Kinetics of the Ligand Exchange Reaction between Tetrakis(acetylacetonato)-thorium(IV) and Free Acetylacetone in CD_3CN and $CDCl_3$

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Kinetics of the ligand exchange reaction between tetrakis(acetylacetonato)thorium(IV) and free acetylacetone in CD_3CN and $CDCl_3$ was studied by ^1H NMR. The rate law was written as rate=k[Th(acac)$_4$][Hacac]$_{enol}$, where k=(1.0±0.1)×10^2 s^{-1} mol^{-1} kg at 0 °C in CD_3CN and (1.7±0.1)×10^2 s^{-1} mol^{-1} kg at −16 °C in $CDCl_3$. The rates were retarded by addition of bases and the retardation effect well correlated with the donor number of the bases. Under the conditions studied, the activation entropies gave large negative values. A ligand exchange mechanism passing through a nine-coordinate intermediate is proposed to interpret the kinetic law.

Thorium(IV) is one of the largest metal ions in size and gives complexes with high coordination numbers. Eight-coordination is usually common and even the existence of nine- and ten-coordinate complexes were reported.[1-6] Tetrakis(2,4-pentanedionato)thorium(IV), where hereafter the common name of the ligand, *i.e.* acetylacetonate (acac) will be used, has been known as one of the typical eight-coordinate complexes having a square antiprismatic structure. The same structure is established in such acac complexes as Zr(acac)$_4$, Hf(acac)$_4$, and U(acac)$_4$.[1]

Little has been known with respect to the kinetics of the ligand substitution in eight-coordinate complexes. Adams and Larsen[7] studied the ligand exchange in Zr(acac)$_4$ and Hf(acac)$_4$ and proposed the mechanism passing through a seven-coordinate intermediate which was formed by the partial breaking of one of the chelate rings. They also studied the ligand exchange in Th(acac)$_4$ but reported that the rate was too fast to be measured by ^1H NMR. On the other hand, the mechanism involving a nine-coordinate intermediate was proposed by Folcher *et al.*[8] in the ligand exchange of U(fod)$_4$ (fod=6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate).

In an earlier study,[9] it was found that the rate of the ligand exchange between Th(acac)$_4$ and Hacac was measurable in chloroform by ^1H NMR. In this paper, we report in detail the kinetic results of the acac exchange in Th(acac)$_4$ and propose a possible mechanism proceeding *via* a nine-coordinate intermediate.

Experimental

Materials. Th(acac)$_4$ was synthesized by the following procedure. The solution containing 0.01 mol of thorium nitrate was stirred with 5 g of acetylacetone; then aqueous ammonia was added slowly until the pH of the solution became 5. White precipitate obtained was dried *in vacuo* for 1 d. Recrystallization of the precipitate was carried out twice first from benzene and then Hacac. Found: C, 38.0; H, 4.3%, Calcd for $C_{20}H_{28}O_8Th$: C, 38.2; H, 4.5%.

Acetylacetone was dried over anhydrous calcium sulfate and distilled twice. Acetonitrile, dichloromethane, tetrahydrofuran (THF) and chloroform-*d* ($CDCl_3$) were distilled, and dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and hexamethylphosphoric triamide (HMPT) were distilled under reduced pressure before use. Acetonitrile-d_3 (CD_3CN) was dried over Molecular Sieve 4A.

Water contents in CD_3CN and $CDCl_3$ were determined by the Karl-Fischer method.

Measurements of UV and ^1H NMR Spectra. The UV spectra of Th(acac)$_4$, Hacac and their mixture were measured by using a Shimadzu 210A spectrophotometer with a 0.1 mm quartz cell. A JEOL JNM-FX100 FT-NMR spectrometer equipped with a JNM-VT-3B temperature controller was used for ^1H NMR measurements. The preparation of NMR samples was carried out by dissolving a small amount of sample materials, which were weighed in 5 mmϕ NMR tubes with a microbalance, in appropriate solvents.

