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Kinetics of the Ligand-exchange Reactions in Th(tta)$_4$ and Th(tta)$_4$dmso in Organic Solvents

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The exchange reactions of 2-thenoyltrifluoroacetonate (tta) in Th(tta)$_4$ and of dimethyl sulfoxide (dmso) in Th(tta)$_4$dmso have been studied by the NMR method. It was found that the first-order rate constant of tta exchange in acetonitrile-d_3 depended linearly on the concentrations of Htta in the enol form, Htta$_{enol}$, and that the rate was retarded markedly by the addition of DMSO. The activation parameters ΔH^* (kJ mol^{-1}) and ΔS^* (JK^{-1} mol^{-1}) were determined to be 43.9±0.5 and −58.4±1.5, respectively and the mechanism including the formation of a nine-coordinate intermediate was proposed. For Th(tta)$_4$dmso, the rate of dmso exchange in acetone-d_6 was much faster than that of β-diketonate exchange, and an interchange mechanism was proposed on the basis of a nonlinear dependency of the first-order rate constant on the free DMSO concentration.

In previous papers,[1,2] we reported the kinetics of the ligand exchange reaction in tetrakis(acetylacetonato)thorium(IV), Th(acac)$_4$, and proposed that the reaction proceeded *via* a nine-coordinate intermediate for the acac exchange. It has been known that thorium(IV) forms an eight-coordinate complex[3] with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, whose common name is 2-thenoyltrifluoroacetone (Htta). On extraction of Th(IV) by Htta, a marked synergic effect was observed in the presence of unidentate donor bases, *e.g.* tributyl phosphate and trioctylphosphine oxide.[4,5,6] This synergic effect suggests that Th(tta)$_4$ may form nine-coordinate complexes with unidentate bases. In fact, several nine-coordinate adducts between Th(tta)$_4$ and bases were isolated.[7,8] From these facts, it is expected that some nine-coordinate intermediate probably plays an important role in the ligand-exchange reaction between Th(tta)$_4$ and Htta. In this paper, we report the formation of nine-coordinate Th(tta)$_4$L(L: unidentate ligand), and the kinetic results of the exchange reaction of tta and dmso in Th(tta)$_4$ and Th(tta)$_4$dmso, respectively.

Experimental

Materials. The Th(tta)$_4$ complex was prepared as follows. An aqueous solution (40 cm^3) containing thorium tetrachloride (0.01 mol) was stirred with the same volume of a benzene solution which contained a large excess amount of Htta. Aqueous ammonia was added to the mixture until the pH of the solution became 5. The brownish yellow benzene phase was separated and a yellow precipitate was obtained by evaporation of benzene under reduced pressure. The precipitate was washed with hexane and recrystallized from hot benzene, and then from 1,2-dichloroethane. Found: C, 34.5; H, 1.4%. Calcd for $C_{32}H_{16}O_8F_{12}S_4Th$: C, 34.4, H, 1.1%.

Purification of 2-thenoyltrifluoroacetone was carried out by recrystallization from hexane. Dimethyl sulfoxide and hexamethyl phosphoric triamide (HMPT) were distilled under reduced pressure. Acetonitrile was dried over phosphorus pentaoxide and distilled. Acetone-d_6 and acetonitrile-d_3 were dried over molecular sieve 4A.

Measurements of UV and NMR Spectra. UV spectra were measured by using Shimadzu 210A and UV-365 spectrophotometers with 0.1 mm and 1.0 mm quartz cells. A JEOL JNM-FX 100 FT-NMR equipped with a JNM-VT-3B temperature controller was used for NMR measurements.

Determination of the Fraction of Keto- and Enol-forms in Htta. The concentration ratio, [enol]/[keto], was determined by area measurements of methine and methylene proton signals for enol- and keto-isomers, respectively. In order to obtain the temperature dependence of the ratio, the area measurements were performed in the temperature range from 30 to 70 °C. The values of enthalpy and entropy were ΔH=−15.5±0.8 kJ mol^{-1} and ΔS=−24.3±2.4 J K^{-1} mol^{-1} in CD_3CN. The fractions of the enol isomer at each temperature were calculated by using these values.

Rate Analysis. The first-order rate constants of ligand-exchange reactions were determined from the line shape analysis of NMR signals by using the two-site model.[2,9] A Sord M-232 microcomputer system was used for the calculation.

