The Solution Chemistry of Organotin Compounds. I. A ^{1}H NMR Study of the Complex Formation between Methyltin Trichloride and 4-Substituted Pyridines

Hideaki Fujiwara,* Fumihiko Sakai, Miyoko Takeyama, and Yoshio Sasaki
Faculty of Pharmaceutical Sciences, Osaka University, 133-1 Yamadakami, Suita, Osaka 565

(Received August 11, 1980)

The formation of donor-acceptor complexes between $MeSnCl_3$ and 4-substituted pyridines has been investigated by analyzing the concentration dependence of NMR parameters. The formation of 1($MeSnCl_3$):2(pyridine) and 1:1 complexes has been proved, and the equilibrium constants(K_1 and K_2) and complex formation shifts ($\varDelta_{AB}$ and $\varDelta_{AB2}$) are determined for the successive formation of these complexes. log K_1 and log K_2 are in a good linear correlation with each other, and they have a tendency parallel with that of pK_a of the pyridine derivative, suggesting a predominant contribution of σ-bonding in the donor-acceptor bond. Both $\varDelta_{AB}$ and $\varDelta_{AB2}$ indicate a high-field shift on the formation of the complex, which is consistent with the expected electron transfer in the donor-acceptor bond. However, $\varDelta_{AB}$ varies inversely to the basicity of the pyridines; the anisotropy effect of the pyridine ring is suggested as the reason for this. The results are also discussed in relation to Hammett's substituent constant.

Among a variety of organometallic compounds, organotins are particularly stable and so are widely used in industry and in pharmaceuticals. They are used, for example, as stabilizers and catalysts for synthetic polymers and such biocides as fungicides, bacteriostasis, and insecticides.[1,2] These facts have stimulated recent studies of the related compounds by means of modern physical techniques.[2,3] In these studies, the physico-chemical properties and geometries of the compounds as well as of their complexes with bases have been the main subject. However, studies from the standpoint of solution chemistry are equally inevitable for a full understanding of the nature of these substances. We are interested in the intermolecular interaction in solution and have, therefore, set about studying the equilibria and thermodynamics as well as the dynamics of the complex formation of organotin compounds.

In the present work the complex formation of methyltin trichloride ($MeSnCl_3$) with several 4-substituted pyridines is investigated by means of analyzing the concentration dependence of the NMR chemical shift, and the equilibrium constant and the complex-formation shift are determined for the 1($MeSnCl_3$):1(pyridine) and 1:2 complexes. The results are discussed in relation to the basicity of pyridines as well as to the substituent effect.

Experimental

The $MeSnCl_3$ and 4-nitropyridine were synthesized from Me_2SnCl_2[4] and 4-nitropyridine *N*-oxide[5] respectively. The other materials were from commercial sources. The $MeSnCl_3$ was purified by sublimation under reduced pressure at ≈30 °C. The NMR spectra showed an impurity of Me_2SnCl_2 of less than 1%. The pyridines were distilled over BaO under normal pressure (pyridine and 4-methylpyridine) and under reduced pressure (4-acetyl- and 4-(methoxycarbonyl)pyridines). The 4-cyanopyridine was sublimed at ≈70 °C, and the 4-nitropyridine was recrystallized several times from petroleum ether. The nitrobenzene was dried over BaO and distilled under reduced pressure. All the materials were stored in desiccators, and all operations of the above distillation and sample preparation for the NMR measurement were made in dry boxes under a relative humidity of <20%. The ^{1}H NMR spectra were observed with a Hitachi R-22 spectrometer operating at 90 MHz and 34.1 °C. The chemical shifts and coupling constants were measured by means of a frequency counter within an error of ±0.1 Hz. As an internal reference, ≈0.02 vol% Me_4Si was added to the solvent. The calculations were done on a NEAC S-900 computer at the Computation Center, Osaka University.

