experiments were carried out in the conventional way. The sample temperature (± 0.30) was calibrated by a thermocouple immersed in nitrobenzene in the sample tube. Chemical shifts (± 0.1 Hz) were measured relative to Me_4Si by means of a YHP5315A frequency counter. ^1H-{^{119}Sn} INDOR experiments were carried out on a Hitachi R-20B n.m.r. spectrometer (60 MHz) equipped with a Anritsu MG514C synthesizer and a radio frequency amplifier. The hydrolysis of Me_2SnCl_2 in nitrobenzene was examined by a Hitachi R-900M Fourier transform n.m.r. spectrometer (90 MHz), employing a pulse sequence for solvent peak suppression, *i.e.* a $(\pi\text{–}5\ s\text{–}\pi/2\text{–}20\ s)_n$ sequence. In this manner the solvent peaks were reduced to *ca.* 1/20 of the normal mode.

Nitrobenzene was used as solvent. When this was replaced by $CHCl_2CHCl_2$, the reproducibility of the value of δ_H (CH_3, base) greatly diminished for samples containing a large excess of Me_2SnCl_2. Dehydrochlorination[5] of $CHCl_2CHCl_2$ must be responsible for this disturbance, which is induced by base in the presence of Me_2SnCl_2.

1,3-Dichloro-1,1,3,3-tetramethyldistannoxane was synthesized as for the butyl analogue[6] (yield >90%), where Me_2SnO was obtained from the hydrolysis of Me_2SnCl_2 with ammonia[7] and thoroughly dried before use.

Calculations were done on a NEAC S-900 computer at the Computation Center in Osaka University. SCD and CONDEP programs[1,4] were used for the equilibrium analysis.

Results and Discussion

Me_2SnCl_2 is known to form a 1 : 2 donor–acceptor complex with picoline, as evidenced by the isolation of the complex from solution.[8] However, it is probable that the 1 : 1 complex coexists in solution. To confirm this we first made up Job plots which are given in Supplementary Publication No. SUP 23427 (14 pp).† The results are explained if the 1 : 1 and 1 : 2 complexes are formed concurrently in solution, each being revealed by the n.m.r. parameters subject to large changes on going from the free molecule to the 1 : 1 complex or from the 1 : 1 to the 1 : 2 complex.

Changes in the N.m.r. Parameters on Complex Formation.— In the Job experiments almost all the ^{13}C shifts changed to the low-field side on addition of Me_2SnCl_2 in the case of picoline, and to the high field side on addition of picoline in the case of Me_2SnCl_2. Therefore, the ^{13}C shifts are concluded to reflect electron donation from the base to the tin atom.‡ The ^1H shift of Me_2SnCl_2 changed inversely with the donation of electrons, and an effect such as magnetic anisotropy of the pyridine ring is suggested. The ^{119}Sn shift changed qualitatively in accord with the electron donation, but the change was drastic, *i.e.*, *ca.* 10 000 Hz compared with *ca.* 40 Hz in ^2J (^{119}Sn, H) and *ca.* 10 Hz in δ_H ($SnCH_3$) in the same system. This is thought to be related to the variation in the co-ordination number of the tin atom.

Although the ^{119}Sn shift is the most suitable if judged from the standpoint of concentration dependence, the ^1H shift of the CH_3 in picoline, δ_H (CH_3, base) was used to determine the

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† For details, see Notice to Authors No. 7 in *J. Chem. Soc.*, *Perkin Trans. 2*, 1981, Index Issue.

‡ The shift of the 2- and 6-carbons in 4-picoline did not fulfill this expectation, as also happens in pyridine subjected to protonation.[9] Thus, these shifts may result from a lowering of the bond order in the C=N=C fragment when the complex is formed or protonation occurs.