Determination of the Fraction of Keto- and Enol-forms in Hacac. Two forms, keto and enol, of Hacac are in tautomeric equilibrium and the concentration ratio, [enol]/[keto], was determined by area measurements of methyl proton signals for keto- and enol-isomers. In order to obtain the temperature dependence of the ratio, the area measurements were performed in the temperature range from −20 to 36 °C.

Rate Analysis. The first-order rate constants of the acac exchange in Th(acac)$_4$, k_{obsd}, were determined from the line shape analysis of the NMR signals by using the two site model.[10]

Results

The absorption spectrum of Th(acac)$_4$ shows a peak at 283 nm with molar extinction coefficients, ε, of 4.9×10^4 M^{-1} cm^{-1} (1 M=1 mol dm^{-3}) in acetonitrile and 4.8×10^4 M^{-1} cm^{-1} in dichloromethane. The spectra of the mixture containing Th(acac)$_4$ and Hacac coincided with the sum of those of each component in acetonitrile and dichloromethane, and remained unchanged for several hours.

The ^1H NMR spectra of the reaction mixture in CD_3CN are shown in Fig. 1. Three methyl proton

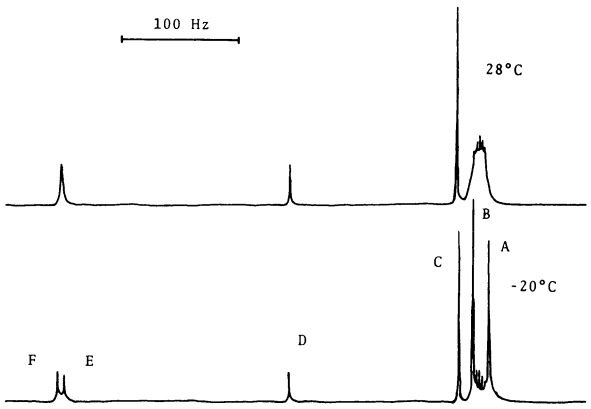

Fig. 1. ^1H NMR spectra of the reaction mixture in CD_3CN at −20 °C and 28 °C. [Th(acac)$_4$]=0.0707 mol kg^{-1} and [Hacac]$_{total}$=0.444 mol kg^{-1}.

signals and two methine proton signals were clearly observed at −20 °C. Two methyl proton signals of $Th(acac)_4$ (A) and Hacac in the enol-form (B) coalesced as the temperature was raised. Similar behavior was observed in methine proton signals of $Th(acac)_4$ (E) and Hacac in the enol-form (F). No line broadening was observed for the methyl proton signal (C) and methylene proton signal (D) of Hacac in the keto-form. Since signals A and B overlapped with the methyl proton signals of the solvent used, the rate analyses were carried out by using signals E and F.

The change of ^1H NMR signals in CD_3CN at various temperatures was very similar to that in $CDCl_3$ in the earlier work.[9] The ligand exchange reaction between $Th(acac)_4$ and Hacac in the enol-form can be described as follows.

$$Th(acac)_4 + Hacac^*_{enol} \rightleftharpoons Th(acac)_3(acac^*) + Hacac_{enol}, \quad (1)$$

where the asterisk denotes the exchanging species.

The life time of acac in the coordination site, τ_c, correlates directly with the first-order rate constant by the following equation.

$$k_{obsd} = 4\tau_c^{-1} \quad (2)$$

Plots of k_{obsd} *vs.* the concentration of $Th(acac)_4$ indicate that the values of k_{obsd} are independent of $[Th(acac)_4]$ (Fig. 2). On the other hand, plots of k_{obsd} *vs.* the concentration of Hacac in the enol-form, $[Hacac]_{enol}$, in CD_3CN and $CDCl_3$ show that the plots are linear passing through the origin (Figs. 3 and 4). These results lead to the following rate equation.

$$Rate = k_{obsd}[Th(acac)_4] = k[Th(acac)_4][Hacac]_{enol}, \quad (3)$$

where k is the second-order rate constant. The values of k and activation parameters are listed in Tables 1 and 2. These results indicate that the exchange rate is influenced by solvents, *i.e.* the rate in $CDCl_3$ is faster than that in CD_3CN. This is mainly due to the difference in activation entropy, ΔS^*, rather than the difference in activation enthalpy, ΔH^*.

