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The Solvation Effect on the Reactions in Solution. I. The Solvation Model for the Interpretation of Entropy Changes in the Complex Formation of Dichlorodimethylstannane with Pyridine

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A complex-formation reaction has been studied for the Me_2SnCl_2 plus pyridine system in dimethyl phthalate (DMP) and dioctyl phthalate (DOP) by means of titration calorimetry. The resulting entropy changes in the reactions of A+B=AB and AB+B=AB_2, with A=Me_2SnCl_2 and B=pyridine, were compared with those calculated for the gas-phase reactions. The values in solution amounted only to 1/3—1/4 of the gas-phase values. Correction for the entropy of solution of each component failed to explain the observed values in the absence of a strong solvation. The solvation model is presented to allow for such a discrepancy, assuming a strong solvation for Me_2SnCl_2 as well as for the 1 : 1 pyridine complex by definite numbers of solvents. To test the applicability of the model, calculations were made based on molecular statistical thermodynamics. The results obtained were reasonable, indicating that a free molecule, Me_2SnCl_2, is solvated by 1.3 molecules of the solvent of DMP, which are released about half by half on the formation of the 1 : 1 and 1 : 2 complexes with pyridine.

Entropy changes upon reactions are generally expressed as the sum of the standard entropies of the products minus those of the starting materials. The standard entropy is equal to the (absolute) entropy of the compound in its standard state at an arbitrary temperature. Based on this concept, entropies of reactions have been calculated from the entropies of relevant compounds, which are either measured as thermodynamic third-law entropies in a calorimetric experiment or estimated statistically from the molecular theory for thermodynamic functions. The calculated entropies usually coincide well with those observed for gas-phase reactions, proving the thermodynamic third law. However, reactions in a solution are almost always accompanied by changes in solvation which affect the entropy change to a great extent. Therefore, solvation is essential for a full understanding of the entropy changes in a solution. In other words, entropy changes can be expected to offer important information regarding the solvation phenomena.

Hitherto, the thermodynamic aspects of reactions in solution have attracted attention mostly in terms of the enthalpy. The well-known Hammett substituent constants have been derived assuming a major contribution from the enthalpy term to the free energy change as a result of a negligible entropy term or a proportional enthalpy-entropy relationship. Some other empirical treatments, such as Drago's *E* and *C* parameters[1] and Gutmann's donor number,[2] have been developed for the enthalpy term in relation to acid-base reactions. Also, a classification of Pearson's hard and soft acids and bases (HSAB)[3] has been discussed quantum chemically[4] in relation to the enthalpy term, although the idea first came from a classification of the free energy changes. In contrast to this, the entropy term has long been overlooked in the discussion of the thermodynamic profiles. Hitherto, ion-pair formation has been discussed with regard to the entropy term, and the entropy of hydration has been obtained for different ion pairs.[5]

The present authors have previously reported that entropy changes upon the complex formation of some chloromethylstannanes with Lewis bases, as measured in halogenated hydrocarbon solvents, amount to only 1/3 of those estimated in the gas phase.[6,7] These results have been interpreted to indicate the release of a definite number of solvent molecules from the solvation sphere upon the complex formation. To take the solvation effect into consideration more exactly, in the present study the entropy term is discussed on the basis of thermochemical cycle. The solvents used are substituted phthalates, for which the entropies of solution can be measured by means of the gas-liquid chromatography.

Experimental

The Me_2SnCl_2 (Tokyo Kasei Co.) was purified by sublimation under a reduced pressure. The pyridine was dried over CaH_2 and distilled in a dry box. The dimethyl phthalate (DMP) and dioctyl phthalate (DOP) were distilled under reduced pressure in a dry box. Alkylbenzenes from commercial sources were used for the gas-liquid chromatography without further purification. The calorimetric titration experiments were performed on a Tronac 550 isothermal/isoperibol calorimeter under an isothermal mode. The details of this experiment were the same as those in Ref. 7. The gas-chromatographic retention data were collected on a Yanagimoto T-1880 gas chromatograph with a TCD detector. The column temperature was measured with a copper-constantan thermocouple. DMP and DOP were coated on 60/80 mesh Chromosorb W AW-DMCS (25 wt%). The temperature ranges measured were from 50 to 70 °C for DMP and from 85 to 135 °C for DOP. The retention data were extrapolated to the vanishing amount of the injection for each solute at each temperature.