Results and Discussion

$MeSnCl_3$ is known to form a 1:2 donor-acceptor complex with pyridine, as evidenced by the isolation of the complex from solution.[6,7] Therefore, in interpreting the equilibrium property of these systems, it is necessary to take into account the concurrent formation of 1:1 and 1:2 complexes. Although equilibrium studies have often been reported with regard to the complex formation of methyltin halides,[6] there have been very few analyses of the simultaneous formation of 1:1 and 1:2 complexes.[8] We have made a computer program, CONDEP,[9] which minimizes the standard deviation(σ) between the observed and calculated NMR parameters—such as the chemical shift and the coupling constant—on the basis of the equilibrium of 1) A+B=AB, 2) A+2B=AB$_2$, and 3) A+B=AB and AB+B=AB$_2$. In this program the NMR parameter can be measured on the side of either A or B, and several selections of the number of adjustable parameters are made possible. The calculations below are made through the use of this program.

Composition of the Complex Formed in Solution. Job plots are shown in Fig. 1 for the $MeSnCl_3$+4-methyl-, +4-acetyl-, and +4-cyanopyridine systems. In the $MeSnCl_3$+4-methylpyridine system, the errors are relatively large in the shift measurement and ^2J(SnH) is difficult to observe because of the signal broadening. The Job plots of this system are almost the same in pattern when the solvent is changed to CH_2Cl_2 from nitrobenzene. Job plots were not obtained for the $MeSnCl_3$+pyridine system because of precipitation during the sample preparation. The Job plots of the $MeSnCl_3$+4-methoxycarbonyl- and +4-nitropyridine systems are similar to those of the $MeSnCl_3$+4-acetyl- and +4-cyanopyridine systems (Figs. 1b and 1c) re-

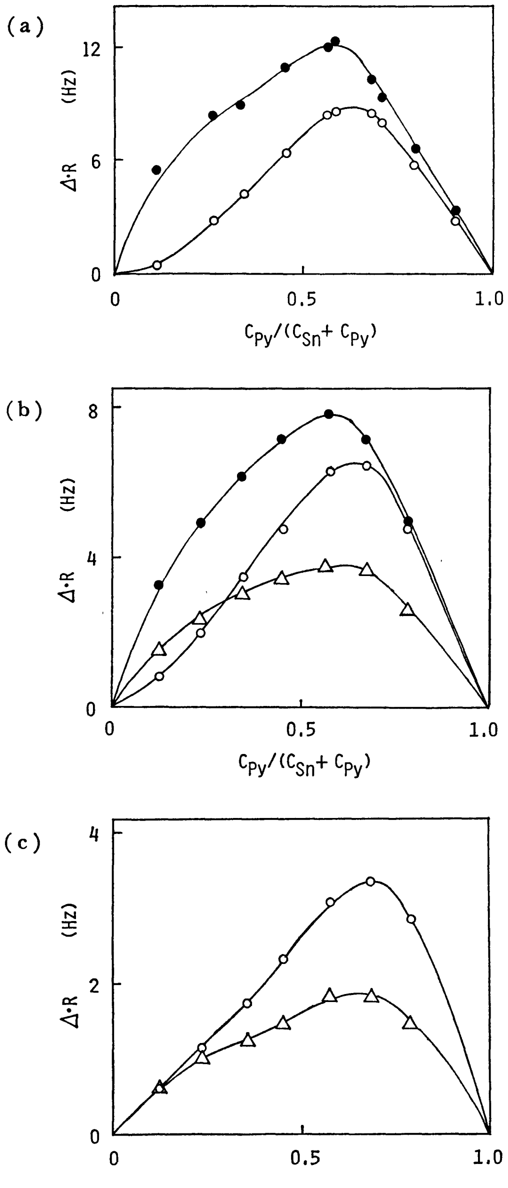

Fig. 1. Job plots for the a) $MeSnCl_3$+4-methylpyridine, b) $MeSnCl_3$+4-acetylpyridine, and c) $MeSnCl_3$+4-cyanopyridine systems.