Influence of the Addition of Bases. The kinetic parameters of the acac exchange in $Th(acac)_4$ were obtained also in the presence of various bases. The results are listed in Table 3. The addition of the bases retarded the exchange rate and this effect is remarkable in the case of strong bases. The order of the retardation effect is found to be as follows;

HMPT > DMSO > DMF > THF, H_2O.
(38.8) (29.8) (26.6) (20.0) (18.0)

It is to be noted that this is the order of Gutmann's

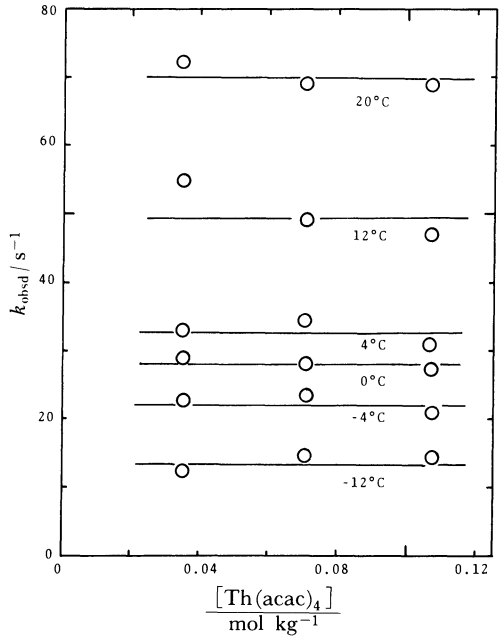

Fig. 2. Dependence of k_{obsd} on $[Th(acac)_4]$ in CD_3CN at various temperatures.

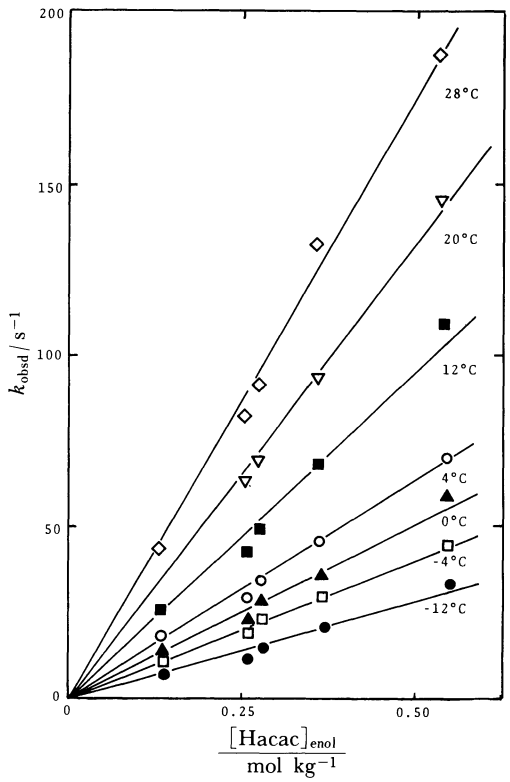

Fig. 3. Plots of k_{obsd} *vs.* $[Hacac]_{enol}$ in CD_3CN at various temperatures.

