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Kinetics of Ligand-Exchange Reactions in Tetrakis(acetylacetonato)-uranium(IV) in Organic Solvents

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The kinetics of ligand-exchange reactions between tetrakis(acetylacetonato)uranium(IV) [U(acac)$_4$] (acac=acetylacetonate) and free acetylacetone Hacac in various organic solvents, $CDCl_3$, C_6D_6, and CD_3CN has been studied by ^{1}H NMR. The rate laws were found to change remarkably with these solvents used. The observed first-order rate constant k_{obsd} in $CDCl_3$ depended linearly on the concentration of free Hacac in the enol form as $k_{obsd}=k_s[\mathrm{Hacac}]_{enol}$, while the plots of k_{obsd} vs. $[\mathrm{Hacac}]_{enol}$ in C_6D_6 deviated from straight lines in higher concentrations of Hacac$_{enol}$. The exchange rate was much slower in CD_3CN than in $CDCl_3$ and C_6D_6, and k_{obsd} increased only slightly with $[\mathrm{Hacac}]_{enol}$. Addition of dimethyl sulfoxide (DMSO) in C_6D_6 yielded the retardation of exchange rate giving a rate law $k_{obsd}^{-1}=p+q[\mathrm{DMSO}]$, where p and q are constants. From the results obtained in these solvents, a mechanism passing through nine-coordinate intermediates was proposed.

Among quadrivalent metal ions which form eight-coordinate complexes with β-diketones, uranium(IV) has been studied most extensively. Earlier studies were much concerned with the solvent extractions of a variety of U(IV) β-diketonato complexes, [U(acac)$_4$], [U(hfaa)$_4$], [U(tta)$_4$], and [U(ba)$_4$], where hfaa=hexafluoroacetylacetonate, tta=2-thenoyltrifluoroacetonate and ba=benzoylacetonate, since the solvent extraction method has been of particular importance in the separation of actinoid elements. Despite a large number of studies little has been known with respect to the kinetics of ligand exchange reactions in the above complexes.1,2)

Recently, we reported the kinetic results of ligand-exchange reactions in tetrakis(β-diketonato) complexes of thorium(IV), [Th(acac)$_4$],3,4) and [Th(tta)$_4$],5) and proposed a mechanism passing through nine-coordinate intermediates. This paper presents the results of kinetic experiments on the acac exchange between [U(acac)$_4$] and free Hacac, and the results are compared with those of earlier studies. A similar mechanism in the reactions of [Th(β-diketonate)$_4$] is also proposed in the present study.

Experimental

The [U(acac)$_4$] complex was synthesized by the same procedure as described in a earlier paper.6) The solution of uranium(IV) chloride which was prepared by electrolytic reduction of uranyl(VI) chloride solution in 0.1 M HCl (M=mol dm^{-3}), was stirred with 0.1 M acetylacetone and the pH of the mixture was adjusted to about 4 with 0.1 M NaOH solution. A green precipitate was dried in vacuo for two days, and then recrystallized from benzene in a glove box filled with dried nitrogen. Identification of the complex was made by measurements of UV-visible and NMR spectra. Both the UV-visible and NMR spectra agreed well with those reported in a earlier paper.7) Acetylacetone was dried over anhydrous calcium sulfate and distilled twice. Chloroform-*d* $CDCl_3$ (Merck 99%) was distilled. Acetonitrile-d_3 CD_3CN (Merck 99.95%) was dried over 4A molecular sieves and distilled. Benzene-d_6 C_6D_6 (Merck 99.6%) was dried over 4A molecular sieves and distilled. Dimethyl sulfoxide was distilled under reduced pressure. The UV-visible spectra were measured by using a Shimadzu 210 spectrophotometer with 10 mm quartz cells. The NMR spectra were recorded on a JEOL JNM-FX 100 NMR spectrometer equipped with a JNM-VT-3B temperature controller. The fraction of keto and enol isomers of Hacac in C_6D_6 were determined by area measurements of methyl proton NMR signals for keto and enol isomers in the temperature regions in which kinetic experiments were carried out.