C_{Sn} and C_{py} are molarities of $MeSnCl_3$ and the pyridines, respectively. $C_{Sn}+C_{py}\simeq 0.1$ mol dm^{-3}. Δ is equal to the variation in NMR parameters from a free state of the molecule under observation. R indicates mole fraction of the molecule under observation. $\Delta \cdot R$ is negative for δ (CH_3 in base) and $^2J(^{119}SnH)$, but absolute value is plotted. ●: Experimental point for δ_H(CH_3 in base), △: experimental point for $^2J(^{119}SnH)$, ○: experimental point for $\delta_H(SnCH_3)$.

spectively. In all these systems, the plots show a plateau between 0.6—0.7 mole fraction of the base, irrespective of the NMR parameters observed, *i.e.*, $\delta_H(SnCH_3)$, δ_H(base), and ^2J(SnH), supporting the idea of the formation of a 1:2 complex in solution as well. On the other hand, the presence of a 1:1 complex is only inferred from the mole fraction corresponding to the plateau, which is a little smaller than 0.67. This is ascertained below from the simulation of the NMR concentration dependences based on several models of the equilibrium. Hitherto, little has been reported about the 1:1 complex.

Determination of the Equilibrium Constant and Complex-formation Shift. The equilibrium constant (K) and the complex-formation shift (Δ), the latter being equal to the variation in chemical shift when complex formation occurs, can be obtained from the simulation of the concentration dependence in the NMR shifts. For this purpose, the concentration of $MeSnCl_3$ is held constant at an appreciably low molarity ($\approx$0.005 M), while that of the base is varied. In this manner, the concentration dependence of δ ($SnCH_3$) is obtained as depicted in Fig. 2. This is analysed on the basis of the equilibrium of 1) $A+2B=AB_2$ and 2) $A+B=AB$ and $AB+B=AB_2$, considering the results of the above Job plots, which strongly support the 1:2 complex. The calculation based on the $A+2B=AB_2$ is shown in Table 1. In this table, the σ

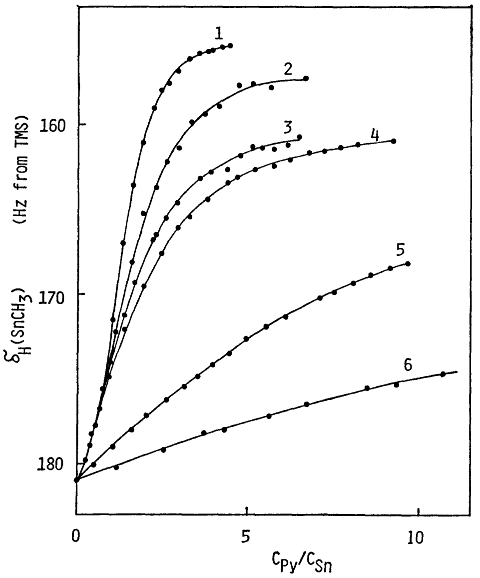

Fig. 2. Concentration dependence of $\delta_H(SnCH_3)$ in the systems of $MeSnCl_3$+4-substituted pyridines. Substituent: 1; CH_3, 2; H, 3; $COCH_3$, 4; $COOCH_3$, 5; CN, 6; NO_2. C_{Sn} is held constant at $\approx$0.005 mol dm^{-3}.

Table 1. Simulation of the NMR concentration dependence according to the equilibrium of $A+2B=AB_2$

4-Substituent in pyridine	log K[a]	Δ_{AB}[b]	σ[c]
CH_3	5.42	26.1	1.05
H	5.16	23.8	0.49
$COCH_3$	5.22	19.4	0.44
$COOCH_3$	4.74	20.0	0.54
CN	3.63	14.2	0.49
NO_2	2.85	11.4	0.54

a) Equilibrium constants, K, in a unit of (dm^3 mol^{-1})^2. b) In a unit of Hz. c) σ = standard deviation between the shifts of observation and calculation(Hz).

TABLE 2. SIMULATION OF THE NMR CONCENTRATION DEPENDENCE ACCORDING TO THE EQUILIBRIUM OF $A+B=AB$ AND $AB+B=AB_2$

4-Substituent in pyridine	$\log K_1$[a)]	$\log K_2$[a)]	Δ_{AB}[b)]	Δ_{AB_2}[b)]	σ[c)]
CH_3	4.07 ± 0.63	3.15 ± 0.11	-6.3 ± 1.2	-26.4 ± 0.5	0.46
H	3.66 ± 0.92	2.79 ± 0.17	-5.8 ± 0.8	-25.3 ± 0.4	0.31
$COCH_3$	3.43 ± 0.34	2.36 ± 0.03	-6.9 ± 0.4	-22.3 ± 0.3	0.19
$COOCH_3$	2.61 ± 0.04	2.35 ± 0.06	-9.2 ± 1.0	-21.7 ± 0.3	0.09
CN	1.51 ± 0.01	1.31 ± 0.01	-13.9 ± 0.2	-22.0 ± 0.3	0.08
NO_2	1.03 ± 0.01	0.83 ± 0.03	-14.8 ± 0.3	-17.4 ± 0.5	0.11

a) K_1 and K_2 in a unit of $dm^3\,mol^{-1}$. b) In a unit of Hz. c) See footnote c) in Table 1.

