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V *. PROTON RELAXATION AND DYNAMIC NMR STUDIES OF SOLUTE–SOLVENT INTERACTIONS IN SOLUTIONS OF DIMETHYLTIN DICHLORIDE PLUS 2,2′-BIPYRIDINE COMPLEX

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Summary

^{1}H T_1 and dynamic NMR measurements (T_1 = relaxation time) were made with Me_2SnCl_2 and its bpy complex in mixed solvents of CH_2Cl_2 and weak bases to elucidate the role of the solvent in the dynamic behaviour of organotin compounds. In the line shape analysis of the exchange reaction between Me_2SnCl_2 and its bpy complex, the dissociation rate constant k_d of the $Me_2SnCl_2 \cdot$bpy complex supported an exchange mechanism of the dissociation followed by a rapid recombination step. Weak bases in the mixed solvents decreased the Eyring activation parameters $\Delta H^‡$ and $\Delta S^‡$ for the dissociation reaction of the complex, indicating more extensive solvation in the activated state than in the ground state of the complex. In the ^{1}H T_1 measurements, the reorientational correlation time τ_c was shorter and its activation energy E_a was larger in Me_2SnCl_2 than in $Me_2SnCl_2 \cdot$ bpy, in conformity with their molecular sizes. E_a and τ_c increased on addition of weak bases, such as nitromethane, nitrobenzene and acetonitrile, even for the $Me_2SnCl_2 \cdot$ bpy complex, whose acidity is reduced considerably from that of the free tin compound. The major cause of this result is suggested to be the interaction of the weak bases with CH_2Cl_2, resulting in a change of the physical properties of the mixed solvent.

Introduction

Solute–solvent interactions play an important role in solutions containing organometallic compounds, where the metal atom can behave as a Lewis acid or as a charge-transfer partner. Usually organometallic compounds exist in solutions in a

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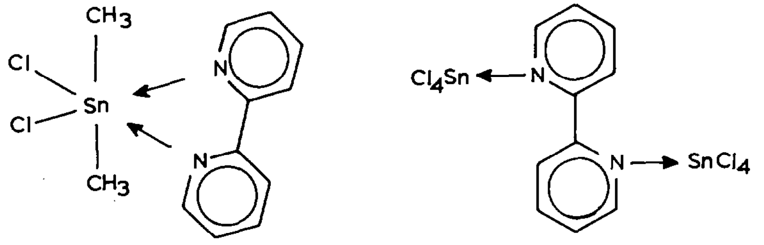
* For part IV see ref. 4.

rather simple form compared to ordinary (Brønsted) acids, making analysis of the solute–solvent interactions much easier.

We have studied acid–base interactions in solutions of organotin compounds by NMR spectroscopy and titration calorimetry [1–4]. In those studies, solute–solvent interactions did not come into explicit consideration. However, solvation phenomena are expected to be important in interpreting entropy changes in the complex formation reaction in solution [5]. In the present study, dynamic NMR and NMR T_1 measurements were applied to investigate the role of the solvent in the dissociation reaction of Me_2SnCl_2 complex with 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). These chelete complexes have been studied in solution by a number of investigators [6–12]. Only the chelete form (Scheme 1) was found for $Me_2SnCl_2 \cdot$ bpy although a bridge form was also suggested for the complex of $SnCl_4$ with bpy [8,9].



(chelete form)

(bridge form)

Experimental

Materials

Me_2SnCl_2, bpy and phen, from commercial sources, were sublimed and stored in desiccators. CH_2Cl_2 was refluxed over CaH_2 for 2 h and distilled. Dimethyl sulfoxide (DMSO)-d_6, acetonitrile-d_3, benzonitrile and dimethylacetamide (DMA) were dried over CaH_2 and vacuum-distilled. Sample solutions were prepared under dry N_2 atmosphere in a dry-box prior to each NMR measurement.