Results

The ^{1}H NMR spectra of the mixture of [U(acac)$_4$] and Hacac in C_6D_6 were measured at various temperatures (Fig. 1), where the signals were assigned as follows: A and C are methine proton signals of [U(acac)$_4$] and Hacac$_{enol}$, respectively, G and F methyl proton signals of [U(acac)$_4$] and Hacac$_{enol}$, respectively, D and E methylene and methyl proton signals of Hacac$_{keto}$, and B refers to the signal of C_6D_5H involved in C_6D_6. The methyl proton signal (G) of [U(acac)$_4$] shifted to the upfield, while the methine proton signal (A) shifted to the downfield. These results agree well with those of earlier studies8,9) suggesting that $\chi_{\parallel}$ is greater than $\chi_{\perp}$ in [U(acac)$_4$].

It can be seen in Fig. 1 that signals A, C, F, and G exhibit the broadening of line widths as the temperature goes up from 4 to 64 °C. This is attributed to the exchange of acac between [U(acac]$_4$] and Hacac$_{enol}$ as follows:

$$[\mathrm{U(acac)_4}] + \mathrm{Hacac^*_{enol}} \rightleftharpoons [\mathrm{U(acac)_3(acac^*)}] + \mathrm{Hacac_{enol}}, \qquad (1)$$

where an asterisk denotes the exchanging species. Since signal G is isolated from other signals and reveals the most clear broadening, the kinetic data were determined from the line-shape analysis of signal G.

In the case of the slow exchange region,[10] the lifetime τ of the ligand at the coordination site is related with the transverse relaxation time of the exchanging nucleus by

$$1/\tau = 1/T_2 - 1/T_{2a}. \tag{2}$$

In the present study T_2 refers to the relaxation time of signal G in the reaction mixture, where acac exchanges between [U(acac)$_4$] and Hacac$_{enol}$, and T_{2a} refers to the relaxation time of signal G in the absence of free Hacac. The first-order rate constant k_{obsd} for reaction 1 is given by the following equation.

$$k_{obsd} = 4/\tau \tag{3}$$

Application of the slow exchange region was tested by plotting k_{obsd} thus determined as a function of temperature, where the plot should obey an Arrhenius type relationship. A typical plot is shown in Fig. 2 indicating that the relaxation process is controlled by the chemical exchange at temperatures studied.

From the plots of k_{obsd} vs. the concentration of the complex (Fig. 3), the exchange reaction is found to be first-order with respect to [U(acac)$_4$] in C_6D_6, i.e. rate=k_{obsd}[U(acac)$_4$]. In Fig. 4, the plots of k_{obsd} determined in $CDCl_3$ vs. [Hacac]$_{enol}$ give straight lines passing through the origin, which are expressed by

$$k_{obsd} = k_s[\text{Hacac}]_{enol}, \tag{4}$$

where k_s denotes the second-order rate constant. The values of k_s ($s^{-1}\,mol^{-1}\,kg$) were determined as: $(1.57\pm0.15)\times10^3$, $(2.66\pm0.30)\times10^3$ and $(4.21\pm0.55)\times10^3$ at 30, 40, and 50 °C, respectively. The corresponding plots with [Hacac]$_{enol}$ in C_6D_6 deviate from a linear relationship, but the plots of k_{obsd}^{-1} vs. [Hacac]$_{enol}^{-1}$ yield straight lines (Fig. 5) giving the following rate law.