Results

Our analysis of the calorimetric titration data is summarized in Table 1 for the complex formation of

Table 1. Analysis of Calorimetric Titration Data for the Me_2SnCl_2+Pyridine System in Dimethyl and Dioctyl Phthalates (DMP and DOP) at 25 °C

Solvent	K_1 a)	K_2 a)	$-\Delta H_1$ b)	$-\Delta H_2$ b)	$-\Delta S_1$ c)	$-\Delta S_2$ c)
DMP	26.7±0.7	4.0±0.2	30.8±0.3	30.7±2.5	76.1±0.9	91.4±8.2
DOP	22.4±0.8	3.8±0.2	32.5±2.1	34.9±0.3	83.3±7.1	106.0±2.1

a) $dm^3 mol^{-1}$. b) $kJ mol^{-1}$. c) $J K^{-1} mol^{-1}$.

Me_2SnCl_2 with pyridine in DMP and DOP. The successive formation of 1 : 1 and 1 : 2 complexes (Eqs. 1 and 2) has already been concluded from the analysis of the NMR[8] and of the calorimetric[9] titration data.

$$A+B=AB \qquad K_1,\ \Delta H_1,\ \Delta S_1 \tag{1}$$

$$AB+B=AB_2 \qquad K_2,\ \Delta H_2,\ \Delta S_2 \tag{2}$$

Table 1 shows that DMP and DOP resemble each other as solvents. Besides these two, the phthalates $C_6H_4(COOR)_2$ with $R=C_2H_5$, C_4H_9, C_7H_{15}, and C_9H_{19} were also tested, but the results showed no clear dependence on the carbon number in R.

The entropy of solution, which is necessary for the comparison of the entropies of reactions in solution and those in the gas phase, was derived from the retention data in gas-liquid chromatography. The basic equation used is as follows;[10]

$$\ln(V_g^0)+\ln(T\rho/273.15)=-\Delta H^s/RT+\Delta S^s/R, \tag{3}$$

where V_g^0 is the specific retention volume, T is the column temperature, ρ is the density of the liquid phase, and ΔH^S and ΔS^S are the enthalpy and entropy of solution, respectively. From the data of benzene, toluene, and ethyl-, propyl-, and isopropylbenzenes, the following relations were obtained between ΔS^S and the thermodynamic third-law entropy, $S^0_{298}(g)$:

$$\begin{array}{ll} \Delta S^s=-0.093\,S^0_{298}(g)-9.0 & r=0.998 \text{ in DOP,} \\ \quad(0.002) \qquad\qquad (8.5) & \end{array} \tag{4}$$

$$\begin{array}{ll} \Delta S^s=-0.097\,S^0_{298}(g)+7.4 & r=0.985 \text{ in DMP.} \\ \quad(0.007) \qquad\qquad (2.6) & \end{array} \tag{5}$$

Here, the values of $S^0_{289}(g)$ have been taken from Ref. 11. In Eqs. 4 and 5, r is the correlation coefficient and the standard errors are listed in parentheses.

