The Solution Chemistry of Organotin Compounds. IV. Thermodynamic Parameters of the Complex Formation between $MeSnCl_3$ and Alkyl Sulfoxides Determined from Titration Calorimetry

Hideaki FUJIWARA,* Fumihiko SAKAI, Akio KAWAMURA, Naoto SHIMIZU, and Yoshio SASAKI
Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamada-Oka, Suita, Osaka 565
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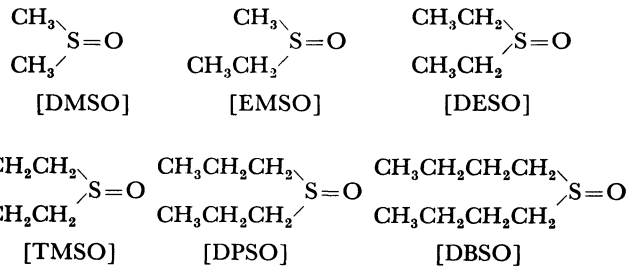
Calorimetric titration data have been analyzed to determine thermodynamic parameters of the interacting system. The system studied is $MeSnCl_3$ plus dialkyl sulfoxide in CH_2Cl_2 and a nonlinear least squares method is utilized to simulate the titration curve. The 1:1 and 1(acid):2(base) complexes are found to coexist in solution, and the effect of alkyl chain length on the complex formation is examined. The complex formation proceeds most favorably under the total carbon number of four, and inductive and steric effects are considered to operate in a compensating way. Entropy changes on the reactions are discussed with the aid of molecular theory of thermodynamic functions, and a new method is suggested that affords the number of solvent molecules released on the complex formation.

Thermodynamic parameters are essential for the discussion of molecular interactions such as complex formation between acids and bases. These parameters are most often determined from the van't Hoff plot after measuring equilibrium constants at different temperatures.[1] However, titration calorimetry may be best suited for such studies, because those parameters are determined precisely and readily from the direct observation of the heat evolved or absorbed on reaction. For the analysis of such titration data it is frequently encountered that more than one type of reaction needs be dealt with concurrently.[2] This arises from the fact that concentration of solute studied is relatively high and the infinite dilution approximation is not applicable. This seems to be a main reason of rather small number of reports regarding the titration calorimetry. Hitherto, a trial and error method has been reported[3] and applied[4] to the complex formation of several organometallic compounds with bases. The authors have established a simulation program for the analysis of concentration dependence of NMR parameters, which optimizes adjustable parameters by means of a nonlinear least squares method under the several types of equilibrium.[5-7] This program is extended in this paper to apply to the titration calorimetry and the complex formation of $MeSnCl_3$ with dialkyl sulfoxides is examined. The sulfoxides used are as follows:



Experimental

An isothermal isoperibol titration calorimeter Model 550 (Tronac Inc.) was used under the isothermal mode at 25 °C. Calibration of the energy equivalent of the reaction solution is unnecessary under this mode. Total sample volume was 50.0 ml and about 2 ml of titrant was added in increment of 0.1315 ml. Solution of the base was added titrimetrically to the solution in vessel containing the tin compound by *ca.* 0.05 mol dm^{-3}. Heat necessary to compensate for the reaction enthalpy was measured in 15 s. after an addition of the titrant. Titration and the subsequent data collection were controlled by the Programmer C-930. Heat of solution of the base was also measured by adding the titrant to the solvent without tin compound in the same manner. Differential heat of these two runs was set to the effective heat of complex formation and analyzed by the computer program. Errors were also estimated in the program for each parameter as equal to the 95% confidence range which makes the σ^2(see Eq. 4 below) larger by 1.96 times, and they were also tested by repeated experiments (more than 3 runs).

$MeSnCl_3$ was synthesized from Me_2SnCl_2 using catalytic reagents[8] and sublimed at *ca.* 30 °C after distillation. EMSO, DESO, and DPSO were synthesized from the corresponding sulfides according to a scheme:[9]

$$R_1R_2S + NaIO_4 \longrightarrow R_1R_2SO + NaIO_3$$

Sulfoxides were dried over BaO and distilled under reduced pressure after decantation. All operations of the purification and sample preparation were done in dry boxes.