^1H dynamic NMR measurements

Studies of the concentration dependence were carried out on two series of solutions for each system studied here. In the first series, the concentration of the ligand was fixed at 0.03 *M* (mol dm^{-3}) for bpy and phen, while that of Me_2SnCl_2 was varied between 0.06 and 0.18 *M*. In the second series, 0.03 *M* bpy and 0.01 to 0.02 *M* Me_2SnCl_2 were used. ^1H NMR spectra were recorded on a Hitachi R-22 NMR spectrometer operating at 90 MHz. The variable temperature experiments were done from -31 to $+8°C$. As an internal reference, 0.02 vol% of TMS was added to the solvent. The spectra were averaged about 10 times by an A-1600B signal averager. Probe temperatures were measured by a calibrated thermocouple (copper-constantan) immersed in CH_2Cl_2 in a separate sample tube. Total line shape analysis was achieved by the DNMR3-IT_2 program [13] on an NEAC S-900 Computer at the Computation Center in Osaka University. The input parameters for the program were w_A and w_{AB} (the chemical shifts of methyl protons in Me_2SnCl_2 in a free state and in a complex, respectively), P_A and P_{AB} (fractional populations), k_A (the initial value for the rate constant), and T_{2A} and T_{2AB} (transverse relaxation times at states A and AB, respectively), which were replaced by $1/\pi\ W_{1/2}$ obtained from the full line width at half-height in the absence of exchange. The values of $W_{1/2}$ for A and AB were equalized and estimated from $W_{1/2}$ of the TMS signal, which was preliminary interrelated to the $W_{1/2}$ value of Me_2SnCl_2 excluding bpy or phen. All parameters other than T_{2A} and T_{2AB} were varied in the program in order to reproduce well the experimental line shape. The spectral pattern was divided into 65 to 91 points by an increment of 2 Hz/point and fed into the computer. The agreement factor $[\Sigma(\text{error})^2/\Sigma(\text{data})^2]^{1/2}$ was less than 6%.

^1H T_1 measurements

T_1 was measured by the inversion recovery method using a pulse sequence of (π-HS-τ-$\pi/2$-acquire) with a homospoil pulse HS. T_1 of the methyl protons in Me_2SnCl_2 was less than 1 s and the pulse repetition time was set to 15 s. The S/N ratio was enhanced by averaging 45 fid's. The $\pi/2$ pulse length was 35 μs. Low temperature was achieved in a conventional way but the carrier gas was supplied from heating liquid N_2 [14]. The temperature variation was less than ±0.3°C during the measurement. Sample solutions were degassed four times with a vacuum line at 10^{-5} Torr and then sealed off.

Method of analysis and results

The variable temperature spectra (experimental and simulated) of the methyl protons in the Me_2SnCl_2 + bpy system in CH_2Cl_2 are shown in Fig. 1. The temperature-dependent residence times on free Me_2SnCl_2 (τ_A) and on the $Me_2SnCl_2 \cdot$ bpy complex (τ_{AB}) were determined according to eq. 1, by observing the ^1H NMR signals from these two species. τ_A and τ_{AB} are equal to $1/k_A$ and $1/k_{AB}$, respectively, and are related to each other by $\tau_A/P_A = \tau_{AB}/P_{AB}$, where P is the fractional population.

$$Me_2SnCl_2 \underset{k_{AB}}{\overset{k_A}{\rightleftharpoons}} Me_2SnCl_2 \cdot bpy \qquad (1)$$