Discussion

In the discussion of entropy changes upon complex-formation reactions in solution, rigorous calculation is very difficult because solvation contributes a great deal to the entropy of each component and because some physical properties, e.g., the fundamental vibrations at low frequencies and the physical properties of the complex especially, are frequently lacking. However, any discussion of the entropy changes in solution can be expected to disclose solvation phenomena in the reaction process. In this section, first, the entropy of reaction is estimated without assuming any specific solvation for each component; it will be compared with the experimental values.

$$\begin{tikzcd} A\ (gas) \arrow[d, "\Delta S^S_A"'] & + & B\ (gas) \arrow[d, "\Delta S^S_B"'] \arrow[r, "\Delta S(gas)"] & AB\ (gas) \arrow[d, "\Delta S^S_{AB}"] \\ A\ (soln) & + & B\ (soln) \arrow[r, "\Delta S(soln)"] & AB\ (soln) \end{tikzcd}$$

Fig. 1. A complex formation reaction of A+B=AB in gas phase and in solution. ΔS^s is the entropy of solution of each component.

i) Estimation of the Entropy Changes Assuming No Specific Solvation. For a simple reaction of A+B=AB, a thermochemical cycle will be given such as the one shown in Fig. 1. Generally, Eq. 6 holds for the gas-phase reaction, and a thermochemical consideration leads to Eq. 7:

$$\Delta S^0(gas)=S^0_{AB}(gas)-S^0_A(gas)-S^0_B(gas), \tag{6}$$

$$\Delta S^0(soln)=\Delta S^0(gas)+(\Delta S^s_{AB}-\Delta S^s_A-\Delta S^s_B). \tag{7}$$

In Eq. 6, $S^0_{AB}(gas)$, $S^0_A(gas)$, and $S^0_B(gas)$ are the standard entropies of AB, A, and B respectively in the gas phase at a standard state. Recently, Wertz proposed a simple relation between the entropy of solution, ΔS^S, and the thermodynamic third-law entropy, $S^0_{298}(g)$; he based this relation on a discussion of relatively simple molecules which interact only weakly with the solvent,[12] i.e.:

$$\Delta S^s=a\,S^0_{298}(g)+b. \tag{8}$$

The coefficents, a and b, in this equation were later reported to change slightly depending on the type of compound.[13] Here, it is clear that the entropy of solution of each component is actually non-vanishing, even if it does not interact strongly with the solvent. In the present case, Eq. 7 is converted to Eq. 9 (see Appendix 1).

$$\Delta S^0_{calcd}(soln)=(1+a)\,\Delta S^0(gas)-b-aR\ln 24.5 \tag{9}$$

where $\Delta S^0_{calcd}(soln)$ means $\Delta S^0(soln)$ as calculated from $S^0(gas)$ and Wertz's equation, $S^0(gas)$ being obtained from an experiment in the gas phase or from the molecular statistical method described above. Equation 9 is applicable to both steps of Eqs. 1 and 2 in the present study, but the coefficients a and b remain undetermined because of the unavailable third-law entropies in the gaseous and liquid states of DMP and DOP. To determine these coefficients, the entropies of solution were measured by means of gas-liquid chromatography for some hydrocarbons which interact only weakly with the phthalates (Eqs. 4 and 5). In this way, Eq. 9 proved to be Eqs. 10 and 11 in DOP and DMP, respectively for the reactions of both Eqs. 1 and 2:

$$\Delta S_{\mathrm{calcd}}(\mathrm{soln}) = 0.907\,\Delta S^0(\mathrm{gas}) + 11.5 \quad \text{in DOP}, \qquad (10)$$

$$\Delta S_{\mathrm{calcd}}(\mathrm{soln}) = 0.903\,\Delta S^0(\mathrm{gas}) - 4.8 \quad \text{in DMP}. \qquad (11)$$