Results

Ligand-exchange between Th(tta)$_4$ and Htta. The absorption spectrum of Th(tta)$_4$ shows a peak at 350 nm with the molar extinction coefficient of 8.3× 10^4 M^{-1} cm^{-1} (1 M=1 mol dm^{-3}) in acetonitrile. The spectrum of the mixture of Th(tta)$_4$ and Htta coincided with the sum of those of each component in acetonitrile, and remained unchanged for several hours. As is shown in Fig. 1, the ^{1}H NMR spectra of the mixture of Th(tta)$_4$ and Htta in CD_3CN and CD_3COCD_3 gave two methine proton signals at room temperature, and the signal in the higher magnetic field was assigned to coordinated tta and that in the lower field to free Htta in the enol-form. The ^{19}F NMR spectra of the reaction mixture in CD_3CN showed also two ^{19}F signals of trifluoromethyl at room temperature, where the one in the higher field was assigned to Htta and the other to Th(tta)$_4$. In both the ^{1}H and ^{19}F spectra

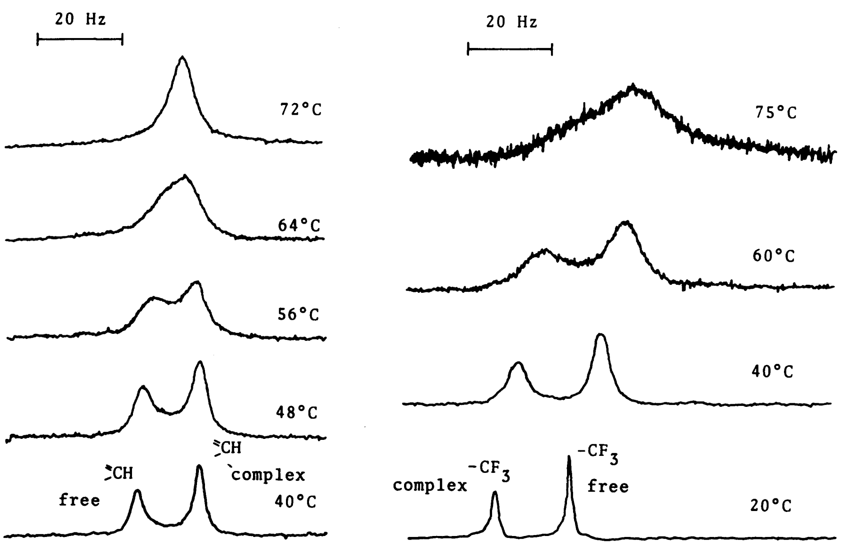

Fig. 1. Changes in methine proton signals (left) and trifluoromethyl ^{19}F signals of the mixture of $Th(tta)_4$ and Htta in CD_3CN with temperature.

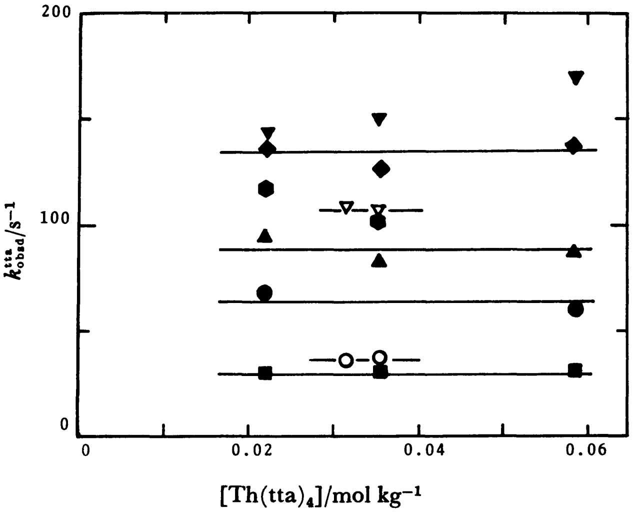

Fig. 2. Dependence of k^{tta}_{obsd} on the concentration of $Th(tta)_4$ in CD_3CN at various temperatures. ■: 30, ●: 40, ▲: 48, ⬢: 52, ◆: 56, ▼: 60 °C.
Open marks: $[Htta]_{total} = 0.130-0.133$ mol kg^{-1},
Closed marks: $[Htta]_{total} = 0.192-0.193$ mol kg^{-1}.