On the other hand, the formation and the dissociation rate constants for the complex formation are defined on the basis of eq. 2 when the reaction is assumed to proceed through a dissociation step followed by recombination [15]. They are

$$Me_2SnCl_2 + bpy \underset{k_d}{\overset{k_f}{\rightleftharpoons}} Me_2SnCl_2 \cdot bpy \qquad (2)$$

related to k_A and k_{AB} by $k_A = k_f \cdot C_B$ and $k_{AB} = k_d$, where C_B is the equilibrium concentration of bpy. Thus, k_d can be obtained directly from the results of line shape analysis. The k_d values thus determined were ascertained to be independent of the concentration changes in Me_2SnCl_2 and bpy, supporting the assumed model of eq. 2. The temperature dependence of k_d was measured and the Eyring activation parameters were obtained from plots of $\ln(k_d/T)$ against $1/T$ (eq. 3 and Fig. 2). To examine the effect of the solvent on the above exchange reaction,

$$\ln(k_d/T) = -\frac{\Delta H^\ddagger}{R} \times \frac{1}{T} + \frac{\Delta S^\ddagger}{R} + 23.76 \qquad (3)$$

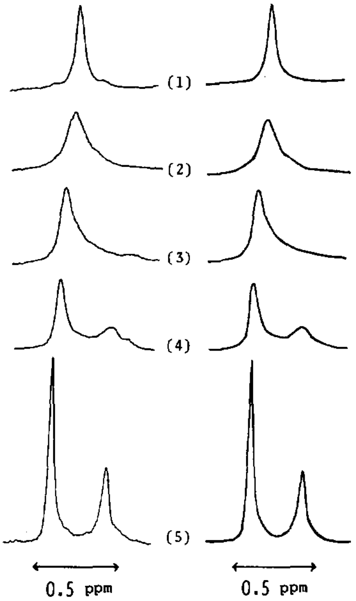


Fig. 1. Experimental (left) and computer-simulated (right) 90 MHz NMR spectra of methyl protons in Me_2SnCl_2 in the exchange reaction with $Me_2SnCl_2 \cdot bpy$. Initial concentrations: $[Me_2SnCl_2]_0 = 0.0927$ *M*, $[bpy]_0 = 0.0300$ *M*. Temperatures: −14.9°C (1), −20.4°C (2), −25.3°C (3), −30.5°C (4), and −38.5°C (5).

k_d was measured in a mixed solution of CH_2Cl_2 containing a definite amount (0.3 *M*) of DMSO-d_6, DMA, acetonitrile-d_3, benzonitrile and nitromethane-d_3. The addition of such weak bases shifted the peak position of "free Me_2SnCl_2" but not that of the $Me_2SnCl_2 \cdot bpy$ complex. In this case, "free Me_2SnCl_2" may be said to correspond to Me_2SnCl_2 averaged statistically between the purely free molecule and the one weakly solvated by the added base. In these experiments the initial concentration of Me_2SnCl_2 (C_A^o) was held constant at 0.03 *M* and that of bpy (C_B^o)

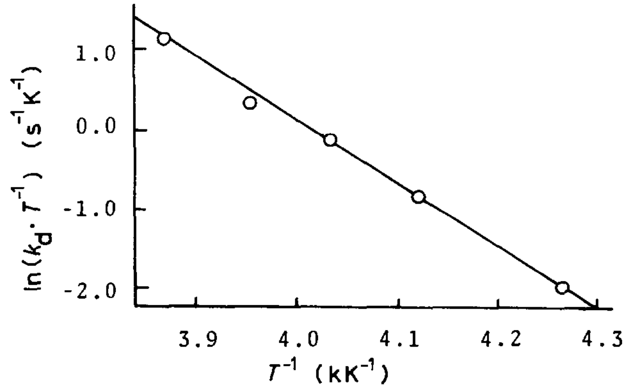


Fig. 2. Determination of the Arrhenius activation parameters from the plot of $\ln(k_d/T)$ against $1/T$ for the $Me_2SnCl_2 + bpy$ system in CH_2Cl_2.