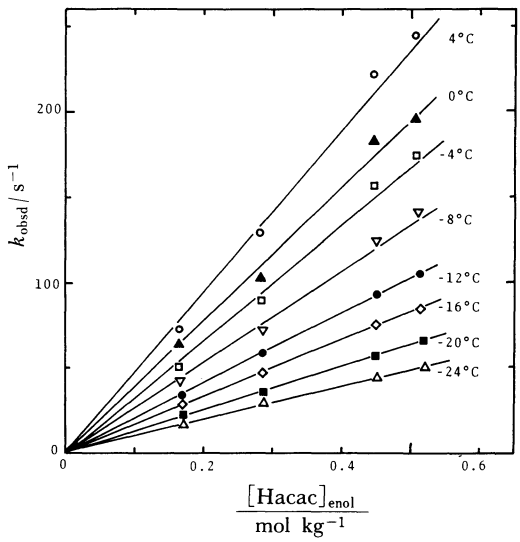

Fig. 4. Plots of k_{obsd} *vs.* $[Hacac]_{enol}$ in $CDCl_3$ at various temperatures.

donor number (DN)[11] which is given in parentheses.

The values of k_{obsd} obtained at various H_2O concentrations in CD_3CN and at various DMSO concentrations in $CDCl_3$ are listed in Tables 4 and 5, respectively. The reciprocal plots of k_{obsd} *vs.* [H_2O] or [DMSO] are shown in Figs. 5 and 6, respectively. From these results,

Table 1. Second-order rate constants and the kinetic parameters for acac exchange in CD_3CN

[Th(acac)$_4$]	[Hacac]$_{enol}$(0°C)	k(0°C)	ΔH^*	ΔS^*
mol kg^{-1}	mol kg^{-1}	s^{-1} mol^{-1} kg	kJ mol^{-1}	J mol^{-1} K^{-1}
0.0394	0.279	100	33.0±1.5	−84.9±5.2
0.0704	0.189	97.0	28.8±1.7	−100.8±6.2
0.0706	0.261	88.4	31.2±0.8	−92.9±2.7
0.0707	0.279	101	31.9±0.7	−102.9±2.4
0.0705	0.365	102	29.1±0.6	−99.2±2.1
0.0707	0.546	110	27.8±1.1	−103.3±3.8
0.107	0.280	96.3	29.8±0.5	−97.1±1.9

The water content in the solvent (CD_3CN) is 0.04 mol kg^{-1}.

Table 2. Second-order rate constants and the kinetic parameters for acac exchange in $CDCl_3$

[Th(acac)$_4$]	[Hacac]$_{enol}$(−16°C)	k(−16°C)	ΔH^*	ΔS^*
mol kg^{-1}	mol kg^{-1}	s^{-1} mol^{-1} kg	kJ mol^{-1}	J mol^{-1} K^{-1}
0.0822	0.170	164	27.9±0.6	−91.2±2.2
0.0817	0.276	166	29.4±0.5	−87.0±1.8
0.0800	0.457	165	32.9±0.7	−73.0±2.7
0.0808	0.517	159	32.8±0.9	−74.1±3.3

The water content in the solvent ($CDCl_3$) is 0.008 mol kg^{-1}.

Table 3. Kinetic parameters of the ligand exchange in the presence of bases

Solvent	Base	k(0°C)	ΔH^*	ΔS^*
		s^{-1} mol^{-1} kg	kJ mol^{-1}	J mol^{-1} K^{-1}
CD_3CN	H_2O	82.3	28.7±0.3	−102±1
	THF	81.1	29.1±1.5	−101±5
	DMF	54.8	30.1±0.6	−101±2
	DMSO	32.4	32.0±0.7	−98±2
	HMPT	9.1	39.7±1.6	−80±5
$CDCl_3$	THF	321	27.7±1.1	−95±4
	DMF	120	37.4±1.8	−68±6
	DMSO	54.3	33.5±2.3	−88±7
	HMPT	16.7	29.8±4.1	−112±13

Conditions: [Th(acac)$_4$]=0.070—0.072 mol kg^{-1}, [Hacac]$_{enol}$=0.27—0.29 mol kg^{-1}, [Base]=0.24—0.25 mol kg^{-1} in CD_3CN; [Th(acac)$_4$]=0.080—0.082 mol kg^{-1}, [Hacac]$_{enol}$=0.27—0.29 mol kg^{-1}, [Base]=0.24—0.25 mol kg^{-1} in $CDCl_3$.

