^{1}H NMR Studies on the Interactions of Acyclic Polyethers with Dimethyltin Dichloride in Aromatic Solvents[1)]

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(Received March 2, 1981)

The interactions between various acyclic polyethers, $RO(CH_2CH_2O)_nR'$(R, R'=CH_3, Ph), and dimethyltin dichloride (DMTC) in aromatic solvents have been studied by means of ^{1}H NMR spectroscopy. On the basis of a continuous variation method, the formation of the 1 : 1 complexes between glymes, $CH_3O(CH_2CH_2O)_nCH_3$ (n=2, 3, 4), and DMTC was revealed in benzene. The $^2J(^{119}Sn-CH_3)$ values suggested distorted *trans*-octahedral configurations for these complexes. From the statistical consideration of stability constants, it was found that the coordination occurred virtually through neighboring two oxygen atoms in these complexes. DMTC gave the complexes of both 1 : 1 and 1 : 2 glyme/DMTC stoichiometry with glymes (n=5, 6) in benzene and with all glymes employed here in toluene and 1-chloronaphthalene. Coexistence of 1 : 1 and 1 : 2 species was also encountered for $PhO(CH_2CH_2O)_nCH_3$ (n=3, 4, 5), whereas no appreciable interaction was observed between $PhO(CH_2CH_2O)_nPh$ (n=2, 3, 4) and DMTC. On the basis of these observations, the additional formation of the 1 : 2 complexes was assumed to be caused by the bulkiness of polyethers.

With recent development of the crown ether chemistry, much attention has also been paid on the metal complexes of acyclic polyethers.[2)] Structural analysis of these complexes in the solid state[2)] and their thermodynamic properties in solution[3)] have been extensively studied. However, it is rather limited to elucidate their behavior, especially their configuration, in solution, because metals employed in these studies were mostly inorganic ions. The structure of some fluorenyl metal complexes of polyethylene glycol dimethyl ethers (glymes) in solution has been investigated by means of ^{1}H NMR[4,5)] and optical spectroscopies.[5)] Coordinating abilities of glymes towards the Na^+ ion have been discussed from kinetical point of view using ^{23}Na NMR spectra.[6)] More recently, ^{1}H NMR spectra of metal complexes with polyethers containing aromatic terminal groups have been reported.[7)]

Molecular complexes of methyltin(IV) halides have been studied for a long time, since their configurations in solution can be deduced easily from their ^{1}H NMR spectra.[8)] Therefore, it seems probable that NMR studies on the polyether/methyltin(IV) halides systems afford various informations on these complexes in solution. In addition, methyltin(IV) halides, unlike the naked metal ions studied so far, possess four substituents attached to the central metal atom. Accordingly, the interactions of methyltin(IV) halides with polyethers are expected to be sterically different from those of inorganic metal ions.

In this paper are presented the results of ^{1}H NMR studies on the interactions of various acyclic polyethers, $RO(CH_2CH_2O)_nR'$ (R, R'=CH_3, Ph), with dimethyltin dichloride (DMTC) in some aromatic solvents.

Experimental

Commercially available DMTC was purified by sublimation. DiG, TrG, and TetG[9)] were of reagent grade and distilled from $LiAlH_4$ before use. The preparative methods for PeG,[10)] HeG,[10)] and $PhO(CH_2CH_2O)_nPh$[3)] have been reported.