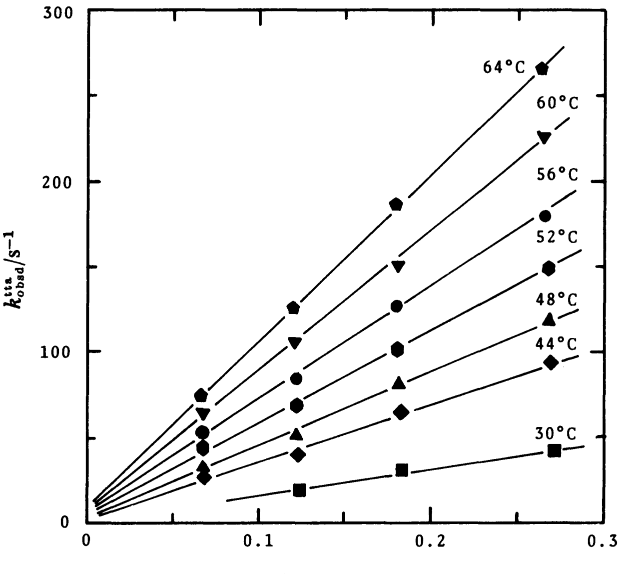

Fig. 3. Dependence of k^{tta}_{obsd} on the concentration of Htta in the enol form in CD_3CN.
$[Th(tta)_4] = 0.0357-0.0363$ mol kg^{-1}.

in CD_3CN, the >CH and $-CF_3$ signals coalesced as the temperature was raised (Fig. 1). These changes in NMR spectra can be attributed to the ligand exchange between $Th(tta)_4$ and Htta in the enol-form. No change was observed in methylene proton signals of Htta in the keto-form. Therefore, the ligand-exchange reaction between $Th(tta)_4$ and Htta in the enol-form can be described as follows.

$$Th(tta)_4 + Htta^*_{enol} \rightleftharpoons Th(tta)_3tta^* + Htta_{enol}, \qquad (1)$$

where the asterisk denotes the exchanging species.

The observed first-order rate constant, k^{tta}_{obsd}, for the tta exchange reaction is given by

$$k^{tta}_{obsd} = 4\tau_c^{-1}, \qquad (2)$$

where τ_c is the life time of tta in the coordination site. Plots of k^{tta}_{obsd} against the concentrations of $Th(tta)_4$ and $Htta_{enol}$ are shown in Figs. 2 and 3, respectively. The first-order rate constant was independent of $[Th(tta)_4]$ though the data at 52 and 60 °C deviated from straight lines and linearly depended on $[Htta]_{enol}$. The intercepts in Fig. 3 might be regarded to be zero within experimental errors. These results lead to the following relationship between k^{tta}_{obsd} and $[Htta]_{enol}$,

$$k^{tta}_{obsd} = k[Htta]_{enol} \qquad (3)$$

where k refers to the second order rate constant, and the values of k are listed in Table 1. The rate of tta

Table 1. Kinetic parameters of the tta exchange of $Th(tta)_4$ in CD_3CN

T / °C	k / $s^{-1}\,mol^{-1}\,kg$
30	153 ± 29
44	337 ± 26
48	432 ± 29
52	517 ± 20
56	647 ± 16
60	814 ± 21
64	981 ± 14
ΔH^* ($kJ\,mol^{-1}$)	43.9 ± 0.5
ΔS^* ($JK^{-1}\,mol^{-1}$)	-58.4 ± 1.5

Table 2. Change in absorbance of $Th(tta)_4$[a] by addition of DMSO in acetonitrile

[DMSO] 10^{-5} mol dm^{-3}	Absorbance (350 nm)
0	0.382
2.0	0.377
4.0	0.374
6.0	0.372
8.0	0.368
10	0.366
12	0.366
14	0.366

a) $[Th(tta)_4] = 4.58 \times 10^{-5}$ mol dm^{-3}.

exchange was retarded in the presence of free DMSO. Under the conditions that $[Th(tta)_4] = 0.0443$ mol kg^{-1}, $[Htta]_{total} = 0.181$ mol kg^{-1} and $[DMSO] = 0.197$ mol kg^{-1} in CD_3CN, the methine proton signals of $Th(tta)_4$ and $Htta_{enol}$ were separated even at 70 °C, and their line widths were slightly broader than those at 20 °C.