Here, $\Delta S^0(\mathrm{gas})$ means $S^0{}_{\mathrm{AB}}(\mathrm{gas})$-$S^0{}_{\mathrm{A}}(\mathrm{gas})$-$S^0{}_{\mathrm{B}}(\mathrm{gas})$ and $\Delta S^0{}_{\mathrm{AB2}}(\mathrm{gas})$-$S^0{}_{\mathrm{AB}}(\mathrm{gas})$-$S^0{}_{\mathrm{B}}(\mathrm{gas})$. In the present study, $\Delta S^0(\mathrm{gas})$ is obtained by means of the molecular statistical calculation (Appendix 2). As a first approximation, the vibrational part of the entropies was omitted in the calculation of $\Delta S^0(\mathrm{gas})$, for the contributions from the products and the starting materials were almost the same. Although detailed structural parameters are not required for the discussion below because of the minor dependence of the calculated entropies on the structural changes, references are cited for Me_2SnCl_2,[14] pyridine,[15] and $Me_2SnCl_2\cdot(\mathrm{pyridine})_2$.[16] As for the 1 : 1 complex, two configurations were assumed, where either pyridine or the Cl group is located at an equatorial position besides the two methyl groups.[17] However, the resulting entropies were virtually unchanged. The comparison of the calculated values with the experimental value shown in Table 2 shows that the correction from the entropy of solution of each component is small and does not explain the difference between the entropies observed in solution and those calculated for the gas-phase reaction. Therefore, a model assuming no specific solvation fails to explain the results in the present study. Where, then, does this difference come from? If it were possible to measure ΔS^{S} for the AB complex similarly to those of A and B, $\Delta S^0(\mathrm{soln})$ could be estimated according to Eq. 7. However, this is impossible because of the labile character of the complex. For reference, the entropies of solution were measured for several methylstannanes (Table 3). These entropies decreased with an increase in the acidity of the stannanes: Me_4Sn exhibits no discernible tendency toward acid, whereas the acidity increases from Me_3SnCl to Me_2SnCl_2. Hence, this decrease is attributed to the increased solvation for the stannanes with increased acidity. In the following, a solvation model is presented which allows for the effect of strong solvation on the entropy of solution and helps to interpret the experimental entropies of reactions in solution measured above.

Table 2. Entropies of the Reactions in Solution and in the Gas Phase

	Solvent	Calculated[a)]	Observed[a)]
$(\Delta S^0{}_{\mathrm{soln}})_1$	DOP	−209.5	−83.3
	DMP	−222.1	−76.1
	Gas phase	−270.3	—
$(\Delta S^0{}_{\mathrm{soln}})_2$	DOP	−227.3	−106.0
	DMP	−239.8	−91.4
	Gas phase	−286.8	—

a) In units of J K^{-1} mol^{-1}.

ii) Solvation Model for the Interpretation of Entropy Changes in Solution. In Fig. 2 a solvation model is depicted for the reactions of A+B=AB and AB+B=AB_2, where A and AB are strongly solvated by *m* and *n* molecules of the solvent respectively, whereas AB_2, in which the tin atom possesses a coordination number of six, and B are not solvated, or are only weakly solvated, so that their entropies of solution are expressed by the Wertz-type equation. From a consideration of the

Table 3. Entropies of Solution ΔS^{s} for Several Methylstannanes as Determined by Means of Gas-Liquid Chromatography[a)]

Mobile phase	Me_2SnCl_2	Me_3SnCl	Me_4Sn
DOP	−73.8±4.7	−58.1±5.6	−34.9±0.3
DMP	−98.6±0.7	−69.9±9.2	−37.6±1.5

a) In units of J K^{-1} mol^{-1}.

Step I

$$\begin{tikzcd}
\mathrm{A\cdot L_m\ (gas)} \arrow[d, "\Delta S^{\mathrm{s}}{}_{\mathrm{AL_m}}"] & + & \mathrm{B\ (gas)} \arrow[d, "\Delta S^{\mathrm{s}}{}_{\mathrm{B}}"] \arrow[r, "\Delta S(\mathrm{gas})_1"] & \mathrm{AB\cdot L_n\ (gas)} \arrow[d, "\Delta S^{\mathrm{s}}{}_{\mathrm{ABL_n}}"] & + & \mathrm{(m-n)L\ (gas)} \arrow[d, "(m-n)\Delta S^{\mathrm{s}}{}_{\mathrm{L}}"] \\
\mathrm{A\cdot L_m\ (soln)} & + & \mathrm{B\ (soln)} \arrow[r, "\Delta S(\mathrm{soln})_1"] & \mathrm{AB\cdot L_n\ (soln)} & + & \mathrm{(m-n)L\ (soln)}
\end{tikzcd}$$

