KINETICS AND EQUILIBRIA OF DIALKYLTHALLIUM(III) COMPLEXES OF SOME THIACROWN-ETHERS IN ACETONITRILE

Yoshikane KAWASAKI* and Takuya MATSUMOTO
Department of Applied Fine Chemistry,
Osaka University,
Yamadaoka, Suita, Osaka 565
JAPAN

ABSTRACT. The rate constants k_1 and activation enthalpies ΔH of complex formation of dialkylthallium(III) perchlorates with some thia-18-crown-6 ethers were determined in acetonitrile. The equilibrium constants K were also obtained. More symmetrical thiacrown-ethers give smaller k_1 and K values, which are mainly regulated by the entropy term rather than the enthalpy term. Diethylthallium(III) ion gives smaller rate constants than those of dimethylthallium(III) ion. The K values of these complexes decrease as oxygen of the 18-crown-6 was replaced by sulfur.

1. INTRODUCTION

Organothallium(III) ions have been found to form stable complexes with several crown-ethers.[1 - 4] In the X-ray crystal structure analyses of dimethylthallium(III) complexes with dibenzo-18-crown-6[2] and two isomers of dicyclohexyl-18-crown-6,[5] the thallium ions were surrounded by six approximately coplanar oxygen atoms with a linear $(CH_3)_2Tl$ skeleton, which is perpendic ular to the plane. In complex formation of dialkylthallium(III) ions with crown-ethers, hydrophobic alkyl groups are necessary to thread through the hydrophilic crown-ether cavity. Therefore, the rates of these reaction are expected to be slower than those of globular ions and depend markedly on the alkyl groups attached to the thallium atom. In fact a smaller rate constant ($k_1 = 1.2 \times 10^{-3}$ $dm^3 \cdot mol^{-1} \cdot sec^{-1}$) and a lager activation energy ($E_a = 74$ kJ$\cdot$mol^{-1}) of complex formation of a $(CH_3)_2TlBF_4$ - dibenzo-18-crown-6 (DBC) system in CH_3CN[6] were obtained as compared to those for a NaNCS - DBC system in DMF ($k_1 = 6 \times 10^7$ $dm^3 \cdot mol^{-1} \cdot sec^{-1}$ and $Ea = 27$ kJ$\cdot$mol^{-1}).[7]

In this paper, we will report the rate constants k_1, activation enthalpies $\Delta H^{\ddagger}$, activation entropies $\Delta S^{\ddagger}$, and equilibrium constants K of eq. 1 in CD_3CN.

$$R_2TlClO_4 \quad + \quad L \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad [R_2Tl(L)]ClO_4 \qquad (1)$$
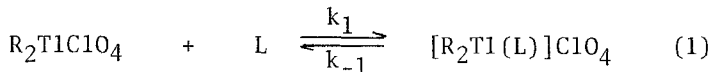
The solvent effect on the equilibrium constants will also be discussed.

2. EXPERIMENTAL

2.1. Materials

Dialkylthallium(III) perchlorates were prepared by heating a mixture of dialkylthallium(III) halides with silver oxide in CH_3OH and an addition of equimolar amount of aqueous $HClO_4$ after filtration of silver halides. The white precipitates obtained after evaporation of solvent under reduced pressure were recrystallized from $CH_3OH/(C_2H_5)_2O$. The compounds were identified by ^{1}H NMR spectra (see Table II).

Monothia-18-crown-6 (MTC), 1,7-dithia-18-crown-6 (1,7-DTC), and 1,4,7-trithia-18-crown-6 (1,4,7-TTC) were prepared by the method of Bradshaw et al. [8] 1,10-dithia-18-crown-6 (1,10-DTC) was obtained by using the method reported by Dann et al. [9] 1,7,13-trithia-18-crown-6 (1,7,13-trioxa-4,10,16-trithiacyclooctadecane) (1,7,13-TTC) was prepared by heating a highly diluted mixture of 1,7-dithia-4-oxaheptane and 1,11-dichloro-3,9-dioxa-6-thiaundecane in C_2H_5OH at reflux in the presence of K_2CO_3 for 72 hr. Bp. 220 °C/ 1 mmHg. MS, m/z 312(M^+). ^{1}H NMR $\delta(CDCl_3)=$ 2.79 (12H,t,-SCH_2-), 3.67 (12H,t,-OCH_2-). Found: C,45.73; H, 8.03; S, 30.62%. Calcd for $C_{12}H_{24}O_3S_3$: C, 46.12; H, 7.74; S, 30.78%.