amounts to 0.4—1.1 Hz. Furthermore, the deviation between the observed and calculated shifts is found to change systematically with the molarity of the base. These facts indicate the inadequacy of the model adopted. When the equilibrium of $A+B=AB(K_1)$ and $AB+B=AB_2(K_2)$ is assumed, four parameters have to be taken into account, *i.e.*, K_1, K_2, δ_{AB}, and δ_{AB_2}, the latter two being identified as the $\delta_H(SnCH_3)$ in the AB and AB_2 species respectively. Under these conditions, it proved necessary to obtain a rough estimate of the four parameters for the simultaneous determination of these parameters in the simulation. That is, the same final values were not always reached if the corresponding initial values were considerably changed. This is not the case in the above two-parameter calculation; it can be interpreted by saying that a small variation in one parameter is compensated for by that in others, with the σ almost unchanged, if the number of adjustable parameters is increased.[10)] When the concentration of the base was increased further in Fig. 2, $\delta_H(SnCH_3)$ was found to level off. This ultimate value of $\delta_H(SnCH_3)$ should correspond to δ_{AB_2}, and so a three-parameter calculation becomes feasible, eliminating δ_{AB_2} from the variables. The values of the 4 parameters thus estimated are next used as the initial ones in the four-parameter calculation. Thus, a final set of all the parameters is obtained (Table 2). Errors are also estimated in the CONDEP program for each parameter as equal to the 95% confidence range, which makes the σ^2 larger by 1.96 times when a parameter under consideration is varied, whereas the others are held constant. The average of such errors was usually a little larger than the reproducibility of each parameter in several repeated experiments; it is also depicted in Table 2. The relatively large σ's in the $MeSnCl_3$+4-methylpyridine and +pyridine systems are due to signal broadening. The relatively large errors in $\log K_1$ are caused by the experimental concentration conditions; that is, our experimental concentrations were rather suitable for the precise determination of small values of K_1 and K_2, but they were too high for the large value of K_1 to be determined more accurately.

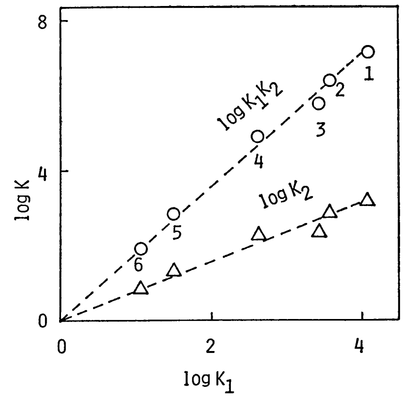

Fig. 3. Plots of log K_1K_2 and log K_2 against log K_1. The numbering corresponds to that in Fig. 2.

Equilibrium Constant. A linear correlation is observable between the stability constants of the 1:1 and 1:2 complexes (Fig. 3). A least-squares fit by means of the $y=ax$ equation proves the satisfactory linearity between them:

$$\log K_1K_2 = 1.78 \log K_1, \quad \sigma = 0.20. \qquad (1)$$

This equation also implies a linear relation between $\log K_1$ and $\log K_2$, a least-squares fit leading to $\log K_2=0.78 \log K_1$, and $\sigma=0.20$. These equations are reflections of the colinearity in the free-energy changes in the formation of 1:1 and 1:2 complexes; the latter equation also means that the absolute value of the free-energy change in the second step is decreased to *ca.* 3/4 of that in the first step. Such a simple relation may be understood as indicative of the absence of a particular derivative in the pyridines treated here, which exerts a specific steric effect or which behaves differently in the complex formation.