Step II

$$\begin{tikzcd}
\mathrm{AB\cdot L_n\ (gas)} \arrow[d, "\Delta S^{\mathrm{s}}{}_{\mathrm{ABL_n}}"] & + & \mathrm{B\ (gas)} \arrow[d, "\Delta S^{\mathrm{s}}{}_{\mathrm{B}}"] \arrow[r, "\Delta S(\mathrm{gas})_2"] & \mathrm{AB_2\ (gas)} \arrow[d, "\Delta S^{\mathrm{s}}{}_{\mathrm{AB_2}}"] & + & \mathrm{nL\ (gas)} \arrow[d, "n\Delta S^{\mathrm{s}}{}_{\mathrm{L}}"] \\
\mathrm{AB\cdot L_n\ (soln)} & + & \mathrm{B\ (soln)} \arrow[r, "\Delta S(\mathrm{soln})_2"] & \mathrm{AB_2\ (soln)} & + & \mathrm{nL\ (soln)}
\end{tikzcd}$$

Fig. 2. The solvation model for the reactions of A+B=AB and AB+B=AB_2. A and AB are solvated strongly by *m* and *n* molecules of the solvent L, respectively.

thermochemical cycles in Fig. 2, the following equations are derived:

$$\Delta S^0(\mathrm{soln})_1 = \Delta S^0(\mathrm{gas})_1 + \Delta S^{\mathrm{s}}{}_{\mathrm{ABL}_n} + (m-n)\Delta S^{\mathrm{s}}{}_{\mathrm{L}} - (\Delta S^{\mathrm{s}}{}_{\mathrm{AL}_m} + \Delta S^{\mathrm{s}}{}_{\mathrm{B}}), \tag{12}$$

$$\Delta S^0(\mathrm{soln})_2 = \Delta S^0(\mathrm{gas})_2 + \Delta S^{\mathrm{s}}{}_{\mathrm{AB2}} + n\Delta S^{\mathrm{s}}{}_{\mathrm{L}} - (\Delta S^{\mathrm{s}}{}_{\mathrm{ABL}_n} + \Delta S^{\mathrm{s}}{}_{\mathrm{B}}). \tag{13}$$

The substitution of Eq. A2 into Eqs. 12 and 13 leads to:

$$\Delta S^0(\mathrm{soln})_1 = (1+a)\Delta S^0(\mathrm{gas})_1 + (m-n-1)(b + aR\ln 24.5), \tag{14}$$

$$\Delta S^0(\mathrm{soln})_2 = (1+a)\Delta S^0(\mathrm{gas})_2 + (n-1)(b + aR\ln 24.5). \tag{15}$$

Here,

$$\Delta S^0(\mathrm{gas})_1 = S^0{}_{\mathrm{ABL}_n}(\mathrm{gas}) + (m-n)S^0{}_{\mathrm{L}}(\mathrm{gas}) - S^0{}_{\mathrm{AL}_m}(\mathrm{gas}) - S^0{}_{\mathrm{B}}(\mathrm{gas}), \tag{16}$$

$$\Delta S^0(\mathrm{gas})_2 = S^0{}_{\mathrm{AB2}}(\mathrm{gas}) + nS^0{}_{\mathrm{L}}(\mathrm{gas}) - S^0{}_{\mathrm{ABL}_n}(\mathrm{gas}) - S^0{}_{\mathrm{B}}(\mathrm{gas}), \tag{17}$$

holds; also, the following equations hold when an additivity rule is assumed for the entropy of the strongly solvated species:

$$S^0{}_{\mathrm{AL}_m}(\mathrm{gas}) = S^0{}_{\mathrm{A}}(\mathrm{gas}) + m\{S^0{}_{\mathrm{AL}}(\mathrm{gas}) - S^0{}_{\mathrm{A}}(\mathrm{gas})\}, \tag{18}$$

$$S^0{}_{\mathrm{ABL}_n}(\mathrm{gas}) = S^0{}_{\mathrm{AB}}(\mathrm{gas}) + n\{S^0{}_{\mathrm{ABL}}(\mathrm{gas}) - S^0{}_{\mathrm{AB}}(\mathrm{gas})\}. \tag{19}$$