MTC   1,7-DTC   1,10-DTC   1,4,7-TTC   1,7,13-TTC
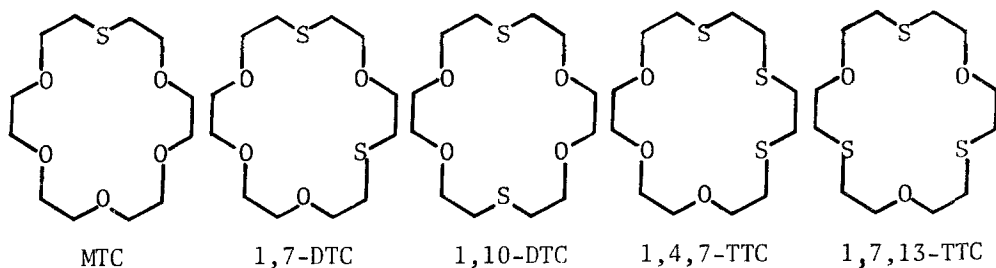
2.2. Preparation of complexes $[R_2Tl(L)]ClO_4$

Equimolar amounts of dimethylthallium(III) perchlorate and thia-crown-ether were dissolved in CH_3CN and the solution was allowed to stand overnight at room temperature. White precipitates obtained after evaporation of solvent under reduced pressure were purified by recrystallization from CH_2Cl_2-THF(3:1)/n-hexane. Diethylthallium(III) complexes were also prepared by the similar method but the mixture was heated at reflux for 8 hr. Purification was made by recrystallization from $CH_3CN/(C_2H_5)_2O$ for 1,10-DTC and 1,4,7-TTC complexes and from CH_2Cl_2-THF(3:1)/n-hexane for MTC,1,7-DTC, and 1,7,13 TTC. Analytical data of the complexes are shown in Table I and relevant ^{1}H NMR data of the complexes measured in CD_3CN are shown in Table II.

2.3. Kinetic measurements and calculations

$(CH_3)_2TlClO_4$ and thiacrown-ether were dissolved in CD_3CN in a NMR

TABLE I. Analytical data of $[R_2Tl(L)]ClO_4$

	R	L	mp (°C)	Found(Calcd) %C	%H
1	CH_3	MTC	241-243	27.67(27.37)	5.10(4.92)
2	CH_3	1,7-DTC	213-214	27.16(26.68)	5.03(4.80)
3	CH_3	1,10-DTC	205	26.88(26.68)	4.81(4.80)
4	CH_3	1,4,7-TTC	143-144	26.48(26.05)	4.90(4.68)
5	CH_3	1,7,13-TTC	210-213	26.48(26.05)	4.87(4.68)
6	C_2H_5	MTC	231-232	30.48(30.68)	5.59(5.47)
7	C_2H_5	1,7-DTC	198-199	29.42(29.19)	5.33(5.21)
8	C_2H_5	1,10-DTC	176-179	28.59(29.19)	5.16(5.21)
9	C_2H_5	1,4,7-TTC	184-186	28.42(28.49)	5.12(5.08)
10	C_2H_5	1,7,13-TTC	190-193	28.70(28.49)	5.37(5.08)

TABLE II. ^1H NMR data of $[R_2Tl(L)]ClO_4$ in CD_3CN

L	R= CH_3 $^2J(Tl-CH_3)$ (Hz)	$\delta(CH_3)$ (ppm)	C_2H_5 $^2J(Tl-CH_2)$ (Hz)	$\delta(CH_2)$ (ppm)	$^3J(Tl-CH_3)$ (Hz)	$\delta(CH_3)$ (ppm)
	400	1.22	339	1.90	612	1.63
18-crown-6[a]	430	0.89	387	1.61	636	1.50
MTC	424	1.03	380	1.70	639	1.50
1,7-DTC	423	1.15	378	1.81	641	1.60
1,10-DTC	416	1.19	367	1.81	635	1.61
1,4,7-TTC	413	1.28	361	1.93	639	1.68
1,7,13-TTC	421	1.29	376	1.91	640	1.67

a) Ref. 3.