Formation of Th(tta)₄L Complexes and the dmso Exchange in Th(tta)₄dmso. The molar extinction coefficient of $Th(tta)_4$ in acetonitrile was measured in the presence of DMSO or HMPT. Slight changes in absorption spectra with an isosbestic point at 340 nm were observed by the addition of DMSO, and the results are shown in Table 2. Similar spectral changes were also observed in the presence of HMPT. These changes in spectra suggest the formation of adduct complexes between $Th(tta)_4$ and DMSO or HMPT. In addition, the ^1H NMR spectra of mixtures of $Th(tta)_4$ and DMSO or HMPT in acetone-d_6 may give additional evidence for 1:1 adduct complex formation. As seen in Fig. 4, the ^1H NMR spectra of the solution containing $Th(tta)_4$ and DMSO gave a sharp signal of methyl protons at −20 °C. As the temperature of the solution was lowered, this signal broadened and then split into two peaks, in which the peak in the higher field was assigned to the methyl protons of free DMSO, while the solution containing $Th(tta)_4$ (0.0662 mol kg^{-1}) and DMSO (0.0270 mol kg^{-1}) whose concentration was less than equivalent showed a single methyl proton signal, and no methyl proton signal of free DMSO was observed at any temperature. The chemical shift of this single methyl proton signal coincided with that of the peak in the lower field in Fig. 4. This fact also suggests that DMSO in the mixture forms a 1:1 adduct complex with $Th(tta)_4$, and the left-hand peak in Fig. 4 can be assigned to the methyl protons of the adduct complex, $Th(tta)_4$dmso. Similar changes in NMR spectra were observed for the mixture of $Th(tta)_4$ and HMPT as is shown in Fig. 5, in which two signals of methyl protons of HMPT were observed at 10 °C and each signal split into two peaks at −40 °C. Left-hand peaks (C) of each signal can be assigned to the methyl protons of the complex, $Th(tta)_4$hmpt. Attempts to determine accurate values of formation constants of 1:1 adduct complexes between $Th(tta)_4$ and DMSO or HMPT in acetonitrile and acetone were unsuccessful because of very large values of molar extinction coefficients for complexes and of rather small changes in absorbance on adduct formation. The value for $Th(tta)_4$dmso is estimated to be some value between 10^4 and 10^5 mol^{-1} kg. A simulated line shape of NMR spectrum, which is obtained from the two-site model by assuming that the left-hand peak in Fig. 4 is the methyl protons of $Th(tta)_4$dmso, and that the dmso exchange reaction takes place between $Th(tta)_4$dmso and free DMSO, shows satisfactory agreement with the observed

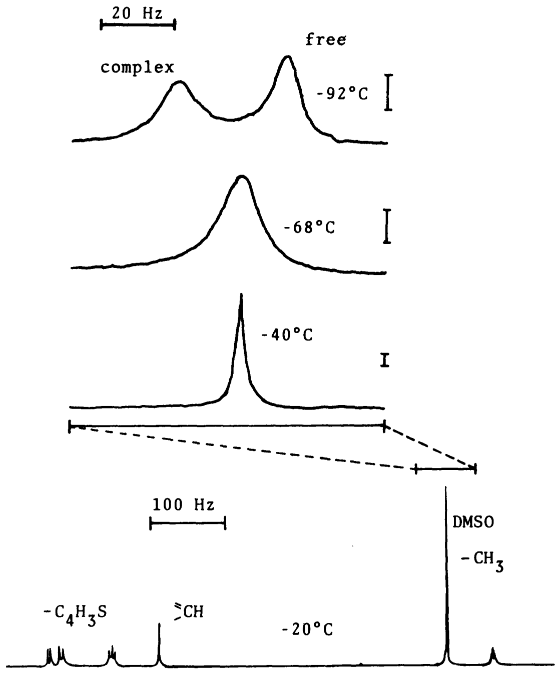

Fig. 4. ^1H NMR spectrum of the mixture of $Th(tta)_4$ and DMSO, and a change in methyl proton signals in CD_3COCD_3 with temperature.
$[Th(tta)_4] = 0.0508$ mol kg^{-1}, $[DMSO] = 0.103$ mol kg^{-1}.