$$k_{obsd}^{-1} = a + b[\text{Hacac}]_{enol}^{-1} \tag{5}$$

In CD_3CN, k_{obsd} changes only slightly with [Hacac]$_{enol}$

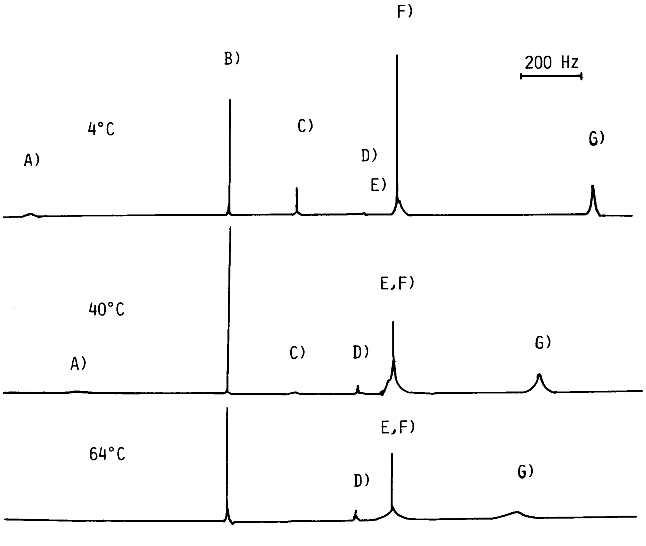

Fig. 1. ^{1}H NMR spectra of the mixture of [U(acac)$_4$] and free Hacac in C_6D_6 at 4, 40 and 64 °C under the following conditions: [U(acac)$_4$]=0.0496 mol kg^{-1}, [Hacac]=0.0128 mol kg^{-1}.

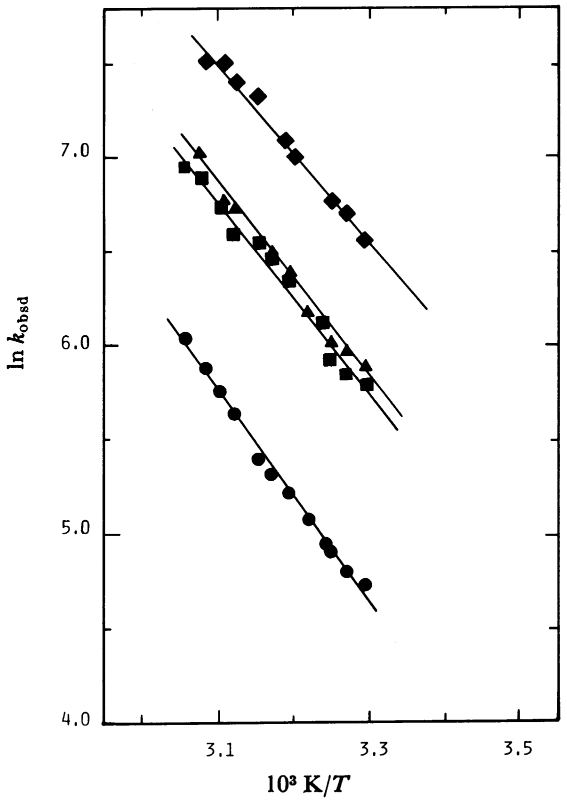

Fig. 2. Typical plots of k_{obsd} as a function of reciprocal temperature in $CDCl_3$. The concentrations of [U(acac)$_4$] and Hacac$_{total}$ (mol kg^{-1}) are as follows: ●: 0.0317, 0.0693; ■: 0.0319, 0.182; ▲: 0.0325, 0.264; ◆: 0.0324, 0.500.

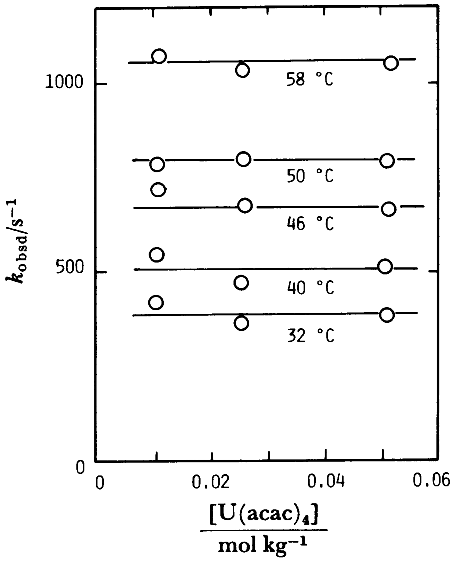

Fig. 3. The dependence of k_{obsd} on the concentration of [U(acac)$_4$] in C_6D_6 at various temperatures. The concentration of total Hacac was kept at 0.545 mol kg^{-1}.

as is illustrated in Fig. 6.