tube and the solution was degassed by the freeze-thaw-freeze method. A typical concentration of $(CH_3)_2TlClO_4$ was 0.08 M and that of thiacrown ether was 0.04 - 0.23 M.   The NMR line shapes of the methyl proton signals were measured at several temperatures(24 - 83 °C).   The line shapes were simulated as a two site ploblem.   Some simulated line

$$A \underset{k_{-1}}{\overset{k_1{'}}{\rightleftharpoons}} B \qquad (2)$$
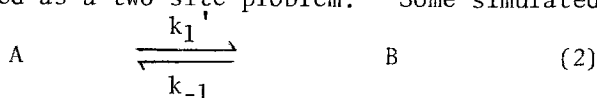
shapes with the observed spectra for a $(CH_3)_2TlClO_4$ - 1,7,13-TTC system are shown in Fig. 1 and Arrhenius plot of this system is shown in Fig.2.
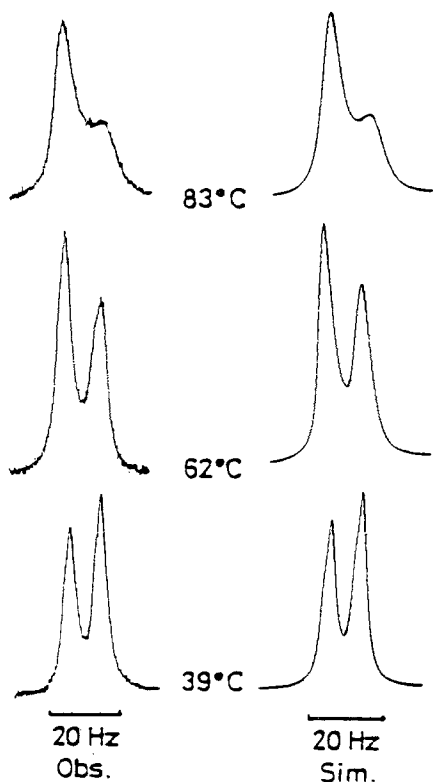
Fig. 1. Observed and calculated spectra of methylsignals of the $(CH_3)_2TlClO_4$ - 1,7,13-TTC system.
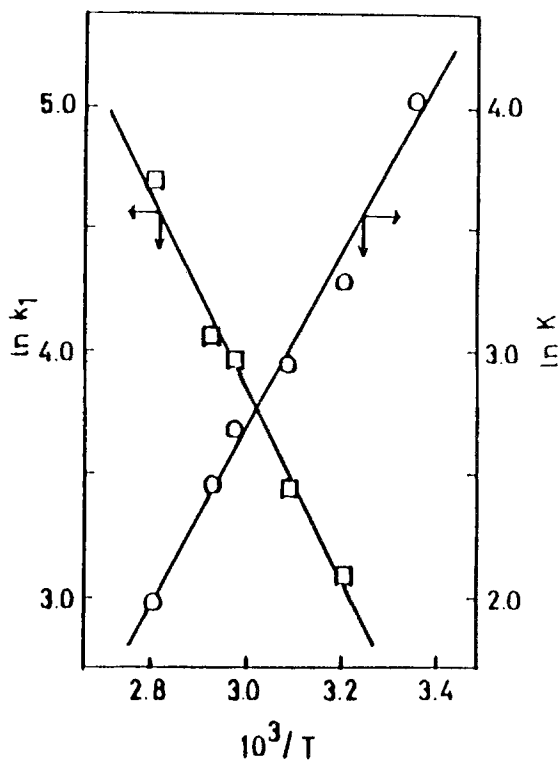
Fig. 2. Arrhenius plot for the $(CH_3)_2TlClO_4$ - 1,7,13-TTC system.