Analysis of Calorimetric Titration Data

Effective heat of the complex formation determined experimentally q_{expt} is expressed as the differential heat between the titration q_{titrn} and the dilution q_{diln} (Fig. 1): $q_{expt}=q_{titrn}-q_{diln}$. The heat q in each incremental step in the succesive titration experiment can be integrated to give the integrated heat Q, for which following eq holds after i-th step of titration.

$$Q_{expt,i} = Q_{titrn,i} - Q_{diln,i} \quad (1)$$

On the other hand, integrated heat of the complex formation such as in Eq. 2 is calculated according to Eq. 3:

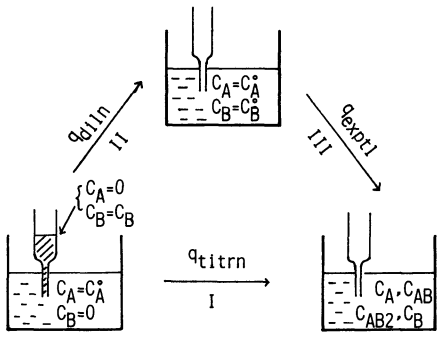


Fig. 1. Heat of titration (step I) can be divided into two parts, *i.e.*, heat of dilution q_{diln} in step II and heat of complex formation q_{exptl} in step III: $q_{titrn}=q_{diln}+q_{exptl}$.

$$\left.\begin{array}{ll} A + B = AB & K_1, \Delta H_1^\circ \\ AB + B = AB_2 & K_2, \Delta H_2^\circ \end{array}\right\}, \quad (2)$$

$$Q_{calcd,i} = (\Delta H_1^\circ \cdot C_{AB} + \Delta H_2^\circ \cdot C_{AB_2}) \cdot V_i, \quad (3)$$

where ΔH_1° and ΔH_2° are the molar enthalpies for the reactions in Eq. 2, and V_i is the volume of solution, *i.e.*, $V_i=V_0+i\cdot\Delta V$, V_0 being the initial volume of the titrated solution and ΔV the incremental volume added in each step. Molarity of the complexes AB and AB_2, C_{AB} and C_{AB_2}, are obtained by solving Eqs. of the chemical equilibrium. In this way, the problem is how to reproduce well the experimental data (Eq. 1) by adjusting K_1, K_2, ΔH_1°, and ΔH_2° in Eq. 2. For this purpose, standard deviation σ as expressed by Eq. 4 needs be minimized by optimizing the four parameters, and to this end a least squares method is surely superior than a trial and error method.

$$\sigma = [\sum_{i=1}^{n} (Q_{expt,i} - Q_{calcd,i})^2/(n-p)]^{1/2} \quad (4)$$

In above equation n is the total number of titration steps and p is the number of adjustable parameters. In our previous case of NMR titration experiments,[5-7] chemical shift or coupling constant (ϕ) is expressed as $\phi_{calcd}=(\phi_A\cdot C_A+\phi_B\cdot C_B+\phi_{AB_2}\cdot C_{AB_2})/C_A^\circ$ instead of Eq. 3 in the present case. Therefore, the method is easily modified to the present case.[10]

Among various kinds of nonlinear least squares analysis, we have adopted a version of so-called DFP (Davidon-Fletcher-Powell) method, which belongs to a variable metric method. This algorithm is widely accepted as one of the most sophisticated search technique, and it appears to be independent of the number of variables involved.[11] The superiority of the DFP method itself is also approved in the MO calculation with geometrical optimization[12] where a large number of variables are usually included but the derivatives of the minimized function are available. However, when we utilized a version of this algorithm, some drawbacks were encountered. A search process failed frequently in improving the variable parameters when started from initial values far from the final ones under the three- or four-parameter simulation. In the original DFP algorithm, an updating formula 5 is used to find a Hessian matrix

$$H_{j+1} = H_j + \delta\cdot\delta^T/\delta^T\cdot\gamma - H_j\gamma\cdot\gamma^T H_j/\gamma^T H_j\gamma, \quad (5)$$

appropriate for the next step. Fletcher[13] demonstrated that use of this equation together with the linear search is unsuccessful in special circumstances and proposed an improved algorithm where the updating formula is switched appropriately between Eq. 5 and the complementary one:

$$H_{j+1} = (I-\delta\gamma^T/\delta^T\gamma)H_j(I-\gamma\delta^T/\delta^T\gamma) + \delta\delta^T/\delta^T\gamma. \quad (6)$$

In the present study the improved algorithm is incorporated and the failure of improving parameters stated above is circumvented.