Preparation of $PhO(CH_2CH_2O)_nCH_3$. n=*2*: The procedure for this compound is as follows;

$$(ClCH_2CH_2)_2O \xrightarrow{+\frac{1}{2}PhONa} Ph(OCH_2CH_2)_2Cl \xrightarrow[+NaI]{+CH_3ONa} PhO(CH_2CH_2O)_2CH_3.$$

To a suspension of NaH (4.8 g, 0.2 mol) in 150 cm^3 of DMF was added phenol (18.8 g, 0.2 mol) in DMF (27 cm^3) with stirring and the mixture was heated at 80 °C for 4 h. After cooling, the mixture was combined with $(ClCH_2CH_2)O$ (57.2 g, 0.4 mol) and heated at 80 °C for 6 h. The reaction mixture was combined with benzene and shaken twice with 0.2 mol dm^{-3} NaOH and with water for several times. The organic layer was dried over sodium sulfate. Evaporation of solvent and distillation gave $Ph(OCH_2CH_2)_2Cl$ (24.4 g, 61%); bp, 104—107 °C (27 Pa). $Ph(OCH_2CH_2)_2Cl$ (24.4 g, 122 mmol) and NaI (33.6 g, 224 mmol) in 100 cm^3 of acetone were heated under reflux for 41 h. After filtration of NaCl and evaporation of acetone, the product was treated with an ether–water mixture. Ether was evaporated and resulting crude $Ph(OCH_2CH_2)_2I$ (29.3 g, 82%) was used in the next reaction without further purification. To 50 cm^3 of methanol was added 1.4 g (60 mmol) of Na and subsequently $Ph(OCH_2CH_2)_2I$ (14.6 g, 50 mmol). The mixture was heated under reflux for 9 h, and combined with water and ether. The organic layer was dried over sodium sulfate and evaporated to leave a yellow oil which was chromatographed on a silica gel column (hexane–ether 10 : 1) to give $PhO(CH_2CH_2O)_2CH_3$ (4.0 g, 41%): ^{1}H NMR (CCl_4) δ=3.23 (s, 3H, CH_3), 3.40—4.07 (m, 8H, CH_2), and 6.58—7.23 (m, 5H, aromatic), high-resolution mass spectrum, 196.2437 (Calcd for $C_{11}H_{16}O_3$, 196.2456).

n=*3*: This compound was prepared by an analogous method for n=2 employing $CH_3OCH_2CH_2ONa$ in place of CH_3ONa: ^{1}H NMR (CCl_4) δ=3.23 (s, 3H, CH_3), 3.43—4.06 (m, 12H, CH_2), and 6.33—7.20 (m, 5H, aromatic), high-resolution mass spectrum, 240.2971 (Calcd for $C_{13}H_{20}O_4$, 240.2986).

n=*4*: This compound was prepared by an analogous method for n=3 employing $(ClCH_2CH_2OCH_2)_2$ in place of $(ClCH_2CH_2)_2O$: ^{1}H NMR (CCl_4) δ=3.23 (s, 3H, CH_3), 3.40—4.07 (m, 16H, CH_2), 6.60—7.20 (m, 5H, aromatic), high-resolution mass spectrum, 284.3511 (Calcd for $C_{15}H_{24}O_5$, 284.3516).

n=*5*: The procedure for this compound is as follows;

$$(HOCH_2CH_2OCH_2CH_2)_2O \xrightarrow{+PBr_3,\ C_5H_5N} (BrCH_2CH_2OCH_2CH_2)_2O \xrightarrow{+\frac{1}{2}PhONa} Ph(OCH_2CH_2)_4Br \xrightarrow{+CH_3OCH_2CH_2ONa} PhO(CH_2CH_2O)_5CH_3.$$