Table 1. Equilibrium constants (K), complex formation shifts (Δ), and thermodynamic parameters for the Me_2SnCl_2–picoline systems in nitrobenzene [a]

	$\frac{K_1}{\text{l mol}^{-1}}$	$\frac{K_2}{\text{l mol}^{-1}}$	$\frac{\Delta_{AB}{}^{b}}{\text{Hz}}$	$\frac{\Delta_{AB2}{}^{b}}{\text{Hz}}$	$\frac{\delta_B{}^{b}}{\text{Hz}}$	$\frac{-\Delta H^\circ_{AB}}{\text{kJ mol}^{-1}}$	$\frac{-\Delta H^\circ_{AB2}}{\text{kJ mol}^{-1}}$	$\frac{-\Delta S^\circ_{AB}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\Delta S^\circ_{AB2}}{\text{J K}^{-1}\text{ mol}^{-1}}$
2-Picoline	6.4	4.8	38.0	88.8	225.4	52	28	152	75
3-Picoline	18.6	14.1	16.7	28.6	202.3	14	14	23	18
4-Picoline	22.0	17.9	25.9	29.8	203.1	17	14	21	16
4-Picoline						60 [c]	18 [c]	167 [c]	34 [c]

[a] K and Δ are taken at 34.1 °C. [b] $\Delta_{AB} = \delta_{AB} - \delta_B$, $\Delta_{AB2} = \delta_{AB2} - \delta_B$, where δ_B is the shift of the free base. [c] In benzene as solvent.[10]

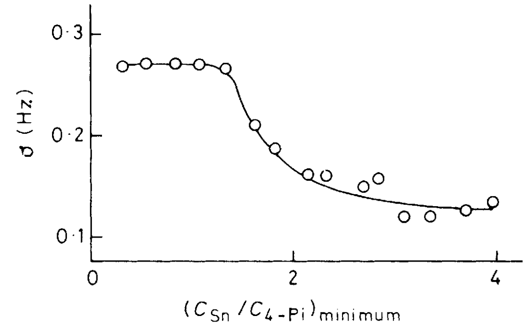

Figure 1. Simulation of the concentration dependence of the Me_2SnCl_2–4-picoline system for the equilibrium $A + B = AB$. $(C_{Sn}/C_{Pi})_{\text{minimum}}$ indicates the minimum molar ratio used in the simulation. σ is the standard deviation between the observed and calculated shifts

equilibrium constant (K) because of its high sensitivity. The concentration dependence of this shift amounted to *ca.* 30 Hz which is adequate to determine K.* The equilibrium constant and the complex formation shift were determined from detailed experiments employing the so-called molar ratio method, where the molarity of the observed component was kept constant and as low as possible, and the unfavourable concentration dependence of the n.m.r. parameters inherent in the free and complexed species was made negligibly small.

Analysis of the Concentration Dependence of the Equilibrium $A + B \rightleftharpoons AB$.—The concentration dependence of δ_H (CH_3, base) was obtained keeping the molarity of picoline constant at *ca.* 0.02M and varying that of Me_2SnCl_2 from 0 to 0.1M. In a preliminary examination, Ketelaar plots were tested; these apply to the formation of the 1 : 1 complex. These plots are also included in SUP 23427. The Ketelaar plots were found to deviate from a linear relation upon decreasing the concentration of Me_2SnCl_2, and interference from equlibria other than the $A + B = AB$ was suggested in the lower concentration range of Me_2SnCl_2.

A similar result was reached by computer calculations freed from any restrictions in the experimental conditions. When the standard deviation (σ) between the observed and calculated shift was plotted for equilibrium (1) while gradually increasing the minimum concentration of calculation from the experimental minimum of C_{Sn}/C_{Pi}, there was found to be a minimum value of the ratio (*ca.* 2) above which σ diminished satisfactorily (Figure 1). This fact also supports some additional equilibrium in the lower concentration range of Me_2SnCl_2. Therefore, parameters for the complex formation according to equilibrium (1) will be obtained from the higher concentration range of Me_2SnCl_2.