The formation rate constant k_1 was obtained by using a following relation. $k_1 = k_1'/[L]$, where $[L] = [L_o] - P_B[Tl_o]$. $[L_o]$ and $[Tl_o]$ are initial concentrations of crown-ether and dimethylthallium(III) perchlorate, respectively and P_B is a relative population of complex $[(CH_3)_2Tl(L)]ClO_4$ at the equilibrium.

In kinetic measurements for the $(C_2H_5)_2TlClO_4$ - thiacrown-ether systems, concentration change of $(C_2H_5)_2TlClO_4$ and $[(C_2H_5)_2Tl(L)]ClO_4$ with time was obtained by measuring the methylene signal area of the upper field signals of the ethyl groups in the ^1H NMR spectra. The concentrations of $(C_2H_5)_2TlClO_4$ were 0.04 - 0.09 M and those of thiacrown-ether were 0.05 - 0.2 M. One of runs of the kinetic measurements for a $(C_2H_5)_2TlClO_4$ - 1,7,13-TTC systems is shown in Fig. 3. The rate constants were obtained by fitting the concentration change of $(C_2H_5)_2TlClO_4$ with time to the rate equation 3 by the least squares

$$d[Tl_c]/dt = k_1[Tl_f][L] - k_{-1}[Tl_c] \qquad (3)$$

method. $[Tl_c]$ and $[Tl_f]$ represent the concentration of $[(C_2H_5)_2Tl(L)]ClO_4$ and $(C_2H_5)_2TlO_4$, respectively.
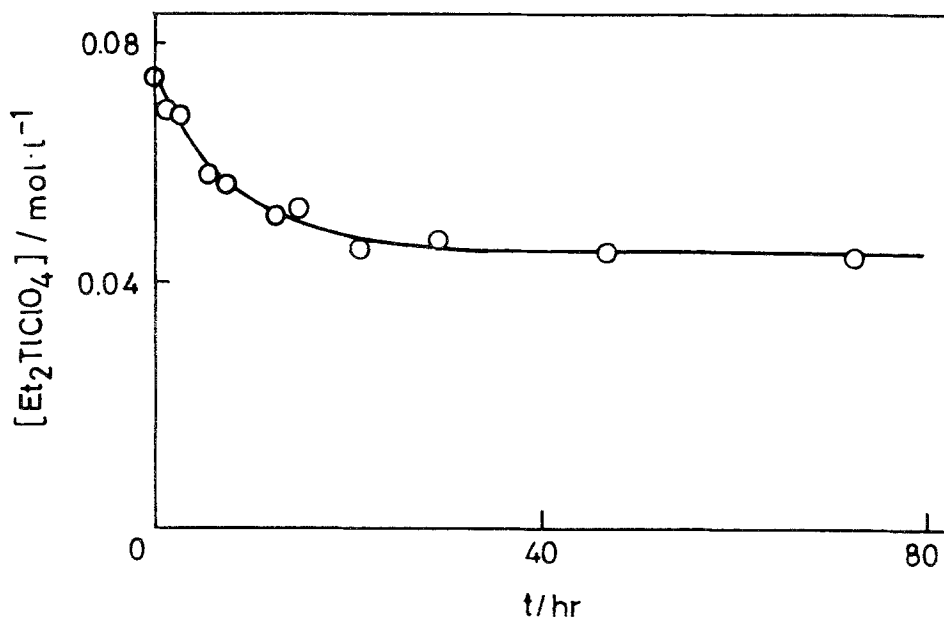
Fig. 3. The change of concentration of $(C_2H_5)_2TlClO_4$ (O) with time and the least squares fitting (——) for the $(C_2H_5)_2TlClO_4$ - 1,7,13-TTC system.