It may be seen from Fig. 4 that $\log K_1$, $\log K_2$, and $\log K_1K_2$ change in parallel with pK_a.[12)] The fact that they are not in a strictly linear relation is obvious from the plots of $\log K_2$, for which the experimental accuracy is excellent. Such deviation is a little improved if $\log K_2$ is plotted against the effective substituent constant($\bar{\sigma}$) determined from the Menschutkin reaction of pyridines with ethyl iodide in nitrobenzene[13)] (Fig. 5). The Hammett ρ value can be determined from the $\log K/K_0$ *vs.* $\bar{\sigma}$ plots and is 2.9, which is equal to the value for the Menschutkin reaction, *i.e.*, 2.94.[13)] This indicates that the donor-acceptor bond formation is less sensitive to changes in electron density on the N atom than is the dissociation of pyridinium ions ($\rho=6.01$[12)] and 6.24[14)]). This is a reasonable result, because the ionicity in the present donor-acceptor bond should be smaller than that in the N^+–H bond of the pyridinium ion. As

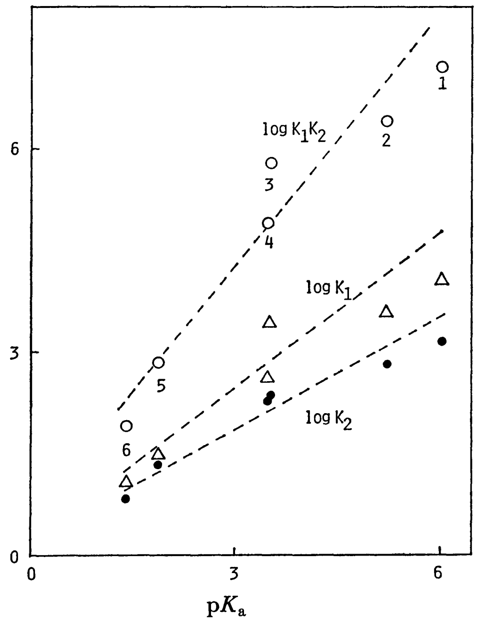

Fig. 4. Correlation between the equilibrium constant and basicity of the pyridine (pK_a).
The numbering corresponds to that in Fig. 2. pK_a's are cited from Ref. 12.

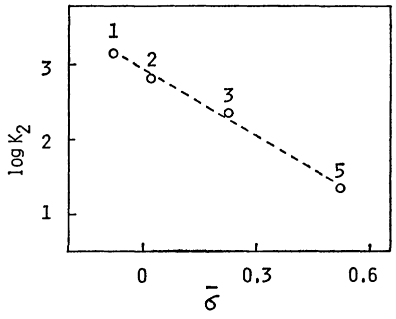

Fig. 5. Correlation between log K_1 and $\bar{\sigma}$ in nitrobenzene.
The numbering corresponds to that in Fig. 2. $\bar{\sigma}$ is cited from Ref. 13 and is available for the four derivatives among the ones treated here.

far as the electron-accepting group is concerned, the σ-effect is known to be a dominant factor in the substituent effect on the dissociation of the pyridinium ion[12,15] and on the above Menschutkin reaction.[13] Therefore, a parallel tendency between the log K's and pK_a as well as $\bar{\sigma}$ can be interpreted as indicating dominant σ-bonding in the formation of the present donor-acceptor complexes.

The distribution curve of $MeSnCl_3$ is shown in Fig. 6 for the $MeSnCl_3$+4-methylpyridine and +4-cyanopyridine systems. This figure clearly demonstrates that an appreciable amount of the 1:1 complex is formed in the solution. In Fig. 6a) the distribution to the free species of $MeSnCl_3$ rapidly falls off with the increase in the molar ratio, $C_{Py}/_{Sn}C$. This is responsible for the relatively large error in log K_1 in this system. If the initial concentration of $MeSnCl_3$ is reduced further, the fall-off will become slower, making the value of K_1 more accurate. However, such an experiment is beyond the sensitivity of the spectrometer used here.