Addition of DMSO to C_6D_6 solutions retarded remarkably the exchange rates (Fig. 7). Under the conditions [DMSO]<0.15 mol kg^{-1} in C_6D_6, plots of k_{obsd}^{-1} vs. [DMSO] are fitted to straight lines (Fig. 8) and the rate law at constant $[Hacac]_{enol}$ is expressed by

$$k_{obsd}^{-1} = p + q[DMSO]. \tag{6}$$

In the presence of high concentration of DMSO ([DMSO]≥0.5 mol kg^{-1}), k_{obsd} (s^{-1}) reaches constant values as follows: 113±14, 179±11, 241±9, and 412±16, at 40, 50, 60, and 70 °C, respectively. The concentrations of $Hacac_{enol}$ in C_6D_6 at various temperatures were calculated by using values of $\Delta H°$ (kJ mol^{-1}) and $\Delta S°$ (J K^{-1} mol^{-1}) for the equilibrium in Hacac, which were determined by the NMR method as above-described. The values obtained are −7.16±0.44 for $\Delta H°$ and −4.35±1.4 for $\Delta S°$. The $\Delta H°$ and $\Delta S°$ values used for calculation in other solvents[4] are as follows: −7.5±0.5 and 10.3±0.2 in $CDCl_3$; −1.6±0.08 and 1.38±0.30 in CD_3CN, respectively.

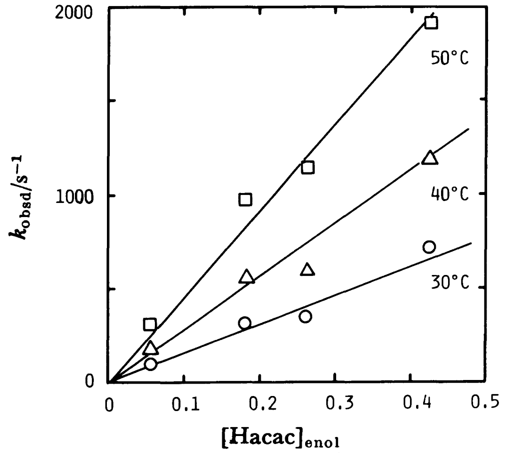

Fig. 4. Plots of k_{obsd} vs. $[Hacac]_{enol}$ in $CDCl_3$ at various temperatures. $[U(acac)_4]=0.0321$ mol kg^{-1}.

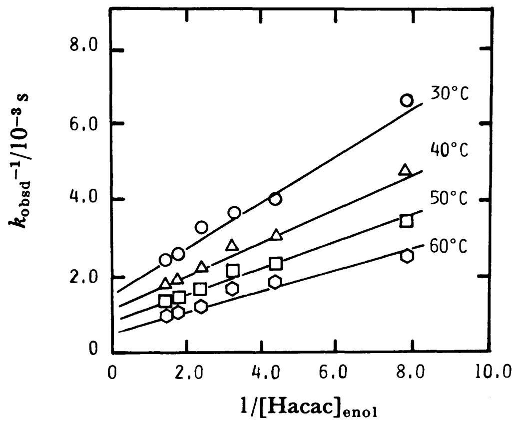

Fig. 5. Plots of k_{obsd}^{-1} vs. $1/[Hacac]_{enol}$ in C_6D_6.