Results and Discussion

Calorimetric titration curves are depicted in Fig. 2

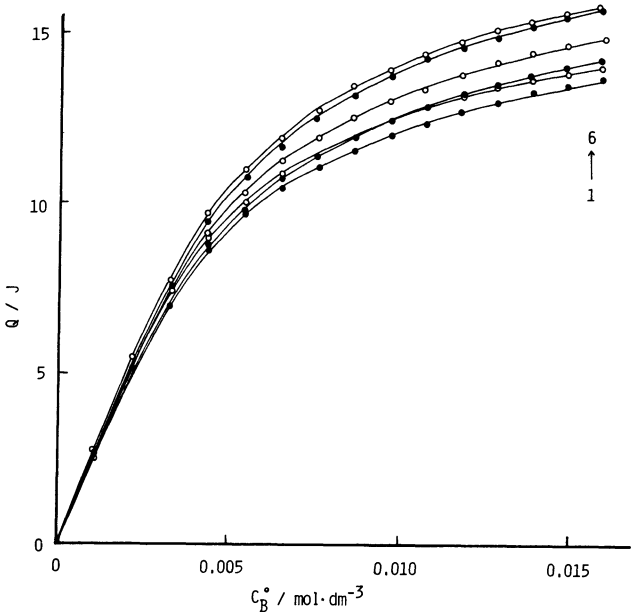


Fig. 2. Calorimetric titration curves for the $MeSnCl_3$ plus alkyl sulfoxide systems in CH_2Cl_2.
Solution of sulfoxide is added titrimetrically into that of $MeSnCl_3$ at 25 °C. Sulfoxides used are: DMSO(1), EMSO(3), DESO(5), TMSO(6), DPSO(4), DBSO(2). C_B° is the initial concentration of sulfoxide and Q the integrated heat of complex formation.

Table 1. Analysis of calorimetric titration data of $MeSnCl_3$ plus DMSO system under some models of chemical equilibrium

Model		K/dm^{3}mol^{-1}	ΔH°/kJ mol^{-1}	σ/J
I	A+B=AB	log K=2.42	ΔH°=−90.8	0.30
II	A+2B=AB_2	log K=7.51	ΔH°=−81.3	1.79
III	A+B=AB	log K_1=3.83	ΔH_1°=−48.0	0.03
	AB+B=AB_2	log K_2=2.00	ΔH_2°=−40.1	

TABLE 2. EQUILIBRIUM AND THERMODYNAMIC PARAMETERS DERIVED FROM CALORIMETRIC TITRATION DATA FOR $MeSnCl_3$ PLUS SULFOXIDE IN CH_2Cl_2 AT 25 °C[a)]

Base	log K_1	log K_2	$-\Delta H_1^\circ$	$-\Delta H_2^\circ$	$-\Delta S_1^\circ$	$-\Delta S_2^\circ$	σ[b)]
DMSO	3.83±0.03	2.00±0.01	48.0±0.2	40.1±0.3	87.7±1.2	96.2±1.1	0.03
EMSO	3.93±0.04	2.18±0.01	47.8±0.3	42.1±0.2	85.2±1.8	99.5±0.8	0.03
DESO	4.13±0.04	2.31±0.01	48.5±0.2	45.1±0.2	83.6±1.5	107.6±0.8	0.03
TMSO	4.13±0.05	2.34±0.01	50.3±0.3	43.5±0.2	89.8±2.0	101.1±0.9	0.04
DPSO	4.12±0.04	2.21±0.01	49.1±0.2	42.3±0.2	85.8±1.4	99.7±0.8	0.03
DBSO	3.94±0.05	2.14±0.01	48.7±0.3	38.2±0.2	88.0±1.9	87.1±0.9	0.04

a) The subscript 1 is used for the reaction of A+B=AB and 2 is for that of AB+B=AB_2. Units used are $dm^3\,mol^{-1}$ for K, $kJ\,mol^{-1}$ for $\Delta H°$, and $J(K\,mol)^{-1}$ for $\Delta S°$. b) Standard deviation between the experimental and recalculated heat of reaction in unit of J.

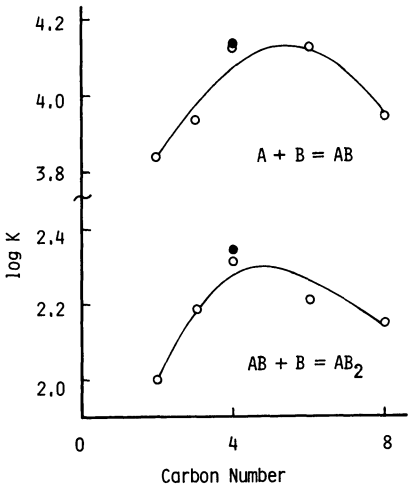


Fig. 3. Dependence of log K on the carbon number of sulfoxide.
●: Indicates data point of TMSO.