$$A + B \overset{K_1}{\rightleftharpoons} AB \qquad (1)$$

Analysis of the Concentration Dependence of the Equilibria $A + B \rightleftharpoons AB$ *and* $AB + B \rightleftharpoons AB_2$.—As mentioned above, a 1 : 2 complex of Me_2SnCl_2-picoline formed as in equilibrium (2) should be taken into account to interpret the concentration dependence. For this purpose, K_1, K_2, Δ_{AB}, and Δ_{AB2} need be determined, Δ being the complex formation shift, *i.e.*, $\Delta_{AB} = \delta_{AB} - \delta_B$, and $\Delta_{AB2} = \delta_{AB2} - \delta_B$. Since K_1 and Δ_{AB} are derived as shown above, these values were fixed for simulation of the whole concentration range and a two-parameter simulation was made for K_2 and Δ_{AB2}. Final values thus obtained were almost unchanged if Δ_{AB} only was fixed at the value derived above and a three-parameter treatment was carried out. Therefore, a two-parameter treatment for K_2 and Δ_{AB2} is accepted as reliable. The reproducibility of K and Δ was checked by repeated runs; errors were within ±5% in K_1, ±10% in K_2, ±0.4 Hz in Δ_{AB}, and ±1 Hz in Δ_{AB2}. The K and Δ values are summarized in Table 1. In the case of $MeSnCl_3$–4-substituted pyridines, the four parameters, which are estimated at first by a three-parameter simulation, were finally refined by varying all the parameters one at a time.[1] However, such a four-parameter simulation was often unsatisfactory in the present case. The final value of Δ_{AB} became too large compared with that of the calculation for equilibrium (1) and with that expected from the shift values for large excesses of Me_2SnCl_2, and K_2 became larger than K_1. The distribution curve for the picoline molecule showed that the percentage of AB_2 is very small compared to that of B and AB. This small percentage is responsible for the relatively large errors in K_2 and Δ_{AB_2} and also for the failure of the four-parameter simulation. The distribution curves are included in SUP 23427 for 2- and 4-picolines.

$$AB + B \overset{K_2}{\rightleftharpoons} AB_2\text{, equlibrium constant} = K_2 \quad (2)$$

Thermodynamic Parameters.—Thermodynamic parameters are useful for understanding the relative stability of complexes formed in solution. The equilibrium constants were determined at several temperatures by analysing the concentration and temperature dependences of the shift such as those shown in Figure 2. van't Hoff plots of these constants lead to the thermodynamic parameters in Table 1. Farhangi and Graddon [10] obtained the parameters in Table 1 from an analysis of calorimetric titration data in benzene by a trial and error method. The enthalpy and entropy changes they derived are larger (absolute values) than those obtained here, especially

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* $\delta_H(SnCH_3)$ exhibited only 1/5 of the concentration dependence of δ_H(CH_3, base) when compared by adding excess amounts of the partner molecule. Hence, $\delta_H(SnCH_3)$ is not suited for our purpose.

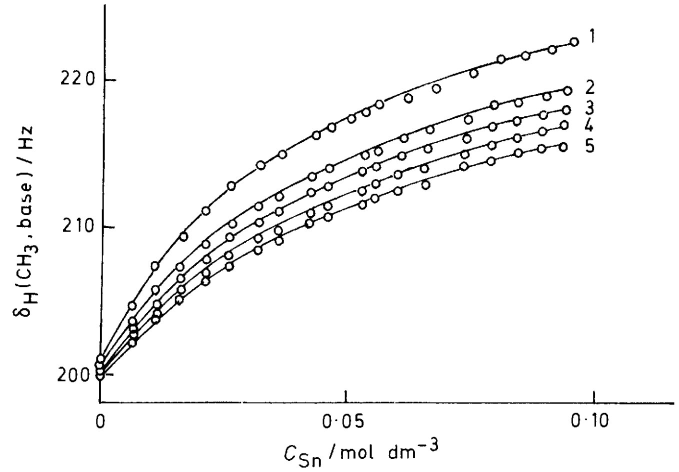


Figure 2. Concentration and temperature dependence of $\delta_H(CH_3$, base) for the Me_2SnCl_2–4-picoline system in nitrobenzene: 1, 34.1 °C; 2, 45.9 °C; 3, 51.0 °C; 4, 56.8 °C; 5, 66.3 °C

for 1 : 1 complex formation. It is suggested that solvation of the free species by nitrobenzene diminished the absolute values in the present study.