TABLE 1

CONCENTRATION DEPENDENCE OF THE RESIDENCE TIMES FOR THE EXCHANGE REACTION BETWEEN Me_2SnCl_2 AND $Me_2SnCl_2 \cdot bpy$

$[Me_2SnCl_2]_0$ [a]	$[bpy]_0$ [a]	τ_A [b]	τ_{AB} [b]	k_d [c]
Experiment I (at − 14.9°C)				
0.0927	0.0300	6.9	4.5	222
0.1124	0.0300	9.1	4.4	227
0.1316	0.0300	10.1	4.4	227
0.1497	0.0300	13.3	4.4	227
0.1658	0.0300	14.8	4.3	233
Experiment II (at − 22.6°C)				
0.0300	0.0104	17.2	9.1	110
0.0300	0.0166	6.9	8.5	118
0.0300	0.0205	4.0	8.6	116
0.0300	0.0219	3.2	8.7	115
0.0300	0.0228	2.7	8.6	116

[a] In *M*. [b] In ms. The errors were estimated to be less than 10%. [c] $k_d = 1/\tau_{AB}$ is given in s^{-1}.

TABLE 2

EYRING ACTIVATION PARAMETERS FOR THE DISSOCIATION REACTION OF $Me_2SnCl_2 \cdot bpy$ COMPLEX IN MIXED SOLVENTS [a]

Base added [b]	$\Delta H^\ddagger$ [c]	$\Delta S^\ddagger$ [d]
none	65	56
nitromethane-d_3	67	59
benzonitrile	59	31
acetonitrile-d_3	52	0.1
DMA	37	−47
DMSO-d_6	25	−93

[a] The errors were estimated to be less than 10%. [b] 0.3 *M* of the weak base was added to CH_2Cl_2. [c] In kJ/mol. [d] In $J\ K^{-1}\ mol^{-1}$.

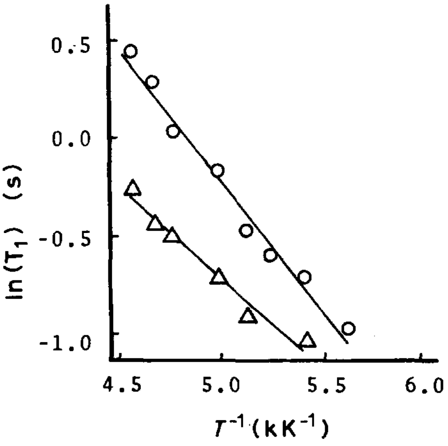


Fig. 3. Plots of $\ln(T_1)$ vs. $1/T$ for the Me_2SnCl_2 + bpy system in CD_2Cl_2. $[Me_2SnCl_2]_0 = 0.04\ M$ and $[bpy]_0 = 0.02\ M$. Experimental points: ○ (Me_2SnCl_2) and △ ($Me_2SnCl_2 \cdot bpy$).

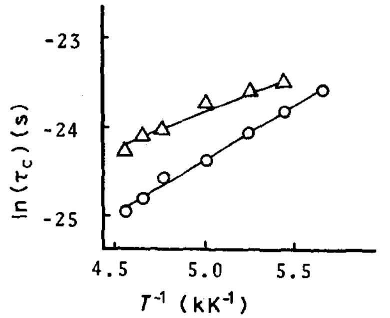


Fig. 4. Plots of $\ln(\tau_c)$ vs. $1/T$ for the Me_2SnCl_2 + bpy system in CD_2Cl_2. See Fig. 3 for details.

was varied between 0.01 and 0.03 *M*. Such mixed solvents enabled the experiments to be carried out at temperatures as low as −100 °C. The results are summarized in Table 2.

To investigate further the role of the solvent molecules on the dynamic features of the metal–ligand complex, the ^1H relaxation time T_1 was measured. A $2(Me_2SnCl_2)/1$ (bpy) mixture in CD_2Cl_2 gives equimolar spectra of Me_2SnCl_2 and its bpy complex because of the large formation constant. The two methyl peaks were well separated below −38 °C and ^1H T_1 was measured for these peaks between −55 and −90 °C. The plots of $\ln(T_1)$ against $1/T$ proved to be linear, as shown in Fig. 3.