To 100 cm^3 of benzene solution containing PBr_3 (189 g, 0.7 mol) and pyridine (32 g, 0.4 mol), tetraethylene glycol (194 g, 1.0 mol) was added with stirring at 0 °C for a period of 4 h. After completion of addition, the mixture was kept on stirring for 72 h at room temperature and extracted with a benzene–water mixture. Drying and evaporation of the organic layer gave crude $(BrCH_2CH_2OCH_2CH_2)_2O$ (206 g, 76%), which was subjected to the reaction with PhONa (0.38 mol) in 100 cm^3 of DMF. After heating at 80 °C for 7 h, the product was poured into a benzene–water mixture. Benznene layer was shaken twice with 0.2 mol dm^{-3} NaOH and with water for several times. Drying and evaporation gave a crude mixture (103 g) of $Ph(OCH_2CH_2)_4Br$ and $PhO(CH_2CH_2O)_4$-Ph in *ca.* 8 : 2 ratio. This mixture (30 g) was treated with $CH_3OCH_2CH_2ONa$ prepared from $CH_3OCH_2CH_2OH$ (20.5 g, 270 mmol) and Na (3.1 g, 135 mmol) and heated at 120 °C for 30 h. Ether and water were added to the reaction product. The organic layer was dried over sodium sulfate and evaporated to yield 19.7 g of an oil. Column chromatography of this oil on silica gel (hexane–ether 5 : 1) gave 2.8 g of pure $PhO(CH_2CH_2O)_5CH_3$: ^1H NMR (CCl_4) δ=3.23 (s, 3H, CH_3), 3.42—4.10 (m, 20H, CH_2), and 6.63—7.22 (m, 5H, aromatic), high-resolution mass spectrum, 328.4011 (calcd for $C_{17}H_{28}O_6$, 328.4046).

Measurements of ^1H NMR spectra were carried out with a Hitachi R-24B spectrometer operating at 60 MHz at 35°C. The chemical shifts (δ) were referred to internal TMS and accurate to $\pm$0.01 ppm. Solvents were purified by standard methods.

Stability constants, K, for the equilibrium (1), $\delta^c(CH_3\text{–}Sn)$, and $^2J^c$ ($^{119}Sn\text{–}CH_3$) were calculated by a least-squares method using Eqs. 2 and 3.[11]

$$(CH_3)_2SnCl_2 + Gly \overset{K}{\rightleftharpoons} (CH_3)_2SnCl_2 \cdot Gly \quad (1)$$

$$\delta = \delta^\circ + \frac{\delta^c-\delta^\circ}{2}[(r+1+1/A_0K) - \sqrt{(r+1+1/A_0K)^2-4r}] \quad (2)$$

$$J = J^\circ + \frac{J^c-J^\circ}{2}[(r+1+1/A_0K) - \sqrt{(r+1+1/A_0K)^2-4r}]. \quad (3)$$

Gly: glyme.
δ, δ°, and δ^c: values of $\delta(CH_3\text{–}Sn)$ for the observed, the uncomplexed, and the 1:1 complexed, respectively.
J, J°, and J^c: values of $^2J(^{119}Sn\text{–}CH_3)$ for the observed, the uncomplexed, and the 1:1 complexed, respectively.
A_0: concentration of DMTC.
r: Gly/DMTC mole ratio.

The calculations were made with a NEAC model 900 computer at the Calculation Center of Osaka University.

Results and Discussion

In Fig. 1 is illustrated the dependence of chemical shifts of methyl protons attached to tin, $\delta(CH_3\text{–}Sn)$, on DiG/DMTC mole ratio (r) in some aromatic solvents and dichloromethane. Marked difference was observed for the change of $\delta(CH_3\text{–}Sn)$ among these solvents; the first group giving rise to little change in $\delta(CH_3\text{–}Sn)$ with r involves benzonitrile, nitrobenzene, and dichloromethane, the second group affecting some dependence on r involves chlorobenzene, bromobenzene, and anisole, and the third group involves benzene, toluene, *p*-xylene, and 1-chloronaphthalene in which the largest dependence of $\delta(CH_3\text{–}Sn)$ on r was observed. In the solvents of the latter two groups, the solvent effect caused by aromatic rings disappeared upon coordination of DiG to tin. This change of $\delta(CH_3\text{–}Sn)$ can be a