By substituting Eqs. 18 and 19 into 16 and 17, we obtain:

$$\Delta S^0(\mathrm{gas})_1 = \Delta S^0{}_{\mathrm{AB}}(\mathrm{gas}) + n\Delta S^0{}_{\mathrm{ABL}}(\mathrm{gas}) - m\Delta S^0{}_{\mathrm{AL}}(\mathrm{gas}), \tag{20}$$

$$\Delta S^0(\mathrm{gas})_2 = \Delta S^0{}_{\mathrm{AB2}}(\mathrm{gas}) - n\Delta S^0{}_{\mathrm{ABL}}(\mathrm{gas}), \tag{21}$$

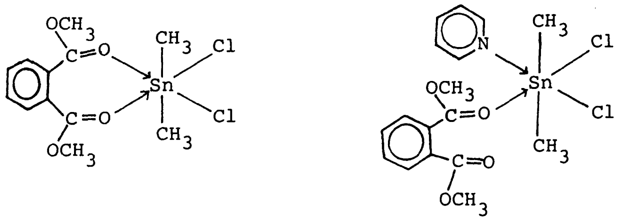
where, $\Delta S^0{}_{\mathrm{AB}}(\mathrm{gas}) = S^0{}_{\mathrm{AB}}(\mathrm{gas}) - S^0{}_{\mathrm{A}}(\mathrm{gas}) - S^0{}_{\mathrm{B}}(\mathrm{gas})$, $\Delta S^0{}_{\mathrm{ABL}}(\mathrm{gas}) = S^0{}_{\mathrm{ABL}}(\mathrm{gas}) - S^0{}_{\mathrm{AB}}(\mathrm{gas}) - S^0{}_{\mathrm{L}}(\mathrm{gas})$, $\Delta S^0{}_{\mathrm{AL}}(\mathrm{gas}) = S^0{}_{\mathrm{AL}}(\mathrm{gas}) - S^0{}_{\mathrm{A}}(\mathrm{gas}) - S^0{}_{\mathrm{L}}(\mathrm{gas})$, and $\Delta S^0{}_{\mathrm{AB2}}(\mathrm{gas}) = S^0{}_{\mathrm{AB2}}(\mathrm{gas}) - S^0{}_{\mathrm{AB}}(\mathrm{gas}) - S^0{}_{\mathrm{B}}(\mathrm{gas})$. Then, Eqs. 14 and 15 turn out to be:

$$\Delta S^0(\mathrm{soln})_1 = (1+a)\Delta S^0{}_{\mathrm{AB}}(\mathrm{gas}) + n\Delta S^0{}_{\mathrm{ABL}}(\mathrm{gas}) - m\Delta S^0{}_{\mathrm{AL}}(\mathrm{gas}) + (m-n-1)(b + aR\ln 24.5), \tag{22}$$

$$\Delta S^0(\mathrm{soln})_2 = (1+a)\Delta S^0{}_{\mathrm{AB2}}(\mathrm{gas}) - n\Delta S^0{}_{\mathrm{ABL}}(\mathrm{gas}) + (n-1)(b + aR\ln 24.5). \tag{23}$$

The rearrangement of Eqs. 22 and 23 gives these expressions for m and n:

$$m = \frac{\Delta S^0(\mathrm{soln})_1 - (1+a)\{\Delta S^0{}_{\mathrm{AB}}(\mathrm{gas}) + n\Delta S^0{}_{\mathrm{ABL}}(\mathrm{gas})\} + (n+1)(b + aR\ln 24.5)}{-(1+a)\Delta S^0{}_{\mathrm{AL}}(\mathrm{gas}) + (b + aR\ln 24.5)}, \tag{24}$$