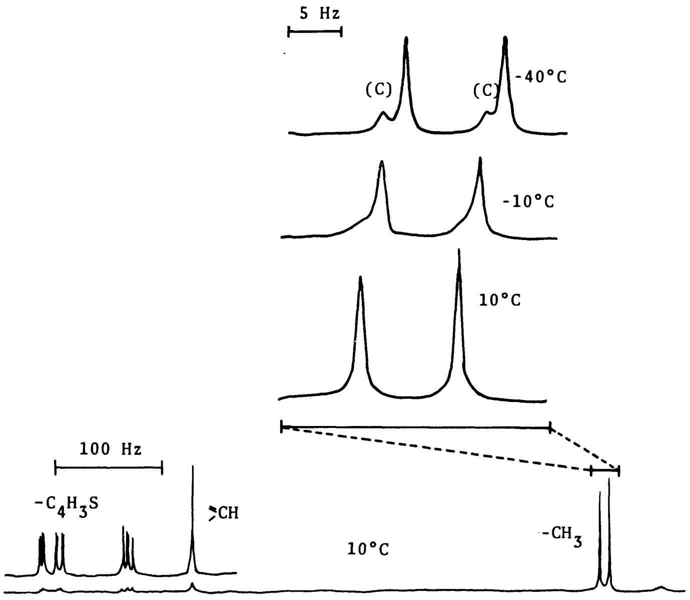

Fig. 5. ^{1}H NMR spectrum of the mixture of $Th(tta)_4$ and HMPT, and a change in methyl proton signals in CD_3COCD_3 with temperature. $[Th(tta)_4]=0.048$ mol kg^{-1}, [HMPT]$=0.210$ mol kg^{-1}.

signals.

All these results indicate that $Th(tta)_4$ and L (L=dmso or hmpt) form the nine-coordinate complex, $Th(tta)_4L$, and the change in ^{1}H NMR spectra in Fig. 4 can be attributed to the dmso exchange reaction in $Th(tta)_4dmso$ as written by Eq. 4.[10]

$$Th(tta)_4dmso + DMSO^* \rightleftarrows Th(tta)_4dmso^* + DMSO \qquad (4)$$

The observed first-order rate constant of the dmso exchange in $Th(tta)_4dmso$, k_{obsd}^{dmso}, does not depend linearly on the concentration of DMSO as shown in Fig. 6. Plots of $k_{obsd}^{dmso^{-1}}$ vs. [DMSO]$^{-1}$ give straight lines with intercepts and yield

$$k_{obsd}^{dmso^{-1}} = p + q[\mathrm{DMSO}]^{-1}, \qquad (5)$$

where p and q are constants.

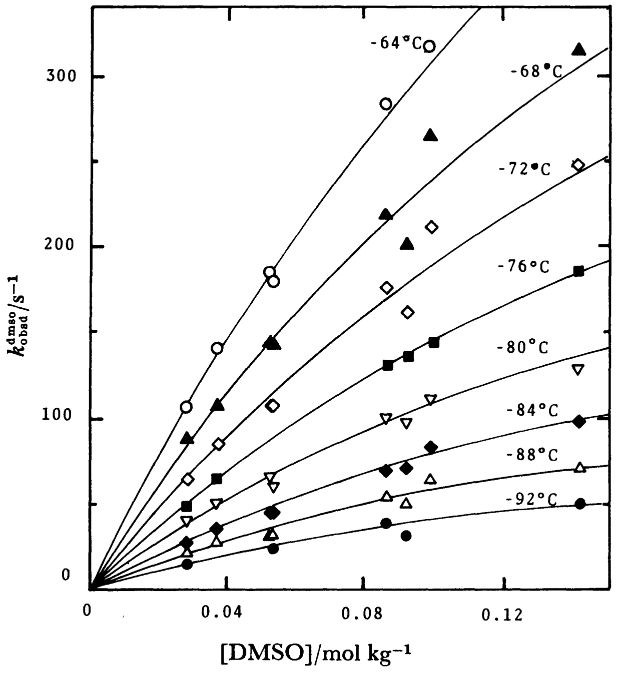

Fig. 6. Plots of k_{obsd}^{dmso} vs. [DMSO] in CD_3COCD_3. $[Th(tta)_4dmso]=0.0227-0.0672$ mol kg^{-1}.