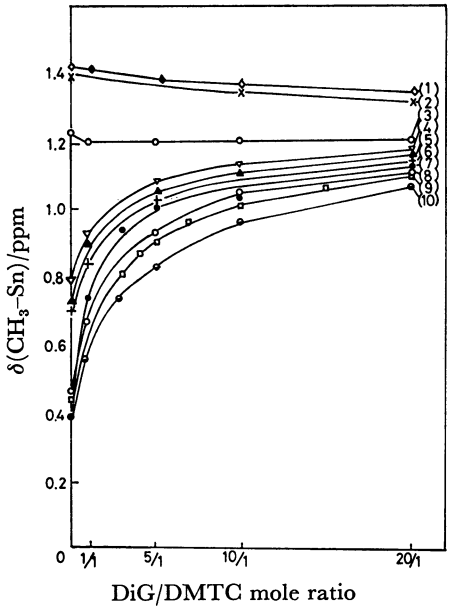


Fig. 1. Dependence of $\delta(CH_3\text{–}Sn)$ on DiG/DMTC mole ratio at constant DMTC concentration (0.15 M) in various solvents.
(1): Nitrobenzene, (2): benzonitrile, (3): dichloromethane, (4): bromobenzene, (5): chlorobenzene, (6): anisole, (7): 1-chloronaphthalene, (8): *p*-xylene, (9): toluene, (10): benzene.

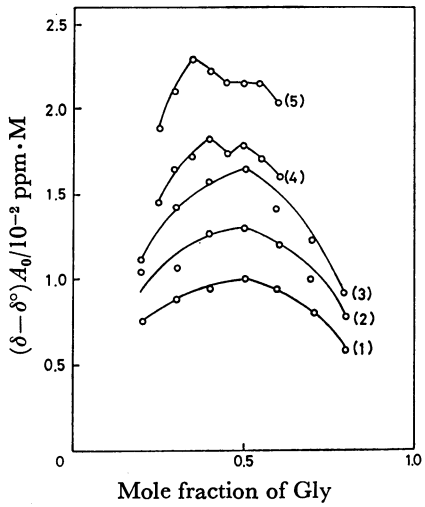
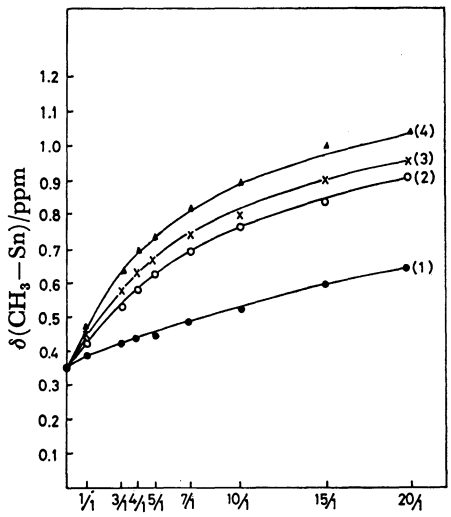
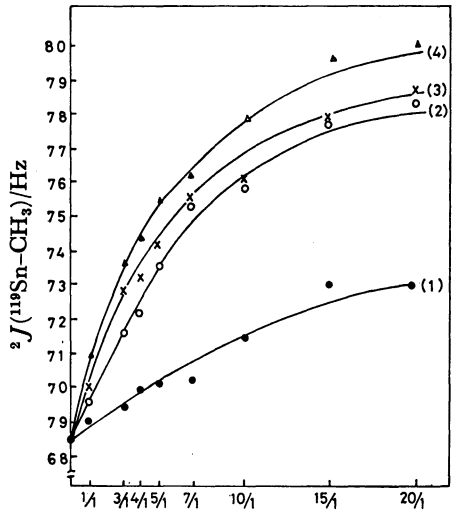


Fig. 2. Job's plot for Gly/DMTC in benzene at total concentration of 0.2 M.
(1): DiG, (2): TrG, (3): TetG, (4): PeG, (5): HexG.