The enthalpy is seen to decrease in the order 2- > 3- ⩾ 4-picoline. This is in accord with that reported for similar systems.[11,12] The result for 2,6-lutidine in ref. 12 is indicative of increased enthalpy upon methyl substitution at the *ortho*-position. Accordingly, the enthalpy term is considered to reflect an electronic effect of methyl substitution. The electron density increase calculated by the MINDO/3 method at the nitrogen atom upon methyl substitution is certainly larger for 2-picoline (0.014) than for 3- (−0.001) and 4-picoline (0.004).

The entropy change is very large for 2-picoline. This leads to the small equilibrium constant, *i.e.*, there is a small free energy change on complex formation, which undoubtedly reflects the steric hindrance of the methyl group at the *ortho*-position.

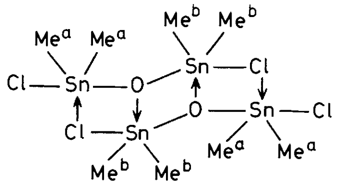
Assignment of N.m.r. Shift Data for 1,3-*Dichloro*-1,1,3,3-*tetramethyldistannoxane formed by Hydrolysis of* Me_2SnCl_2.—Me_2SnCl_2 is known to form a distannoxane $(ClMe_2SnOSnMe_2Cl)_2$ in water on adding equimolar pyridine dissolved in ethanol.[13] This distannoxane is also obtained by refluxing a solution of Me_2SnCl_2 and dimethyltin oxide in benzene,[6] and so the above reaction is thought to proceed *via* formation of Me_2SnO by hydrolysis [7] of Me_2SnCl_2. Therefore, the formation of distannoxane will become serious if the solution is contaminated with water as well as strong base. The authors suggest that this side-reaction caused the unsuccessful fitting of the calorimetric titration curves in the Me_2SnCl_2–2-picoline system in ref. 10. In the present work, all sample handling was performed in a dry box. In this manner the formation of the distannoxane was suppressed effectively to an amount below 1% if any.*

We are able to assign the distannoxane structure from the signals which appeared on addition of water to a sample prepared in a dry box. The n.m.r. data coincided with those for the distannoxane prepared according to refs. 6 and 7. No detailed assignment have been reported for this n.m.r. data.[14] However, with the aid of an INDOR experiment, the signal with the larger coupling of ^2J (^{119}Sn, H) as well as the lower field shift of δ_{Sn} is assignable to the $Sn^b(Me^b)_2$ fragment in the ladder structure (A) of the distannoxane.

Table 2. ^1H and ^{119}Sn n.m.r. parameters of 1,3-dichloro-1,1,3,3-tetramethyldistannoxane [a]

Assignment [b]	δ_H [c] (p.p.m.)	δ_{Sn} [d] (p.p.m.)	$^2J(^{119}Sn, H)$/Hz
a	1.187	−218	79.8
b	1.240	−265	84.1

[a] 0.1M in $CHCl_2CHCl_2$. [b] See text. [c] Me_4Si internal reference. [d] Me_2SnCl_2 external reference (0.2M in $CHCl_2CHCl_2$). The minus sign denotes high field shift, errors being within ±4 p.p.m.



(A)

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* 2-Picoline was most liable to produce the distannoxane of the picolines treated here. DMSO and HMPA had no effect when tested in nitrobenzene saturated with water. Therefore, the basicity in water, and not the basicity towards the tin atom, may be the dominant factor in producing the distannoxane.

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