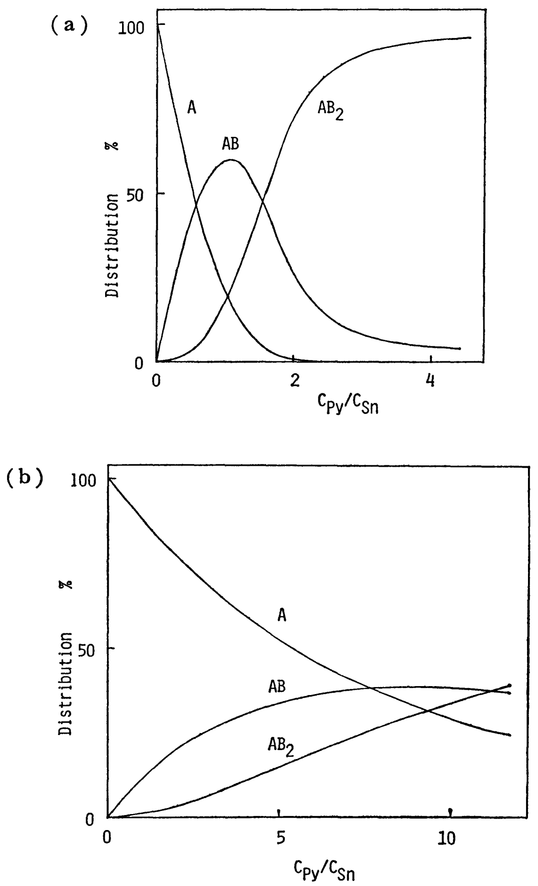

Fig. 6. Distribution curves of $MeSnCl_3$ in the a) $MeSnCl_3$+4-methylpyridine and b) $MeSnCl_3$+4-cyanopyridine systems.
C_{Sn} and C_{Py} are molarities of $MeSnCl_3$ and the pyridines, respectively. C_{Sn} is held constant at $\approx$0.005 mol dm^{-3}. A=$MeSnCl_3$. B=Pyridine derivative.

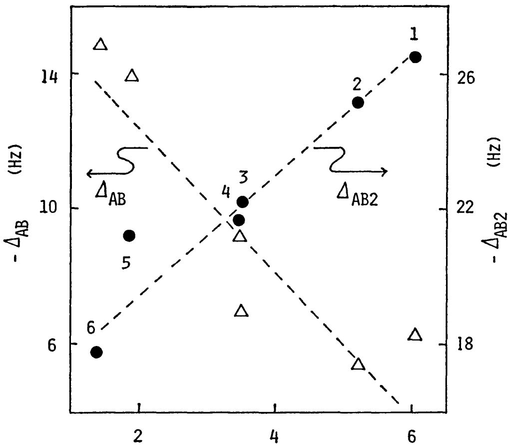

Fig. 7. Plots of Δ_{AB} and Δ_{AB2} against pK_a.
The numbering corresponds to that in Fig. 2. pK_a is cited from Ref. 12. See text for the definition of Δ_{AB} and Δ_{AB2}.

Complex-formation Shift. The complex-formation shifts, Δ_{AB} and Δ_{AB2}, which are defined as $\Delta_{AB}=$

$\delta_{AB}-\delta_A$ and $\Delta_{AB2}=\delta_{AB2}-\delta_A$, are all negative, indicating a high-field shift on the formation of the complex. This is consistent with the expectation from the electron transfer in the donor-acceptor bond. When Δ_{AB} and Δ_{AB2} are plotted against pK_a, a nearly linear relation is obtained (Fig. 7). It is reasonable that Δ_{AB2} is varied to the high-field side by the more basic pyridine derivative. On the contrary, Δ_{AB} is seen to vary inversely with the basicity of the pyridine derivative, although the plots in Fig. 7 are scattered, reflecting the relatively large errors in log K_1. As a reason for this inverse dependency, the anisotropy of the pyridine ring may be pointed out; it originates from the ring current effect. That the anisotropy effect really acts is also suggested by the variation of $\delta_H(SnCH_3)$ in Me_2SnCl_2, which moves toward the low-field side on the addition of pyridine, contrary to the case when DMSO or HMPA is added. A detailed analysis of this effect will be worthwhile for the elucidation of structural problems in solution; it will be the subject of further work.

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$$\Delta pK_a = 6.49\sigma_i + 9.50\sigma_\pi^+ + 2.20\sigma_\pi^- - 0.04.$$