[$Me_2SnCl_2 \cdot DMP$] [$Me_2SnCl_2 \cdot Py \cdot DMP$]

Fig. 3. Structures assumed as the strongly solvated species.

$$n = \frac{\Delta S^0(\mathrm{soln})_2 - (1+a)\Delta S^0{}_{\mathrm{AB2}}(\mathrm{gas}) + (b + aR\ln 24.5)}{-(1+a)\Delta S^0{}_{\mathrm{ABL}}(\mathrm{gas}) + (b + aR\ln 24.5)}, \tag{25}$$

Therefore, n can be determined from Eq. 25, the value of which will enable m to be determined from Eq. 24. In making these calculations, $\Delta S^0(\mathrm{soln})_1$ and $\Delta S^0(\mathrm{soln})_2$ can be replaced by experimental values, but definite structures need be assigned to AL and ABL in order to calculate the entropy of these strongly solvated species. The structures shown in Fig. 3 were assumed for the case of L=DMP. The molecular structures of pyridine[15] and DMP were taken to be the same in both free and complexed states, and also the structural data of the $Me_2SnCl_2 \cdot$(*N*,*N*-dimethylformamide)$_2$[18] complex was used for the Sn····O=C distance and angle in $Me_2SnCl_2 \cdot$DMP. The structure of DMP was determined on the basis of the standard bond lengths[19] and angles for sp^2 and sp^3 hybridization. Calculations were also performed under somewhat different structures for the complexes (e.g., a cis configuration with regard to the two Cl groups in $Me_2SnCl_2 \cdot$(pyridine)$_2$ or $Me_2SnCl_2 \cdot$pyridine$\cdot$DMP), but the resulting entropies showed no discernible changes. In this way, $m=1.34$ and $n=0.70$ were obtained. This means that, when judged from the point of view of the entropy change, a free molecule of Me_2SnCl_2 is solvated by ca. 1.3 molecules of DMP, half of which are released when the 1 : 1 and 1 : 2 complexes are each formed with pyridine. As for the molecular structures of these strongly solvated species, the structures shown in Fig. 3 can be imagined. However, in the case of the solvated $Me_2SnCl_2 \cdot$pyridine complex, the solvent (DMP) molecule needs be either in a rapid exchange between the solvated state and a released state or in a rather weak solvation to make the averaged solvation number equal to 0.7. This number is probable since the tin atom is already coordinated by a strong base of pyridine before solvation occurs with a relatively weak base of DMP. Also, $Me_2SnCl_2 \cdot$DMP is solvated by an extra 0.3 molecule of DMP, on the average. This situation may be explained by a partial contribution from a solvated structure where two DMP molecules are involved.

iii) An Effect of the Entropy of Vibration in the Solvation Model. New vibrational degrees of freedom contribute to the entropy of reaction when new chemical bonds are formed between the two participant molecules, leading to a complex. This number is six when one bond is formed to make a new complex, but such a vibrational term has been reported to be nontrivial from a comparison of the calculated sum of the translational and rotational entropies with the experimental total entropy for several gas-phase reactions.[20)] When a linear relationship is assumed between the vibrational term, $\Delta S^0{}_{\mathrm{vib}}(\mathrm{gas})$, and $\log \mu$ according to Ref. 20, μ being the reduced mass of the complex, Eq. 26 is obtained from the data in the reference, excluding the complexes with a cyclic structure:

$$\Delta S^0{}_{\mathrm{vib}}(\mathrm{gas}) = 35.4 \log \mu - 20.4. \tag{24}$$

When this equation was used to estimate the vibrational terms in $\Delta S^0(\mathrm{gas})_1$, $\Delta S^0(\mathrm{gas})_2$, $\Delta S^0{}_{\mathrm{AL}}(\mathrm{gas})$, and $\Delta S^0{}_{\mathrm{ABL}}(\mathrm{gas})$, the latter values decreased by ca. 16% in absolute value and m=1.25 and n=0.65 resulted. That is, the conclusion given in this section does not change considerably even if the vibrational term is included in the calculation.