3. RESULTS AND DISCUSSION

As shown in Table II, spin-spin coupling constants between methyl protons and the thallium nucleus $^2J(Tl-CH_3)$ of the thiacrown-ether complexes of dimethylthallium(III) ion in CD_3CN are somewhat larger than that of the free dimethylthallium(III) ion in the same solvent. These values have a tendency to decrease, accompanied by a downfield shift of the methyl proton chemical shift, as the number of sulfur atom in 18-crown-6 increases. Similar results were obtained in $^2J(Tl-CH_2-)$ and $\delta(Tl-CH_2-)$ values of diethylthallium(III) complexes. The magnitude of $^2J(Tl-CH_3)$ values has been found to be an indication of increasing interaction between solvent molecules and the thallium atom in the solvent dependence of $^2J(Tl-CH_3)$ values of dimethylthallium ion.[10] The ^2J values obtained for thiacrown-ether complexes of dialkylthallium (III) ions, therefore, suggest that interaction between thiacrown-ether and the thallium atom decreases with substitution of oxygen of 18-crown-6 with sulfur.

The equilibrium constants K for thiacrown-ether complexes of dimethylthallium(III) ions obtained in CD_3CN are shown in Table III and those of diethyl thallium(III) ions in Table IV. The K values of trithiacrown-ether complexes of dimethylthallium(III) ion are found to be larger than those of diethylthallium(III) ion. The symmetry of ligands also influences these K values. More symmetrical 1,7,13-TTC

gives smaller K values than 1,4,7-TTC. In this case the unfavorable entropy term offsets the favorable enthalpy term. In the complexes with more symmetrical thiacrown-ethers, the structure of the complexes might be enforced to take a restricted configuration, which causes a large negative entropy.

In contrast to the trithiacrown-ether complexes of dialkylthallium-(III) ions, ^{1}H NMR spectra of monothia- and dithia-crown-ether complexes in CD_3CN give only signals of complex species $[R_2Tl(L)]ClO_4$ and those of free ions and uncomplexed crown-ether were very small if present at all. Therefore, K values of monothia- and dithia-crown-ether complexes of dialkylthallium(III) ions are much larger than those of trithiacrown-

TABLE III. Kinetic and equilibrium data of $(CH_3)_2TlClO_4$ - L systems at 25 °C

L=	1,7-DTC[a]	1,10-DTC[a]	1,4,7-TTC[b]	1,7,13-TTC[b]
$k_1/dm^3 \cdot mol^{-1} \cdot sec^{-1}$	c)	c)	160	11
$\Delta G^{\ddagger}/kJ \cdot mol^{-1}$	c)	c)	61	67
$\Delta H^{\ddagger}/kJ \cdot mol^{-1}$	c)	c)	35	31
$\Delta S^{\ddagger}/J \cdot K^{-1} \cdot mol^{-1}$	c)	c)	-85	-120
$K/dm^3 \cdot mol^{-1}$	80	8.5	122	48
$\Delta G/kJ \cdot mol^{-1}$	-11	-5.3	-19	-28
$\Delta H/kJ \cdot mol^{-1}$	-26	-18	-12	-9.6
$\Delta S/J \cdot K^{-1} \cdot mol^{-1}$	-50	-41	-22	-62

a) In CD_3OH. b) In CD_3CN. c) Could not be obtained.

TABLE IV. Kinetic and equilibrium data of $(C_2H_5)_2TlClO_4$ - L systems in CD_3CN at 25 °C

L=	MTC	1,7-DTC	1,10-DTC	1,4,7-TTC	1,7,13-TTC
$k_1/dm^3 \cdot mol^{-1} \cdot sec^{-1}$	3.3×10^{-4}	2.2×10^{-4}	1.7×10^{-4}	140×10^{-4} [a]	3.2×10^{-4}
$\Delta G^{\ddagger}/kJ \cdot mol^{-1}$	93	94	95	b)	93
$\Delta H^{\ddagger}/kJ \cdot mol^{-1}$	50	67	49	b)	45
$\Delta S^{\ddagger}/J \cdot K^{-1} \cdot mol^{-1}$	-140	-89	-150	b)	-160
$K/dm^3 \cdot mol^{-1}$	$> 10^3$	$> 10^3$	$> 10^3$	36	31
$\Delta G/kJ \cdot mol^{-1}$	b)	b)	b)	-8.9	-8.5
$\Delta H/kJ \cdot mol^{-1}$	b)	b)	b)	-21	-41
$\Delta S/J \cdot K^{-1} \cdot mol^{-1}$	b)	b)	b)	-40	-110

a) Value at 24 °C. b) Could not be obtained.

ethers, in accordance with the results obtained by $^2J(Tl-CH_3)$ and $^2J(Tl-CH_2)$ values, although precise K values could not be obtained.