(a) Gly/DMTC mole ratio



(b) Gly/DMTC mole ratio

Fig. 3. Dependence of $\delta(CH_3\text{–}Sn)$ (a) and $^2J(^{119}Sn\text{–}CH_3)$ (b) on Gly/DMTC mole ratio at constant DMTC concentration (0.05 M) in benzene.
(1): MoG, (2): DiG, (3): TrG, (4): TetG.

TABLE 1. STABILITY CONSTANT, K, $\delta^c(CH_3\text{–}Sn)$ AND $^2J^c(^{119}Sn\text{–}CH_3)$ FOR Gly/DMTC IN BENZENE AT 35 °C

	K	δ^c $(CH_3\text{–}Sn)$ ppm	$^2J^c(^{119}Sn\text{–}CH_3)$ Hz
MoG[a]	0.47±0.11	1.18	85.4
DiG	2.0±0.2	1.20	83.5
TrG	2.9±0.4	1.19	82.0
TetG	3.5±0.5	1.26	83.4

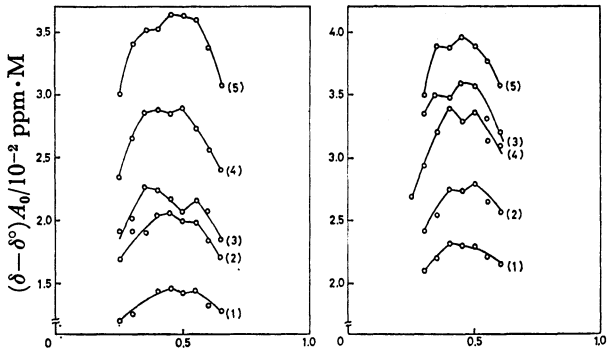
a) MoG was assumed to give 1 : 1 stoichiometry.

good measure for the interactions between glymes and DMTC. Therefore, we have studied, in detail, the ^1H NMR spectra of a series of Gly/DMTC system in benzene, toluene, and 1-chloronaphthalene.

First, the results obtained in benzene will be described. The stoichiometry of complexation was successfully disclosed by the Job's continuous variation method[12] as shown in Fig. 2. While no reliable curve could be drawn in the case of MoG, the evident 1 : 1 stoichiometry was found for DiG, TrG, and TetG. Figure 3 shows plots of $\delta(CH_3\text{–}Sn)$ and $^2J(^{119}Sn\text{–}CH_3)$ *vs.* r.[13] Stability constants, K, for the equilibrium (1), along with the values of $\delta^c(CH_3\text{–}Sn)$ and $^2J^c(^{119}Sn\text{–}CH_3)$ calculated by a least squares method using the above data are given in Table 1. The K values reveal a large gap of complexing ability between MoG and DiG. This trend is similar to the results obtained for some alkali metal salts in THF, in which the K value for DiG is larger by 10^2 times than that for MoG.[5a,b] The values of $^2J^c(^{119}Sn\text{–}CH_3)$ are comparable to those of *trans*-octahedral dimethyltin(IV) compounds with a slightly bent C–Sn–C moiety such as dimethyltin diacetate[14] and dikojate.[15] Since the benzene solutions containing Gly and DMTC in a 10 : 1 mole ratio at the DMTC concentration of 10^{-4} M (1 M=1 mol dm^{-3}) found to be nonelectrolytes by conductivity measurements indicative of nonionic structures, analogous distorted *trans*-octahedral configurations are suggested for the 1 : 1 complexes formed in this study.[16]

In the glyme complexes of inorganic metal ions, the coordination mode of the oxygen atoms has been the subject of considerable interest. While naked metal ions such as Li^+, Na^+, and K^+ can accommodate four to eight coordinating oxygen atoms on the interaction with glymes,[5,6] DMTC can accept two oxygen atoms at most due to the existence of four substituents. If we assume that all oxygen atoms are equivalent in coordinating ability and the coordination takes place virtually through neighboring two oxygen atoms in our 1 : 1 complexes, the total number of possible coordination modes should be 2, 3, and 4 for DiG, TrG, andTetG, respectively, leading to the increase in K values by the same factors. The observed K values of 2.0, 2.9, and 3.5 for these glymes are almost in accordance with the above statistical consideration.