Discussion

The rate laws (Eqs. 4 and 5) can be well explained by assuming the presence of a preequilibrium between [U(acac)$_4$] and free $Hacac^*_{enol}$ prior to the acac exchange as follows:

$$[U(acac)_4] + Hacac^*_{enol} \overset{K_1}{\rightleftharpoons} [U(acac)_4\cdots Hacac^*_{enol}], \tag{7}$$

where K_1 is the equilibrium constant and [U-

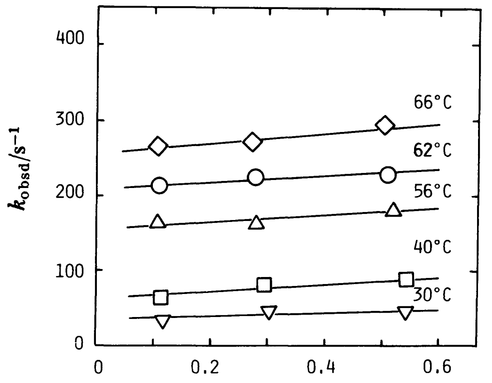

Fig. 6. Plots of k_{obsd} vs. $[Hacac]_{enol}$ in CD_3CN at various temperatures. $[U(acac)_4]=0.0521$ mol kg^{-1}.

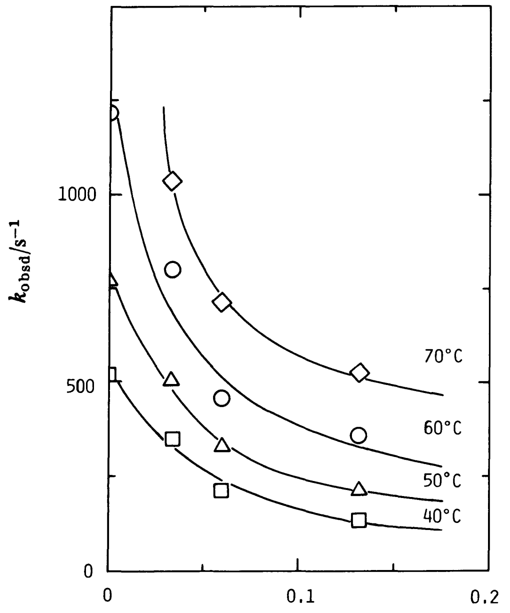

Fig. 7. Effect of added DMSO on the exchange rate in C_6D_6 at various temperatures. $[U(acac)_4]=0.0485$ mol kg^{-1}, $[Hacac]_{total}=0.556$ mol kg^{-1}.

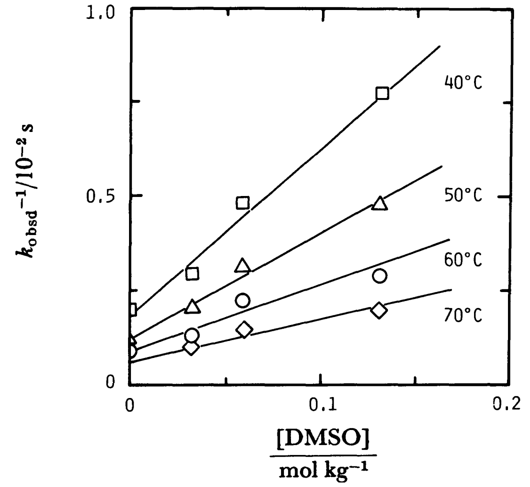

Fig. 8. Plots of k_{obsd}^{-1} vs. [DMSO] in C_6D_6 at various temperatures.

Table 1. Values of K_1, K_3, and k_2 at Various Temperatures in C_6D_6

Temperature °C	K_1 kg mol^{-1}	K_3 kg mol^{-1}	k_2 s$^{-1}\times10^3$
40	2.72	63.8	0.901
50	2.68	40.0	1.24
60	2.69	36.6	1.69

$(acac)_4\cdots Hacac^*_{enol}]$ denotes an intermediate complex. If the acac exchange takes place only through the intermediate, k_{obsd} can be expressed by

$$k_{obsd} = \frac{k_2K_1[\mathrm{Hacac}]_{enol}}{1+K_1[\mathrm{Hacac}]_{enol}} \tag{8a}$$

or

$$k_{obsd}^{-1} = 1/k_2 + 1/(k_2K_1[\mathrm{Hacac}]_{enol}), \tag{8b}$$

where k_2 refers to the rate constant for acac exchange in the intermediate, which is accompanied by a proton transfer from $Hacac^*_{enol}$ to one of the coordinated acac.