Table 4. Dependence of the first-order rate constants on [H_2O] in CD_3CN

[Th(acac)$_4$]	[Hacac]$_{enol}$		[H_2O]	k_{obsd}	
mol kg^{-1}	mol kg^{-1}		mol^{-1} kg	s^{-1}	
	(0°C)	(20°C)		(0°C)	(20°C)
0.0706	0.278	—	0.074	31.5	—
0.0706	0.278	0.273	0.246	22.6	55.5
0.0701	0.276	0.271	0.477	19.0	49.4
0.0699	0.275	0.270	0.816	16.2	45.4
0.0706	0.278	0.273	1.01	12.4	40.4

Table 5. Dependence of the first-order rate constants on [D_MSO] in $CDCl_3$

[Th(acac)$_4$]	[Hacac]$_{enol}$		[DMSO]	k_{obsd}	
mol kg^{-1}	mol kg^{-1}		mol^{-1} kg	s^{-1}	
	(24°C)	(32°C)		(24°C)	(32°C)
0.0810	0.273	0.270	0.068	128	184
0.0812	0.274	0.271	0.135	83.6	127
0.0812	0.271	0.268	0.249	49.9	76.6
0.0811	0.270	0.267	0.401	31.6	50.0
0.0812	0.275	0.272	0.672	21.2	31.8

The water content in the solvent ($CDCl_3$) is 0.008 mol kg^{-1}.

k_{obsd}^{-1} can be expressed by the following equation.

$$k_{obsd}^{-1} = a + b[H_2O \text{ or DMSO}], \quad (4)$$

where a and b are constants. The intercepts of these plots agree well with the values of k_{obsd}^{-1} in the absence of bases.

Discussion

It is generally considered that the ligand exchange processes in (acetylacetonato)metal complexes consist of several steps. Two types of initiation mechanism are presented for the acac exchange reactions: 1) bond breaking of one end of the chelate bond; 2) bond formation with free Hacac at the additional coordination site without a ring opening of the chelate.

Type (1) has been proposed for the acac exchanges in $Al(acac)_3$,[12] $Co(acac)_3$,[13] and type (2) has been proposed for those in $Cr(acac)_3$, $Rh(acac)_3$, $V(acac)_3$ and $Fe(acac)_3$.[13] In the case of the acac exchange in $Al(acac)_3$, a complete dissociation of one of the coordinated acac occurs prior to an attack of entering Hacac to the complex. For most of the other acac exchange reactions which belong to type (1) or type (2), a proton transfer from incoming Hacac to coordinated acac is involved in the acac exchange processes.

The ionic radius of Th^{4+} is large enough to make nine- or ten-coordinate complexes, *e.g.* $Th(tta)_4topo$ and $Th(tta)_4tbp$, where tta, topo and tbp are 2-thenoyltrifluoroacetonate, trioctylphosphine oxide and tributyl phosphate, respectively.[3] This fact suggests that type (2) seems to be probable for the acac exchange in $Th(acac)_4$.

As shown in Fig. 7, $Th(acac)_4$ (I) forms a nine-coordinate intermediate, $Th(acac)_4Hacac^*$ (II), by the attack of free acetylacetone, and the proton of entering Hacac* is transferred to one of the coordinated acac, followed by the Th–O bond breaking of the chelate ring. Then the protonated ligand (Hacac) leaves rapidly from the coordination sphere.