The longitudinal relaxation time T_1 is generally divided into several parts [16,17]:

$$\frac{1}{T_1}=\frac{1}{T_1^{DD}}+\frac{1}{T_1^{Q}}+\frac{1}{T_1^{SC}}+\frac{1}{T_1^{CA}}+\frac{1}{T_1^{SR}} \qquad (4)$$

But all the parts except the dipole–dipole interaction term T_1^{DD} may be safely omitted in the present case, because quadrupole nuclei (T_1^Q) or direct bonding to a rapidly relaxing nucleus (T_1^{SC}) was not included and because the experiments were performed in a low magnetic field (T_1^{CA}). In addition, the contribution of the spin rotation term T_1^{SR} is excluded from the temperature dependence of T_1 in Fig. 3. T_1^{DD} is next separated into two parts, i.e. intramolecular and intermolecular ones, but the latter may be ignored because the dilute solutions (0.02 *M* of Me_2SnCl_2 and of its bpy complex) are treated in perdeuterated solvent. T_1^{DD} (intra) is related to the

TABLE 3

REORIENTATIONAL CORRELATION TIME τ_c AT −90 °C AND REORIENTATIONAL ACTIVATION ENERGY E_a IN CD_2Cl_2 MIXED SOLVENTS FROM THE ^1H T_1 MEASUREMENTS [a]

Base added [b]	Me_2SnCl_2		$Me_2SnCl_2\cdot$bpy	
	τ_c	E_a	τ_c	E_a
none	0.046	10.6	0.067	7.4
nitromethane-d_3	0.051	12.5	0.068	7.9
nitrobenzene-d_5	0.051	12.6	0.068	8.8
acetonitrile-d_3	0.079	13.5	0.101	10.9

[a] τ_c in ns and E_a in kJ/mol. [b] 0.5 *M* of the weak base was added to CH_2Cl_2.

correlation time τ_c by eq. 5 [16], where b is the H---H distance in the CH_3 group

$$T_1^{DD}(\text{intra}) = N\frac{3}{10}\frac{\gamma^4\hbar^2}{b^6}\left\{\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right\} \tag{5}$$

(1.822 Å [18]), N is the number of protons contributing to the relaxation ($N = 2$), and the other symbols have their usual meanings. In this equation, protons in the same methyl group are taken into account and those in another group are omitted because of the large distance. The temperature dependence of the correlation time τ_c is expressed by eq. 6, and from the plot of $\ln(\tau_c)$ against $1/T$ the reorientational

$$\tau_c = \tau_0 \exp(E_a/kT) \tag{6}$$

activation energy E_a is obtained (Fig. 4). τ_c and E_a were also determined after 0.5 M of various weak bases was added to investigate the effect of solvation (Table 3).

Discussion

In eq. 2, k_f, which is given by $1/(\tau_A C_B)$, is much larger than k_d because the equilibrium concentration of bpy (C_B) is very small owing to the large formation constant [12] of the bpy complex. Therefore, the exchange reaction is seen to proceed via a dissociation step followed by rapid recombination, i.e.

$$Me_2SnCl_2 \cdot bpy^1 \xrightarrow{\text{slow}} Me_2SnCl_2 + bpy^1 \tag{7}$$

$$Me_2SnCl_2 + bpy^2 \xrightarrow{\text{fast}} Me_2SnCl_2 \cdot bpy^2 \tag{8}$$

A linear correlation exists between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the dissociation reaction (Fig. 5), and $\Delta H^\ddagger$ decreases with the donor number [19] of the solvent (Fig. 6), i.e. the basic solvent energetically stabilizes the activated complex more than the complex in the ground state. This means that the activated complex is solvated more strongly or by a larger number of solvent molecules than the complex in the ground state. The

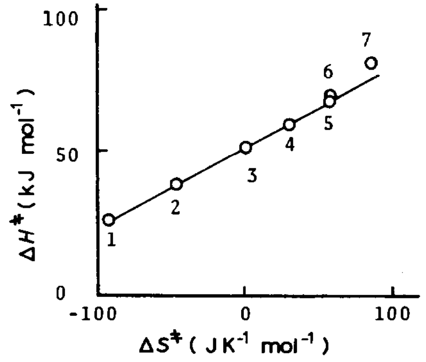


Fig. 5. Correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the exchange reaction of Me_2SnCl_2 with its bpy complex in mixed solvents. The solvents consisted of CH_2Cl_2 and 0.3 M of: DMSO-d_6 (1), DMA (2), acetonitrile-d_3 (3), benzonitrile (4), and nitromethane (5). Also included are the data in neat CH_2Cl_2 (6) and those for phen in neat CH_2Cl_2.