If K_1 is small enough to apply the condition $K_1[\mathrm{Hacac}]_{enol} \ll 1$, Eq. 8 is simplified as

$$k_{obsd} = k_2K_1[\mathrm{Hacac}]_{enol}. \tag{9}$$

Equation 9 is essentially the same as Eq. 4. This is the case for the reaction in $CDCl_3$, where $k_s=k_2K_1$, and k_2 and K_1 can not be determined independently. Under the conditions $K_1[\mathrm{Hacac}]_{enol}\simeq1$ with relatively large values of K_1, a linear relationship is no longer expected for the plot of k_{obsd} vs. $[\mathrm{Hacac}]_{enol}$. On the other hand, Eq. 8b shows that the plot should be linear if k_{obsd}^{-1} is plotted against $[\mathrm{Hacac}]^{-1}{}_{enol}$. This is the case for the reaction in C_6D_6, where Eq. 5 coincides with Eq. 8b, and the values of K_1 and k_2 can be determined. The results are listed in Table 1.

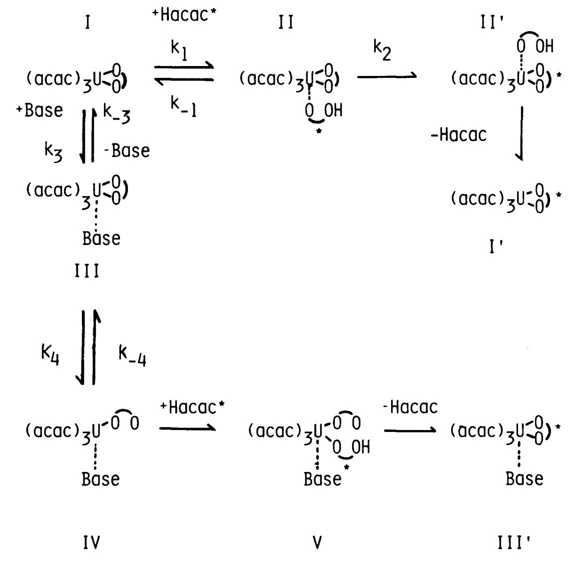

Fig. 9. Possible mechanism for the exchange of acac between $[U(acac)_4]$ and $Hacac^*_{enol}$. $\overset{\frown}{O\,O}$ and $\overset{\frown}{O\,OH}$ represent acac and $Hacac_{enol}$, respectively.

From the rate analysis, K_1 is expected to be smaller in $CDCl_3$ than in C_6D_6. This might be attributed to the difference in dielectric constant of these solvents, because K_1 is supposed to be smaller in the solvent with a larger dielectric constant, if the electrostatic interaction is responsible for the nine-coordinate adduct formation.[12]

Khvostik et al.[1] studied the kinetics of the same reaction in benzene. Although their results were not quantitative, the following data were reported: $k_2=1\times10^3\ s^{-1}$ and $K_1=0.4\ M^{-1}$ (no description of temperature was given). Compared with the present study, k_2 has the same order, but K_1 is much smaller than the values in Table 1. Since they determined the values of K_1 and k_2 from a plot of k_{obsd} vs. [Hacac] under the condition $K_1[\mathrm{Hacac}] \ll 1$, where [Hacac] includes both keto and enol isomers, the K_1 and k_2 values obtained seem not to be correct.