Since the rate of ligand exchange of unidentate ligands is generally much faster than that of bidentate ligands in the complexes of the same metal ion [10,14] it can be assumed that complexes (I) and (II) are in fast

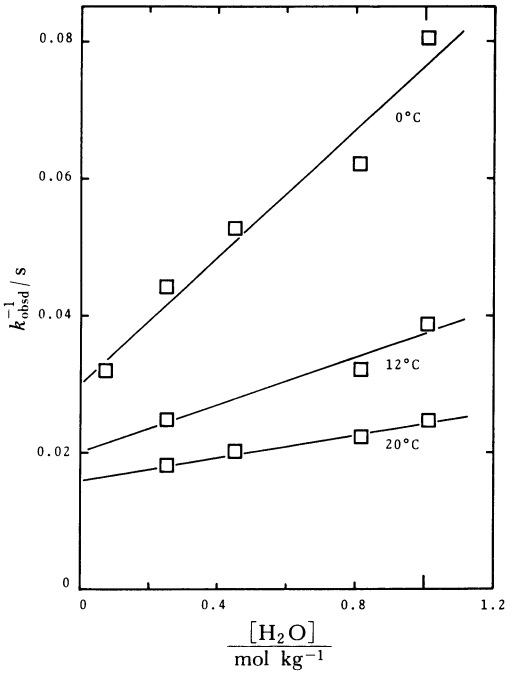

Fig. 5. Plots of k_{obsd}^{-1} against $[H_2O]$ in CD_3CN at various temperatures.

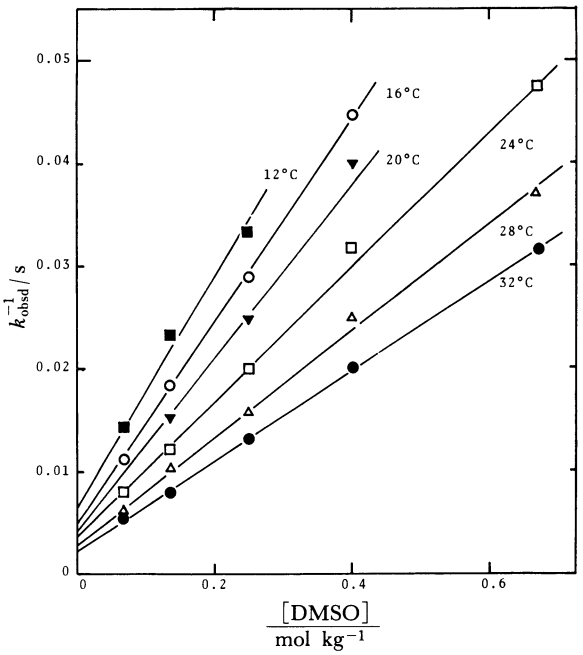

Fig. 6. Plots of k_{obsd}^{-1} against [DMSO] in $CDCl_3$ at various temperatures.

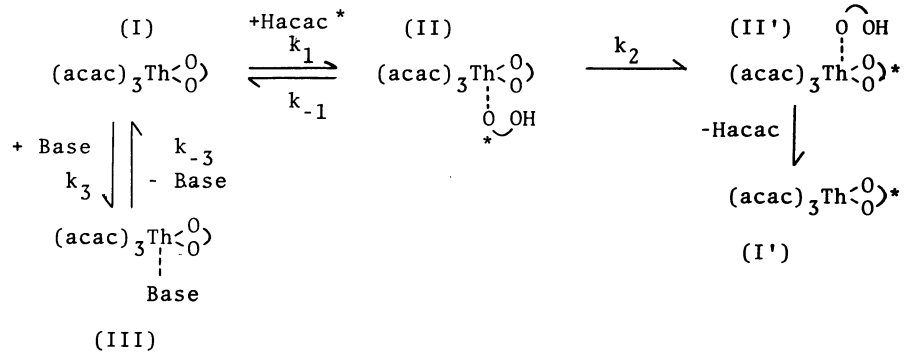

Fig. 7. Possible mechanism of the ligand exchange in $Th(acac)_4$. HO̅O represents Hacac in the enol-form.

equilibrium. Based on this assumption, the rate of exchange is expressed by Eq. (5).