Izatt et al. reported a decrease in the K values of Tl^+ and Pb^{2+} complexes by replacement of oxygen of 18-crown-6 with sulfur. In Ag^+ and Hg^{2+}, however, an increase of the K values was obtained.[11]

In the ^{1}H NMR spectra of the 1,7,13-TTC complex of dimethylthallium (III) ion in CH_3OH, signals observed were only those of free dimethyl- thallium(III) ion and uncomplexed 1,7,13-TTC and those of the complex species were not detected, although very small amounts of the complex species were detected in the 1,4,7-TTC complex. The results indicate that almost complete decomplexation has occured in the 1,7,13-TTC complex and the 1,4,6-TTC complex is more stable than the 1,7,13-TTC complex. In the case of dithiacrown-ether complexes, however, considerable amounts of the complex species were detected even in CH_3OH, indicating that these crown-ethers form more stable complexes with dimethylthallium(III) ion than trithiacrown-ethers. The K values of these complexes are shown in Table III. Decrease of the K values of these complexes in CH_3OH may mainly be due to large stabilization of dimethylthallium(III) ion, rather than the complexes, by strong solvation of CH_3OH as compared to CH_3CN, since $^2J(Tl-CH_3)$ value of dimethylthallium(III) ion in CH_3OH (414 Hz)[10] is larger than that in CH_3CN (400 Hz). On the other hand, in less polar solvents such as $CDCl_3$ or CH_2Cl_2, the complex species only were detected in these trithiacrown- ether complexes in the ^{1}H NMR spectra and the presence of the uncom- plexed species were very small if present at all.

As can be seen from Table III, the rate constant k_1 of complex formation of dimethylthallium(III) ion with less symmetrical 1,4,7-TTC is found to be larger than that of 1,7,13-TTC. In these cases, activation entropy is negatively large and is a dominant factor for deciding the rate constant. The result may be explained by the same mechanism as discussed for the K values. The large rate constant k_1 of trithiacrown-ethers is associated with favorable small activation enthalpy and unfavorable negative large activation entropy as compared to DBC ($\Delta H^{\ddagger}$ = 71 kJ·mol^{-1} and $\Delta S^{\ddagger}$ = -60 J·K^{-1}·mol^{-1}).[6] In the uncom- plexed state, trithiacrown-ethers may be more flexible and can take more conformations than DBC. At the transition state of complex formation, the activated complex might take rather restricted conforma- tions, which may lead a large reduction of entropy for trithiacrown- ethers than DBC. On the other hand, the cavity of DBC is considered to be smaller than that of trithiacrown-ethers, since DBC does not form a complex with diethylthallium(III) ion. This result may reflect large activation enthalpy of the DBC complex. The rate constants k_1 of dithia- and monothia-crown-ether complexes of dimethylthallium(III) ion could not be obtained, since line broadening of the methyl proton signals did not occur in the ^{1}H NMR spectra even in a presence of excess dimethylthallium(III) ion or thiacrown-ethers and at elevated temperatures in CH_3CN and CH_3OH. This may indicate that the rate of decomplexation k_{-1} is very slow on the NMR time scale, which is consistent with large K values of these crown-ether complexes.

There is no large difference of the rate constants k_1 of MTC, 1,10- DTC, 1,7-DTC, and 1,7,13-TTC complexes of diethylthallium(III) ion (see Table IV). The rate constants of diethylthallium(III) ion are smaller by a factor of 10^4 than those of dimethylthallium(III) ion. This

difference may be explained by the fact that more bulky ethyl group must thread though the crown-ether cavity in the complex formation, which is necessary, as have been observed, to impose large activation enthalpy.   In the 1,4,7-TTC complex of diethylthallium(III) ion, reliable kinetic data could not be obtained at elevated temperatures by the method used in this experiment.   The activation parameters, there-fore, could not be obtained.   The rate constant at room temperature is larger than that of 1,7,13-TTC, as in the case of dimethylthallium(III) complexes.

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