Appendix 1

Correction of Eq. 8 for the difference in standard states.

In Eq. 8, ΔS^{S} corresponds to the entropy changes of a gas at unit atm, and a and b are constants, which are determined from the entropies and other physical properties of the solvent. In the present study, the equilibrium constant is given in units of mol dm^{-3}: hence, $\Delta S^0(\mathrm{soln})$ and $\Delta S^0(\mathrm{gas})$ are given on that basis also, the standard state corresponding to a unit mol dm^{-3}. As this contrast, the third-law entropy, $S^0{}_{298}(\mathrm{g})$, is expressed relative to a standard state of 25 °C and 1 atm. Therefore, the gas-phase entropy, $S^0(\mathrm{gas})$, in Eq. 6, which corresponds to a unit mol dm^{-3} at 25 °C, is connected with the $S^0{}_{298}(\mathrm{g})$ by the following equation under an ideal gas assumption:

$$S^0(\mathrm{gas}) = S^0{}_{298}(\mathrm{g}) - R \ln 24.5. \tag{A1}$$

Hence, Eq. 8 is converted to Eq. A2 for the present purposes:

$$\Delta S^{\mathrm{s}} = a\,S^0(\mathrm{gas}) + b + aR \ln 24.5, \tag{A2}$$

since ΔS^{S} itself does not change on this conversion of the standard state. The substitution of Eqs. 6 and A2 into Eq. 7 leads to Eq. 9.

Appendix 2

Calculation of entropies according to molecular statistical thermodynamics.

The entropy of a molecule is composed of several parts (translational, rotational, vibrational, and internal-rotational ones); i.e., $S=S_{\mathrm{tr}}+S_{\mathrm{rot}}+S_{\mathrm{vib}}+S_{\mathrm{ir}}$. Each part relates to the physical properties of the molecule:[21)]

$$S_{\mathrm{tr}} = R(1.5\ln M + 2.5\ln T - \ln P - 1.1650), \tag{A3}$$

$$S_{\mathrm{rot}} = R(0.5\ln I_{\mathrm{A}} I_{\mathrm{B}} I_{\mathrm{C}} + 1.5\ln T - \ln\sigma - 2.7106), \tag{A4}$$

$$S_{\mathrm{rot}} = R(\ln I + \ln T - \ln\sigma - 2.1886) \text{ for linear molecules,} \tag{A5}$$

$$S_{\mathrm{vib}} = R\sum_i[(\theta_i/T)\exp(-\theta_i/T)/\{1-\exp(-\theta_i/T)\} - \ln\{1-\exp(-\theta_i/T)\}], \qquad \theta_i = h\nu_i/k, \tag{A6}$$

$$S_{\mathrm{ir}} = S_{\mathrm{fir}} - (S_{\mathrm{f}} - S), \tag{A7}$$

where R is the gas constant, M is the molecular weight, T is the absolute temperature, h is Planck's constant, k is the Boltzmann constant, ν_1 is the wavenumber, and P is the pressure in atm, equal to 1/24.5 atm for an ideal gas of unit mol dm^{-3} at 25 °C. $I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}}$ in Eq. A4 is the product of the principal moments of inertia and is calculated simply by using the moments of inertia with regard to any Cartesian axes x, y, or z, which go through the center of gravity:

$$I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}} = \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix} \tag{A8}$$

where $I_{xx}=\sum m_i(y_i^2+z_i^2)$ and $I_{xy}=\sum m_i x_i y_i$.

σ is the symmetry number, which is equal to the number of rotational operations by which the molecule remains the same as before when all the atoms are numbered. Thus, the accurate calculation of entropies is feasible according to the above formalism. Some computer programs have also published,[22)] in which several refinements such as "vibrational anharmonicity" are included.

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