Discussion

A pathway which is similar to the mechanism proposed for the acac exchange in $Th(acac)_4$[2] is proposed for the mechanism of the tta exchange reaction in $Th(tta)_4$. As shown in Fig. 7, $Th(tta)_4$ forms a nine-coordinate intermediate, $Th(tta)_4Htta^*$, with $Htta_{enol}^*$, and the proton of $Htta_{enol}^*$, is transferred to one of the coordinated tta (II→II′), followed by rapid dissociation of $Htta_{enol}$ from the coordination sphere (II′→I′). If complexes I and II are in fast equilibrium, and [II] is much smaller than [I], the first-order rate constant, k_{ex}, can be written by

$$k_{ex} = k_2K_1[\mathrm{Htta}]_{enol}, \qquad (6)$$

where K_1 is the formation constant of complex II, and k_2 is the rate constant for the proton transfer reaction. Equation 6 is the same as Eq. 3 obtained experimentally, where k corresponds to k_2K_1.

The retardation effect by the addition of DMSO can be interpreted by the formation of nine-coordinate adduct complex (III). It seems reasonable to assume that the formation of $Th(tta)_4Htta$ is hindered by DMSO. The rate of the tta exchange reaction in

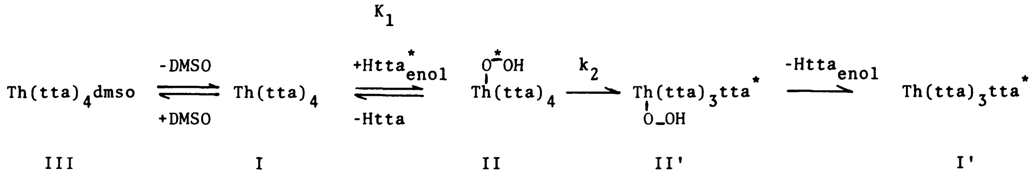

Fig. 7. Mechanism of the tta exchange in $Th(tta)_4$ in CD_3CN.

Table 3. Activation parameters for the second-order rate constants of ligand exchange reactions in *β*-diketonato complexes

Complex	Solvent	ΔH^{*} / kJ mol^{-1}	ΔS^{*} / JK^{-1} mol^{-1}	Ref
$VO(acac)_2$	DCE$^{a)}$	46.7	−61.9	13
$Zr(tfac)_4$$^{b)}$	C_6H_6	46.4	−63	12
$Hf(tfac)_4$	C_6H_6	49.8	−54	12
$U(fod)_4$$^{c)}$	CCl_4	21.8	−109	11
$Th(acac)_4$	AN$^{d)}$	29.4	−98	2
$Th(tta)_4$	AN	43.9	−58	This work
$V(acac)_3$	AN	73	−90.7	14
$Ga(acac)_3$	THF$^{e)}$	79	−84	15
$Zr(acac)_4$	C_6H_6	76.9	37	12
$Hf(acac)_4$	C_6H_6	74.0	26	12

a) 1,2-Dichloroethane. b) 1,1,1-Trifluoroacetylacetonate. c) 6,6,7,7,8,8,8-Heptafluoro-2,2-dimethyl-3,5-octanedionate. d) Acetonitrile. e) Tetrahydrofuran.

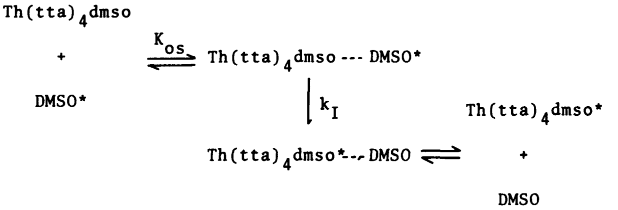

Fig. 8. Mechanism of the dmso exchange in $Th(tta)_4$ dmso in CD_3COCD_3.

$Th(tta)_4$ was slower than that of the acac exchange reaction in $Th(acac)_4$. According to the proposed mechanism (Fig. 7), the difference in reaction rate might be ascribed to the following causes: (1) The formation constant of $Th(tta)_4Htta$ is smaller than that of $Th(acac)_4Hacac$. (2) Replacement of coordinated tta by incoming $Htta_{enol}$ is slower than the acac replacement in $Th(acac)_4Hacac$. However, it is difficult at present to determine which causes to be predominant.