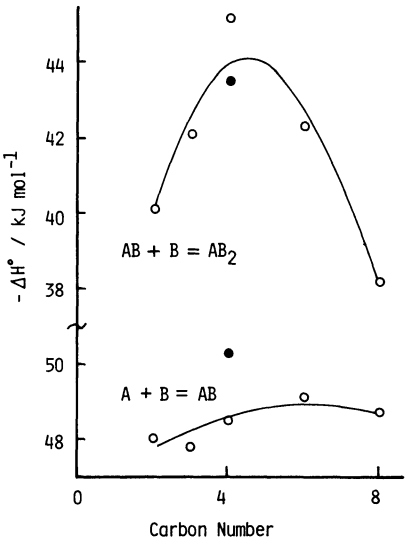


Fig. 4. Dependence of $-\Delta H°$ on the carbon number of sulfoxide.
●: Indicates data point of TMSO.

for the $MeSnCl_3$ plus sulfoxide systems in CH_2Cl_2. Analysis of such experimental data basing on a few models of chemical equilibrium which may occur is

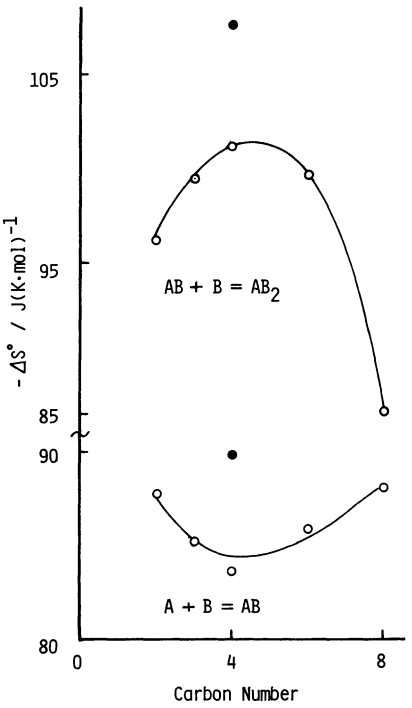


Fig. 5. Dependence of $-\Delta S°$ on the carbon number of sulfoxide.
●: Indicates data point of TMSO.

compared in Table 1 for the DMSO system typically. It is clear that 1:1 and 1(acid):2(base) complexes are formed in solution. Analysis under the model III in Table 1 is summarized in Table 2 for all the systems studied here, including error limit estimated from the program and repeated runs whichever is larger. Equilibrium constants, enthalpies, and entropies are plotted in Fig. 3 to 5 against the total number of carbon atoms in the alkyl groups in sulfoxide. It is interesting to note that the complexes AB and AB_2 are most stable for the sulfoxide with the carbon number of four (Fig. 3). For the 2nd step of the complex formation, $-\Delta H°$ and $-\Delta S°$ also show the similar dependency on the carbon number (Figs. 4 and 5). This means that the enthalpy term contributes positively but the entropy term negatively in the 2nd step. That is, the dependency comes out of the enthalpy term. Introduction of a methylene group into the substituent of the functional

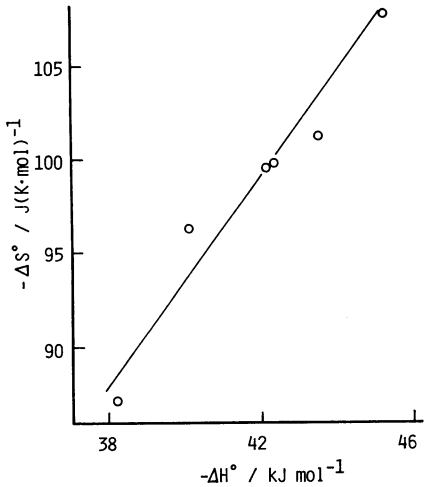


Fig. 6. Enthalpy-entropy compensation relation for the reaction of AB+B=AB$_2$. A=MeSnCl$_3$ and B=alkyl sulfoxide.

S=O group will increase the electron-donating ability of the functional group through an effect such as called "hyperconjugation." On the contrary, increase in the number of methylene groups will induce the steric hindrance, weakening the chemical bond between Sn and S=O.[14] This steric effect is, however, not such a strong and specific one as to disturb the enthalpy-entropy compensation relation as revealed in Fig. 6 for the 2nd step.