For the complexes of PeG and HexG, unexpected Job's plots were encountered (Fig. 2). Appearance of two peaks at *ca.* 0.33 and 0.5 in mole fraction of Gly suggests the formation of the 1 : 2 and 1 : 1 complexes[17] as shown in the equilibrium (4).[18] An intramolecular chelation of glyme molecule resulting in a six-coordinate



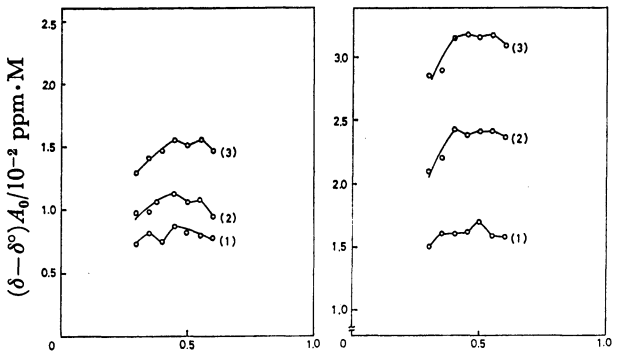
(a) Mole fraction of Gly (b) Mole fraction of Gly

Fig. 4. Job's plot for Gly/DMTC in toluene (a) and 1-chloronaphthalene (b) at total concentration of 0.2 M.
(1): DiG, (2): TrG, (3): TetG, (4): PeG, (5): HexG.

$$2(CH_3)_2SnCl_2 \underset{K_1}{\overset{Gly}{\rightleftharpoons}} [(CH_3)_2SnCl_2]_2\cdot Gly$$

$$\underset{K_2}{\overset{Gly}{\rightleftharpoons}} 2(CH_3)_2SnCl_2\cdot Gly \quad (4)$$

configuration obviously becomes sterically unfavored on increasing chain length of glymes. The additional formation of the 1 : 2 species was found for all glymes in toluene and 1-chloronaphthalene as shown in Fig. 4. On the basis of $(\delta-\delta^\circ)A_0$ values in the Job's plots which are proportional to stability constants,[12] overall stability constants in these solvents seem to be larger than those in benzene for respective glymes.



(a) Mole fraction of Gly (b) Mole fraction of Gly

Fig. 5. Job's plot for $PhO(CH_2CH_2O)_nCH_3$/DMTC in benzene (a) 1-chloronaphthalene (b) at total concentration of 0.2 M.
(1): n=3, (2): n=4, (3): n=5.

Steric effect on stoichiometry and complexation was further confirmed with polyethers involving terminal phenoxy groups. As shown in Fig. 5, replacement of one of the methoxy groups in glymes by a bulkier phenoxy group resulted in the coexistence of 1 : 2 and 1 : 1 complexes in both benzene and 1-chloronaphthalene even for lower members of the polyethers. It should be noted that each $PhO(CH_2CH_2O)_nCH_3$ (n=3, 4, 5) shows a smaller $(\delta-\delta^\circ)A_0$ value than that of $CH_3O(CH_2CH_2O)_{n-1}CH_3$ and no reliable Job's plot could be obtained for n=2. When a series of $PhO(CH_2CH_2O)_nPh$ (n=2, 3, 4) was employed, no appreciable interaction was detected in all cases. It is rather unexpected that little interaction was observed even for $PhO(CH_2CH_2O)_4Ph$, since this polyether involves three oxygen atoms linked by ethylene units and accordingly should be equivalent to $CH_3O(CH_2CH_2O)_2CH_3$ or $PhO(CH_2CH_2O)_3CH_3$ in coordinating ability. These observations suggest that the coordination behavior of polyethers towards DMTC is affected to a considerable degree by the bulkiness of the terminal groups.

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