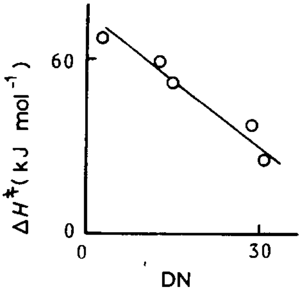


Fig. 6. Correlation between $\Delta H^{\ddagger}$ and DN (donor number). The numbering corresponds to that given in Fig. 5.

smaller $\Delta S^{\ddagger}$ value for the more basic solvent supports this idea. Activation parameters were also measured for the ligand of phen in CH_2Cl_2; the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values fell close to the same line corresponding to bpy in Fig. 5, indicating the increased basicity of phen. From these data a loosely bonded complex such as $[Me_2SnCl_2\text{---}bpy]^{\star}$ can be visualized as the activated state. An alternative state where only one N atom is released from the bonding to the Sn atom is not probable because the phen complex showed a similar tendency in Fig. 5.

From the ^1H T_1 experiments, the solvation effect of the $Me_2SnCl_2 \cdot bpy$ complex in the ground state can be discussed. τ_c is known to be approximated by eq. 9,

$$\tau_c = 4\pi\eta a^3/3kT \tag{9}$$

where a is the molecular diameter, k is the Boltzmann constant and η is the macroscopic shear viscosity [20]. In the above equation, η also reflects the solute–solvent interactions, if present at all, which will act to suppress the molecular reorientational motion of the solute. The temperature dependence of η is usually expressed by eq. 10, where E_{vis} is the

$$\eta = A\ \exp(E_{vis}/kT) \tag{10}$$

activation energy in viscosity and depends mainly on the intermolecular forces present in solution. From eqs. 6, 9, and 10, E_a will be approximately parallel to E_{vis}. It is seen from Table 3 that the Me_2SnCl_2 free molecule has shorter τ_c and larger E_a values than those of the bpy complex. This is due to the smaller size and the enhanced acidity of the free molecule compared to the complex. Experiments using the mixed solvents showed that τ_c and E_a increase, even in the $Me_2SnCl_2 \cdot bpy$ complex for which solute–solvent interactions are expected to be reduced considerably compared to the free molecule. The changes of τ_c and E_a in Me_2SnCl_2 as well as in the bpy complex are linearly correlated to the donor number (DN) of the weak base added to CD_2Cl_2: DN equals almost zero for CD_2Cl_2, 2.7 for nitromethane, 4.4 for nitrobenzene and 14.1 for acetonitrile. The molecular interactions between CD_2Cl_2 and the weak bases in the mixed solvents are indicated as the major cause of this correlation since methylene chloride can act as a hydrogen-bond donor. Such an interaction will increase the viscosity of the mixed solvent, increasing the values of τ_c and E_a. A detailed discussion is, however, prevented by the lack of viscosity data for the mixed solvents at low temperatures.

In conclusion, from the study of line shape analysis and T_1 measurement of the Me_2SnCl_2 + bpy system in CH_2Cl_2 solutions mixed with weak bases, the weak base was shown to play an important role in the dissociation reaction of the $Me_2SnCl_2 \cdot$ bpy complex, by solvating to the activated state of the complex, whereas the weak base only influences indirectly the ^1H T_1 of the complex which is in the ground state by probably associating with CH_2Cl_2 in the mixed solvent.

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