We studied the ligand-exchange reactions in tetrakis(β-diketonato)thorium(IV) [Th(β-diketonate)$_4$] and proposed a mechanism passing through a nine-coordinate intermediate.[3-5] On the basis of the kinetic data and structures of Th(IV) and U(IV) β-diketonato complexes, a mechanism similar to that in Th(IV) complexes is proposed in the present study as is illustrated in Fig. 9. Addition of free $Hacac^*_{enol}$ to $[U(acac)_4]$ leads to the formation of a nine-coordinate complex (I → II), and a proton is transferred from $Hacac^*_{enol}$ to one of the coordinated acac (II → II′), followed by rapid dissociation of $Hacac_{enol}$ from the coordination sphere (II′ → I′). In $CDCl_3$ and C_6D_6 the pathway I → II → II′ → I′, which is consistent with a mechanism reported by Folcher et al. for the ligand exchange in $[U(fod)_4]$,[2] appears to be the principal exchange pathway.

In the presence of such a free base as DMSO, another nine-coordinate complex (III) might be formed. On the assumption that complexes I, II, and III are in equilibrium and that only the pathway I ⇀ II ⇀ II′ ⇀ I′ contributes to the exchange of acac, k_{obsd} can be expressed by

$$k_{\mathrm{obsd}} = \frac{k_2K_1[\mathrm{Hacac}]_{\mathrm{enol}}}{1+K_1[\mathrm{Hacac}]_{\mathrm{enol}}+K_3[\mathrm{Base}]} \tag{10a}$$

or

$$k_{\mathrm{obsd}}^{-1} = \frac{1+K_1[\mathrm{Hacac}]_{\mathrm{enol}}}{k_2K_1[\mathrm{Hacac}]_{\mathrm{enol}}} + \frac{K_3[\mathrm{Base}]}{k_2K_1[\mathrm{Hacac}]_{\mathrm{enol}}}, \tag{10b}$$

where K_3 refers to the equilibrium constant for the reaction, $\mathrm{I}+\mathrm{Base} \rightleftharpoons \mathrm{III}$. In Eq. 10b, k_{obsd}^{-1} is a linear function of the concentration of the base at constant $[\mathrm{Hacac}]_{\mathrm{enol}}$, and consistent with Eq. 6 obtained experimentally. In other words, the retardation effect of DMSO can be accounted for by the adduct complex formation. Additional evidence for the adduct formation came from the solvent extraction study[11] and the NMR chemical shift measurement.[2]

It should be noted, however, that k_{obsd} approaches constant values as [DMSO] increases over 0.5 mol kg^{-1}. The results suggest an alternative exchange pathway, which corresponds to the pathway I ⇀ III ⇀ IV ⇀ V ⇀ III′. The existence of two exchange processes is demonstrated clearly by the exchange reaction in CD_3CN, where k_{obsd} changes only slightly with $[\mathrm{Hacac}]_{\mathrm{enol}}$ (Fig. 6) giving an observed rate law

$$k_{\mathrm{obsd}} = k_{\mathrm{AN}} + k'_{\mathrm{AN}}[\mathrm{Hacac}]_{\mathrm{enol}}. \tag{11}$$

Since CD_3CN acts as a base even though its basicity is not so strong as DMSO, the reaction might proceed via both the pathways. In the pathway I ⇀ III ⇀ IV ⇀ V ⇀ III′ the rate determining step is expected to be the bond breaking of an acac chelate ring (III ⇀ IV), because the rates of paths IV ⇀ V (coordination of $\mathrm{Hacac}^{*}_{\mathrm{enol}}$) and V ⇀ III′ (proton transfer) should be comparable with those of paths I ⇀ II and II ⇀ II′, respectively and hence are much faster than the observed rates in Fig. 6. Therefore, k_{obsd} can be written by

$$k_{\mathrm{obsd}} = \frac{k_2K_1[\mathrm{Hacac}]_{\mathrm{enol}}+k_4K_3[\mathrm{CD_3CN}]}{1+K_1[\mathrm{Hacac}]_{\mathrm{enol}}+K_3[\mathrm{CD_3CN}]}. \tag{12}$$

If $K_3[\mathrm{CD_3CN}] \gg (1+K_1[\mathrm{Hacac}]_{\mathrm{enol}})$ is assumed in CD_3CN, Eq. 12 can be simplified as

$$k_{\mathrm{obsd}} = k_4 + \frac{k_2K_1[\mathrm{Hacac}]_{\mathrm{enol}}}{K_3[\mathrm{CD_3CN}]}. \tag{13}$$