The values of activation parameters for the second-order rate constant of ligand-exchange reactions in *β*-diketonato complexes are listed in Table 3. In spite of a variety of ligands and solvents, it seems that there is a linear relationship between the values of ΔH^{*} and ΔS^{*} for the ligand-exchange reactions in $Th(acac)_4$, $Th(tta)_4$, $U(fod)_4$, $Zr(tfac)_4$, $Hf(tfac)_4$, and $VO(acac)_2$.[2,11–13] Although it is hardly discernible whether this relationship is held by accident or implies a mechanistic similarlity, almost the same mechanism has been proposed for the ligand-exchange reactions in $Th(acac)_4$, $Th(tta)_4$ and $U(fod)_4$, while different reaction mechanisms are proposed for $V(acac)_3$[14] and $Ga(acac)_3$.[15]

As described above, k_{obsd}^{dmso} does not follow the linear relationship with respect to free DMSO concentration. This fact suggests that neither the dissociative mechanism (D) nor the associative mechanism (A) fits the dmso exchange mechanism in $Th(tta)_4dmso$. On the other hand, the interchange mechanism (I)[16] seems to be probable as seen in Fig. 8, where free DMSO and $Th(tta)_4dmso$ form an outer-sphere complex, and the interchange process between the coordinated dmso and DMSO in the outer-sphere is the rate-determining step. On the basis of the I mechanism, the first-order rate constant of dmso exchange, k_{ex}^{dmso}, is expressed by

$$k_{ex}^{dmso} = \frac{k_I K_{os}[DMSO]}{1+K_{os}[DMSO]}, \tag{7a}$$

or

$$k_{ex}^{dmso^{-1}} = \frac{1}{k_I} + \frac{1}{k_I K_{os}}[DMSO]^{-1}, \tag{7b}$$

where k_I is the rate constant of the interchange process and K_{os} is the formation constant of the outer-sphere complex. Equation 7b is identical with Eq. 5, which was determined experimentally. Hence, the proposed I mechanism can interprete well the dmso exchange reaction in $Th(tta)_4dmso$ in acetone-d_6. Values of k_I and K_{os}, which were obtained from $k_I=1/p$ and $K_{os}=1/qk_I$, are listed in Table 4. The rate of the dmso exchange in $Th(tta)_4dmso$ is much faster than that of the tta exchange in $Th(tta)_4$. This fact supports the assumption that $Th(tta)_4$ and $Th(tta)_4Htta$ are in a fast equilibrium as shown in Fig. 7.

The *N*,*N*-dimethylformamide (dmf) exchange in eight-coordinate complexes, $[Tb(dmf)_8]^{3+}$, $[Er(dmf)_8]^{3+}$, and $[Tm(dmf)_8]^{3+}$, were studied by Merbach *et al.*[17–18] and they reported that the smaller the size of the central metal ion was, the more dissociative the character of the exchange mechanism was. In spite of the large negative value of ΔS^{*}, the I_d mechanism was proposed for $[Tb(dmf)_8]^{3+}$, where Tb(III) has a large ionic radius, and the D mechanism was proposed for $[Tm(dmf)_8]^{3+}$. Based on these facts, we

TABLE 4. KINETIC PARAMETERS OF dmso EXCHANGE IN Th(tta)$_4$dmso IN CD_3COCD_3

$\frac{T}{^\circ C}$	$\frac{k_I}{10^2\,s^{-1}}$	$\frac{K_{os}}{mol^{-1}\,kg}$
−64	11.8±4.1	3.5
−68	7.4±1.9	4.7
−72	7.9±3.1	3.2
−76	5.8±0.2	3.3
−80	3.0±1.6	5.3
−84	3.2±1.2	3.2
−88	1.6±0.8	4.9
−92	1.0±0.3	6.1
	$\Delta H^{\ddagger}=25.1\pm2.5$ kJ mol^{-1}	
	$\Delta S^{\ddagger}=-65\pm13$ J K^{-1} mol^{-1}	

can not rule out the possibility of the I_d mechanism in the dmso exchange in Th(tta)$_4$dmso, though the I_a mechanism seems to be more likely by considering a large ionic radius of Th(IV) and the negative $\Delta S^{\ddagger}$ value.

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