$$\text{Rate} = \frac{k_1 k_2}{k_{-1}}[\text{I}][\text{Hacac}]_{\text{enol}} \quad (5)$$

If $[\text{I}] \gg [\text{II}]$ or $K_1[\text{Hacac}]_{\text{enol}} \ll 1$, where $K_1 = k_1/k_{-1}$, the first-order rate constant for the exchange of acac, k_{ex}, can be written by Eq. (6).

$$k_{\text{ex}} = k_2 K_1 [\text{Hacac}]_{\text{enol}} \quad (6)$$

Equation (6) is basically the same as Eq. (3), where k corresponds to k_2K_1 in the absence of water. The k_2 pathway involves two processes, *i.e.* the proton transfer from entering Hacac* to coordinated acac and the Th–O bond breaking in the chelate ring. It appears difficult to determine which process is the rate determining step from the above results.

In the case of tris(acetylacetonato) complexes,[12,13] it was often observed that the ligand exchange was accelerated in the presence of water. However, the retardation by the addition of bases including water was observed for the acac exchange in $Th(acac)_4$ as described above. A good correlation between $\ln k$ and DN as shown in Fig. 8 suggests that the donicity of bases might be important for the retardation effect. Strong donor bases may bind to $Th(acac)_4$ tightly forming adduct complex (III) and hence hinder the formation of (II).

On the assumption that complex (III) is in fast equilibrium with (I) and that the concentration of (II) is much low compared with that of (I) or (III), k_{ex} in the presence of bases is written by Eq. (7).

$$k_{\text{ex}} = \frac{k_2 K_1 [\text{Hacac}]_{\text{enol}}}{1 + K_3[\text{Base}]}, \quad (7)$$

or by Eq. (8).

$$k_{\text{ex}}^{-1} = \frac{1}{k_2 K_1 [\text{Hacac}]_{\text{enol}}} + \frac{K_3[\text{Base}]}{k_2 K_1 [\text{Hacac}]_{\text{enol}}}, \quad (8)$$

where $K_3 = k_3/k_{-3}$. Hence, when the concentration of Hacac is kept constant, the plots of k_{ex}^{-1} *vs.* [Base] should give a straight line. This relationship is the same as Eq. 4 which was determined experimentally.

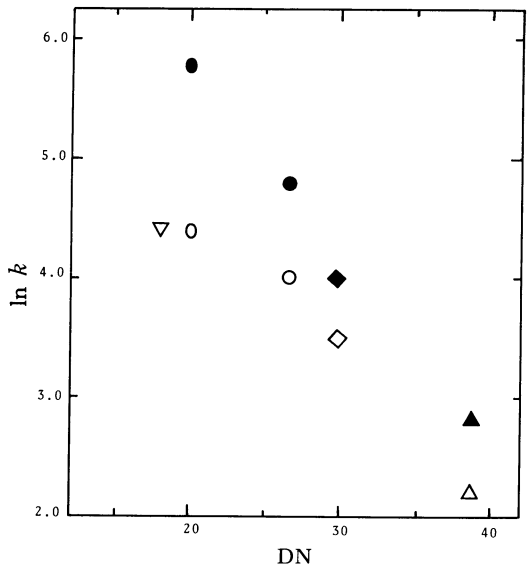

Fig. 8. Relationship between $\ln k$ and the donor number (DN) at 0 °C. ▽: H_2O, 0: THF, ○: DMF, ◇: DMSO, △: HMPT in CD_3CN, and ●: THF, ●: DMF, ◆: DMSO, ▲: HMPT in $CDCl_3$.

Thus, the proposed mechanism can explain well the experimental results. The large negative values of activation entropies shown in Table 3 might support the formation of nine-coordinate intermediate.