Equation 13 is consistent with Eq. 11, where

$$k_{\mathrm{AN}} = k_4$$

and

$$k'_{\mathrm{AN}} = k_2K_1/K_3[\mathrm{CD_3CN}]. \tag{14}$$

The fact that the values of $k'_{\mathrm{AN}} \approx 50$ kg mol^{-1} at 56 °C, which was determined from the plots in Fig. 6, are about hundred times smaller than those of k_2K_1 in $CDCl_3$ supports the above assumption, $K_3[\mathrm{CD_3CN}] \gg (1+K_1[\mathrm{Hacac}]_{\mathrm{enol}})$. The values of k_{AN} in Fig. 6 are comparable with those of k_{obsd} obtained in the presence of high DMSO concentration in benzene, though the latter is slightly larger than the former. This fact also supports that the path III ⇀ IV controls the rates. The larger values of k_{obsd} in the presence of DMSO, as compared with k_{AN}, might be attributed to the stronger affinity of DMSO than CD_3CN toward [U(acac)$_4$], because the adduct formation with the strong base in complex III may contribute to weaken the U(IV)–acac bonds and hence accelerate the rate in the k_4 path.

The activation parameters for the ligand-exchange reactions in [U(acac)$_4$] are summarized in Table 2 together with those of [Th(acac)$_4$]. Similar values, particularly the large negative values of ΔS^{*}, suggest the similarlity in mechanism for the ligand exchange reactions in both U(IV) and Th(IV) complexes, although the pathway III ⇀ IV ⇀ V ⇀ III′ was not observed in the latter complex. In the case of ligand exchange in [Th(acac)$_4$], the rate law was expressed by Eq. 4 under the condition $K_1[\mathrm{Hacac}]_{\mathrm{enol}} \ll 1$ in solvents $CDCl_3$ and CD_3CN. As compared with the results of the present study, K_1 appears relatively smaller for [Th(acac)$_4$] than for [U(acac)$_4$]. Since the exchange rate in [Th(acac)$_4$] is faster than in [U(acac)$_4$] and the values of k_2K_1 for [Th(acac)$_4$] and [U(acac)$_4$] are 4.5×10^2 and 1.0×10^2 kg s^{-1} mol^{-1} at 20 °C in $CDCl_3$ respectively, k_2 for [Th(acac)$_4$] is expected to be much larger than for [U(acac)$_4$]. This fact may account for that the pathway III ⇀ IV ⇀ V ⇀ III′ is observed only in [U(acac)$_4$], because the pathway I ⇀ II ⇀ II′ ⇀ I′, whose rate is controlled by the k_2 path, is so fast in [Th(acac)$_4$] that the probability of taking pathway III⇀IV⇀V⇀III′ becomes negligible. A marked difference in k_2 value might be attributed to a difference in size of these complexes: the distance between Hacac* and acac in complex II is presumed to be more favorable for the proton transfer in Th(IV) complex than in U(IV) complex.

Table 2. Activation Parameters of acac Exchange in [U(acac)$_4$] and [Th(acac)$_4$]

Complex	Solvent	Rate constant	ΔH^{*} / kJ mol^{-1}	ΔS^{*} / J mol^{-1} K^{-1}
[U(acac)$_4$]	$CDCl_3$	$k_s(=k_2K_1)$	37.6±0.9	−69.8±3.0
[U(acac)$_4$]	C_6D_6	k_2	40.4±6.6	−62.6±2.1
[U(acac)$_4$]	CD_3CN	$k_4(=k_{\mathrm{AN}})$	46.4±0.1	−63.6±3.5
[Th(acac)$_4$]	$CDCl_3$	k_2K_1	30.8±0.7	−81.3±2.5
[Th(acac)$_4$]	CD_3CN	k_2K_1	30.2±1.0	−97.3±3.5

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