In contrast to the 2nd step of the complex formation, the results are not straightforwardly explained in the 1st step. That is, the entropy change is oppositely dependent on the carbon number (Fig. 5), and the enthalpy change is not clearly dependent on this number (Fig.4).[15] The 1st step of the complex formation is considered entropy-dependent, because the trend in reactivity in Fig. 3 is consistent with that in the entropy term and because difference in the enthalpy term is small among the sulfoxides listed in Fig. 4. Only an exception is TMSO, for which enhanced reactivity surely comes from the enthalpy term.

Entropy change on the complex formation is generally expressed by the difference in standard entropies of the components, *e. g.*, $\Delta S^\circ_{calcd}=S^\circ_{AB}-(S^\circ_A+S^\circ_B)$ for A+B=AB. The entropies can be calculated from molecular theory of thermodynamic functions, and it is composed of several contributions of translational, rotational, vibrational, and internal rotational parts, *i.e.*, $S^\circ=S^\circ_{tr}+S^\circ_r+S^\circ_v+S^\circ_{fir}-(S_f-S)$.[16] This value of ΔS°_{calcd} is considered to correspond to the gas-phase value of ΔS°. Such calculations have been applied precisely to various chemical reactions and equilibria to approve the third-law of thermodynamics, and the results are also useful for the discussion of internal motions in the relevant substances.[17] Although similar discussion should be applicable to the case of complex formation,

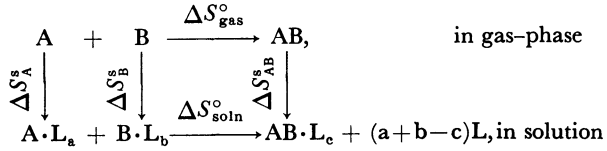


Fig. 7. Entropy changes related to the complex formation in gas phase and in solution.
The species A, B, and AB are assumed solvated weakly by the solvent L, and the numbers of solvation are a, b, and c, respectively, the related entropies of solution being denoted by ΔS^s's.

those studies are very limited in number.[18] This is probably because only the enthalpy change is interested and the entropy one is overlooked. However, if the entropy is measured carefully in gas phase, the result can be compared with the calculation. As an example, $\Delta S^\circ=-166.9$ J K^{-1} mol^{-1} determined for the complex formation of B(CH$_3$)$_3$ with NH$_3$ in gas phase at 100° C[19] can be interpreted by the moment of inertia and vibration-spectral data of each species, calculated value being -168.9 J K^{-1} mol^{-1}.[20]

For the present case of MeSnCl$_3$ plus sulfoxides, experimental values of ΔS° are measured in solution and the values will not correspond with the calculated ones, and also exact calculations of the vibrational and the internal rotational entropies are prevented by a lack of necessary physicochemical constants. However, it is interested to compare the experimental values with the calculated ones which include predominant parts, *i.e.*, translational and rotational ones, of the entropies. The calculated value is -253.1 J K^{-1} mol^{-1} against the observed one of -87.7 for A+B=AB, and is -259.8 against -96.2 for AB+B=AB$_2$ when B is DMSO. Since the vibrational and the internal rotational contributions are very small for the simple molecule such as DMSO, the entropy changes observed in CH$_2$Cl$_2$ are said to be about 1/3 of the net entropy changes in gas phase. If, as in a model calculation described in the previous paper,[21] DMSO is assumed to be solvated by one molecule of CH$_2$Cl$_2$ and the latter be released on the complex formation, the entropy changes are reduced in absolute value to -19.2 for A+BS=AB+S and -25.5 for AB+BS=AB$_2$+S. Therefore, experimental entropies can be said to indicate the solvation number of 0.7 or the release of solvent molecules by 0.7 mol on the complex formation of both A+B=AB and AB+B=AB$_2$. In these calculations entropies are also estimated by assuming different geometries of the complexes as well as the solvated species, but the result does not change considerably. This situation may be discussed more precisely by a thermodynamic cycle as shown in Fig. 7. The entropy change in solution ΔS°_{soln} is expressed as follows:

$$\Delta S^\circ_{soln} = \Delta S^\circ_{gas} + (\Delta S^s_{AB}-\Delta S^s_A-\Delta S^s_B) + (a+b-c)S^\circ_L \quad (7)$$

where S°_L means the entropy of solvent.[22] Therefore,

a+b−c, the number of solvent molecules released on the complex formation, is seen to be obtained from the Eq.:

$$a+b-c = \{\Delta S^{\circ}_{soln} - \Delta S^{\circ}_{gas} - (\Delta S^{s}_{AB} - \Delta S^{s}_{A} - \Delta S^{s}_{B})\}/S^{\circ}_{L}. \quad (8)$$