Nishizawa and Saito[14] studied the kinetics of acac exchange in $VO(acac)_2$ and found that the reaction was retarded by the addition of DMSO. They proposed that the retardation effect was attributed to the formation of an outer-sphere intermediate with DMSO, which prohibits an associative attack by free Hacac. Unlike their interpretation in $VO(acac)_2$, the retardation by bases in the present study arises from the competition between bases and Hacac in the enol-form at the ninth coordination site. From the slopes and intercept in Figs. 5 and 6, the formation constant of the nine-coordinate adduct complex (III) was determined to be *ca.* 0.9 $mol^{-1}kg$ at 12 °C for $Th(acac)_4H_2O$ in CD_3CN, and *ca.* 20 $mol^{-1}kg$ at 32 °C for $Th(acac)_4dmso$ in $CDCl_3$. These values indicate that the presence of such strong bases as DMSO and HMPT in solution leads to the adduct formation with bases.

In this study, it was found that $Th(acac)_4$ was the most labile of acetylacetonato complexes of quadrivalent metal ions. The order of the lability for the ligand exchange reaction is as follows:[7,15,16]

$$\text{Th(acac)}_4 \geq \text{U(acac)}_4 > \text{Zr(acac)}_4 \simeq \text{Hf(acac)}_4 > \text{Ti(acac)}_3^+.$$

As the ionic size of Th^{4+} is much larger than the ionic radii of Zr^{4+} and Hf^{4+}, and the electronic configuration of Th^{4+} is $5f^0$ and $6d^0$, the electric repulsion between electrons of donor molecule and Th^{4+} might be weak. These facts also support the proposed mechanism in which the reaction proceeds through the nine-coordinate intermediate for the ligand exchange reaction between $Th(acac)_4$ and Hacac.

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References

1) S. J. Lippard, "Eight-Coordination Chemistry," in "Progress in Inorganic Chemistry," ed by F. A. Cotton, Wiley-Interscience, New York (1967), Vol. 8, pp. 108—193.
2) M. Lenner and O. Lindgvist, *Acta Crystallogr., Sect. B*, **35**, 600 (1979).
3) L. D. C. Bok, G. F. S. Wessels, and J. G. Leipordt, *Z. Anorg. Allg. Chem.*, **404**, 76 (1974).
4) J. G. Leipordt, G. F. S. Wessels, and L. D. C. Bok, *J. Inorg. Nucl. Chem.*, **37**, 2487 (1975).
5) R. J. Hill and C. E. F. Rickard, *J. Inorg. Nucl. Chem.*, **37**, 2481 (1975).
6) M. M. Akhtar and A. J. Smith, *Acta Crystallogr., Sect. B*, **31**, 1361 (1975).
7) A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 814 (1966).
8) G. Folcher, N. Keller, C. Kiener, and J. Paris, *Can. J. Chem.*, **55**, 3559 (1977).
9) N. Fujiwara, H. Tomiyasu, and H. Fukutomi, *Chem. Lett.*, **1983**, 377.
10) Y. Ikeda, H. Tomiyasu, and H. Fukutomi, *Bull. Chem.*

Soc. Jpn., **56**, 1060 (1983).
11) V. Gutmann, "Coordination Chemistry in Non-aqueous Solution," Springer-Verlag, Wien (1968).
12) K. Saito, *Pure Appl. Chem.*, **38**, 325 (1974).
13) a) H. Kido, *Bull. Chem. Soc. Jpn.*, **53**, 82 (1980); b) H. Kido and K. Saito, *ibid.*, **53**, 428 (1980); c) A. Watanabe, H. Kido, and K. Saito, *Inorg. Chem.*, **20**, 1107 (1981).
14) M. Nishizawa and K. Saito, *Bull. Chem. Soc. Jpn.*, **51**, 483 (1978).
15) G. M. Khvostik, V. N. Sokolov, G. K. Grebenshchikov, S. A. Toropov, and G. P. Kondratenkov, *Koordinatsionnaya Khimiya*, **5**, 680 (1979).
16) M. Nishizawa, H. Kido, I. Kinoshita, Y. Soma, and K. Saito, *Bull. Chem. Soc. Jpn.*, **49**, 819 (1976).