This number may be interpreted as reflect the solvation number judged from the entropy effect. It is, however, not easy to estimate exactly the entropy of solution for the complex, *i. e.*, ΔS^{s}_{AB}. Usually ΔS°_{gas} is more negative than ΔS°_{soln} as is shown in above case. Therefore, if the entropies of solution ΔS^{s}'s are smaller than ΔS°_{gas} in absolute value or if ΔS^{s}_{AB} almost cancells out with $\Delta S^{s}_{A}+\Delta S^{s}_{B}$, above equation is simplified as:

$$a+b-c = (\Delta S^{\circ}_{soln} - \Delta S^{\circ}_{gas})/S^{\circ}_{L}. \quad (9)$$

From this equation and by putting ΔS°_{calcd} in place of ΔS°_{gas}, a+b−c is calculated as 0.6 for $MeSnCl_3$ plus DMSO in CH_2Cl_2, in consistent with above preliminary calculations. In this way, entropy changes in the complex formation is expected to give a number of solvent molecules released on the reaction. Further study is under way including other systems.

References

1) M. D. Joesten and L. J. Schaad, "Hydrogen Bonding," Marcel Dekker, New York, 1974.

2) For a simple case of A+B=AB, see: T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 5730 (1966).

3) Y. Farhangi and D. P. Graddon, *J. Organomet. Chem.*, **87**, 67 (1975).

4) D. P. Graddon and B. A. Rana, *J. Organomet. Chem.*, **136**, 19 (1977).

5) H. Fujiwara, F. Sakai, and Y. Sasaki, *J. Phys. Chem.*, **83**, 2400 (1979).

6) H. Fujiwara, F. Sakai, M. Takeyama, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **54**, 1380 (1981).

7) H. Fujiwara, F. Sakai, and Y. Sasaki, *J. Chem. Soc. Perkin Trans. 2*, **1983**, 11.

8) H. W. Jung, R. Maul, S. Kintopf, N. Kloss, and R. Knapp, Ger. Patent: 2437586 (1975), also see *Chem. Abstr.*, **83**, 1040n (1975).

9) N. J. Leon and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

10) Activity coefficients were assumed to be unity because of the lack of necessary data for the alkyl sulfoxides. They would be easily incorporated into the computer program by expressing activities as an appropriate function of the analytical concentration.

11) D. A. Pierre, "Optimization Theory with Applications," John Wiley, New York, (1969), p. 320.

12) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975) and M. J. S. Dewar and W. Thiel, *ibid.*, **99**, 4907 (1977). Fletcher's improvement is not included therein.

13) R. Fletcher, *Compt. J.*, **13**, 317 (1970).

14) That such a steric effect surely acts when a carbon number exceeds two in each alkyl substituent may be seen from a molecular model of the complex AB_2 assuming a bent form for S=O···Sn (angle=≈120°). Such a bent form has been observed in some tin halide complexes with DMSO and DMF: L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin, and V. S. Petrosyan, *Zhur. Strukt. Khim.*, **19**, 109 (1978).

15) The authors suggest that a weak solvation of the complex AB has obscured a clear dependency.

16) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945.

17) S. C. Schumann and J. G. Aston, *J. Chem. Phys.*, **6**, 480 (1938) and the references cited therein.

18) Only a case known to the authors is an ion-pair formation: R. Fujishiro, G. Wada, and R. Tamamushi, "Yoeki no Seishitsu. II," (in Japanese), Tokyo-Kagaku-Dojin, (1968) p. 136, and references cited therein.

19) H. C. Brown, "Boranes in Organic Chemistry," Cornell Univ. Press, (1972).

20) If methyl groups become restricted in rotation in the complex, the calculated value is reduced by an amount of $-(S_f-S)$ for these groups, and if the NH_3 fragment can rotate around the N-B bond, it is increased by $S_{fir}-(S_f-S)$. But these effects are not included here because of a lack of necessary data.

21) Part III, H. Fujiwara, F. Sakai, Y. Mikawa, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **58**, 1741 (1985).

22) S°_{L}=270.3 $J\,K^{-1}\,mol^{-1}$ for CH_2Cl_2 from: S. W. Benson, "Thermochemical Kinetics," John Wiley, New York, (1968), Japanese ed by H. Sakurai, T. Fueno, and M. Kira, Hirokawa, Tokyo.