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A Nuclear Magnetic Resonance Study of the Kinetics of Ligand Exchange Reactions in Uranyl Complexes. VI. *N,N*-Dimethylformamide Exchange in Bis(acetylacetonato) (*N,N*-dimethylformamide)dioxouranium(VI)

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The exchange reaction of *N,N*-dimethylformamide(dmf) in [$UO_2(acac)_2dmf$](acac=acetylacetonato) has been studied by the NMR line-broadening method in CD_3COCD_3 and CD_2Cl_2. In CD_3COCD_3, the rate of dmf exchange is independent of the free DMF concentration. The rate constant(s^{-1}) at 25 °C and activation parameters ΔH^{*}(kJ mol^{-1}) and ΔS^{*}(JK^{-1} mol^{-1}) are 1.19×10^3, 42.0±1.3, and −45.8±5.5, respectively. In CD_2Cl_2, the exchange rate depends on the free DMF concentration. The exchange rate constant (k_{ex}) is expressed by $k_{ex}=k_1+k_2$[DMF], where k_1(25 °C)=1.90×10^2 s^{-1}, ΔH^{*}=32.8±1.7 kJ mol^{-1}, and ΔS^{*}=−92.0±5.9 JK^{-1} mol^{-1}, and k_2 (25 °C)=5.66×10^3 M^{-1} s^{-1}(1M=1 mol dm^{-3}), ΔH^{*}=37.0±2.1 kJ mol^{-1}, and ΔS^{*}=−49.6±8.8 JK^{-1} mol^{-1}. The D and I mechanisms are proposed for the dmf exchange in [$UO_2(acac)_2$ dmf].

The uranyl β-diketonato complexes, [UO_2(β-diketonato)$_2$L] (L=adduct ligand) have been studied extensively in view of the extraction of uranyl ions[1] and the IR laser separation of uranium isotopes.[2] In particular, the synergistic effect on the extraction[1] and the relationship between the bond-strength and basicity[3] have been studied for the adduct ligands. However, only limited kinetic data are available with respect to the reactivity of adduct ligands.[4,5]

Recently, we studied exchange reactions of dimethyl sulfoxide(dmso) in [$UO_2(acac)_2dmso$] and [$UO_2(dbm)_2$ dmso] (dbm=dibenzoylmethanate) by using NMR[6] and proposed the exchange mechanism to be either D or I.[7] The dmso exchange rates in these complexes are much slower than that in [$UO_2(dmso)_5$]$^{2+}$.[8] This result suggests that the steric hindrance is regarded as significant for the ligand exchange reactions in uranyl complexes. In order to examine the steric effect on the ligand exchange reaction in uranyl complexes and the relationship between the reactivity and basicity of adduct ligands, the exchange reaction of dmf in [$UO_2(acac)_2$·dmf] was studied and compared with the dmso exchange in [$UO_2(acac)_2dmso$] and the dmf exchange in [UO_2 (dmf)$_5$]$^{2+}$.[9]

Experimental

The [$UO_2(acac)_2dmf$] complex was prepared by the same method as described in a previous paper.[5] Calcd for [UO_2-(acac)$_2$dmf]: C, 28.84; H, 4.28; N, 2.59. Found: C, 28.79; H, 3.89; N, 2.55. Acetone-d_6 (CD_3COCD_3, Merck 99.8%) and dichloromethane-d_2 (CD_2Cl_2, Merck 99%), which were used as solvents, were dried over 3A and 4A molecular sieves (Wako Pure Chemical Ind. Ltd.), respectively. *N,N*-Dimethylformamide (Wako) was distilled over barium oxide *in vacuo*, followed by distillation with molecular sieves, and stored over 3A molecular sieves. Sample solutions for NMR measurements were prepared by weighing the complex, DMF and solvents in a 1 cm^3 volumetric flask and some of each solution was placed in an NMR sample tube and sealed. All samples were prepared in a glove box filled with dried nitrogen. The measurement of the ^{1}H NMR spectra was carried out at 100 MHz on a JEOL JNM FX-100 FT-NMR spectrometer equipped with a JNM-VT-3B temperature controller. The infrared spectra of [$UO_2(acac)_2$·dmf] in CD_2Cl_2 were recorded in the 200—4000 cm^{-1} range by using a JASCO DS-701G IR spectrophotometer. The dmf exchange reaction in [$UO_2(acac)_2dmf$] was measured by the NMR linebroadening method. The kinetic parameters were calculated by using a computer program on the assumption of a two-site exchange process as described in the previous paper.[5]

Results and Discussion

The Structure of [$UO_2(acac)_2dmf$] in Solutions. Figure 1 shows the ^{1}H NMR spectrum of a solution containing [$UO_2(acac)_2$·dmf], DMF, and CD_3COCD_3 at −75 °C. In the spectrum, signals (a) and (d) are assigned to the methyl protons and the 3-H protons of coordinated acac, respectively, and signals (b) and (c), and signals (e) and (f) are the methyl protons, and the formyl protons of free and coordinated DMF, respectively. The area ratio of (f) to (d) to (c) to (a) was 1:2:6:12, and this ratio remained constant in solutions i, ii, and iii listed in Table 1. This fact indicates

TABLE 1. SOLUTION COMPOSITION AND KINETIC PARAMETERS FOR THE EXCHANGE OF dmf IN [$UO_2(acac)_2dmf$]

Solution	[$UO_2(acac)_2dmf$]	[DMF]$^{a)}$	[CD_3COCD_3]	[CD_2Cl_2]	ΔH^{*}	ΔS^{*}	k_{ex}(25 °C)$^{b)}$
	10^{-2} M	10^{-2} M	M	M	kJ mol^{-1}	J mol^{-1} K^{-1}	10^3 s^{-1}
i	3.25	3.83	13.6		42.0±1.3	−45.8±5.5	1.19
ii	6.45	6.57	13.4		42.0±1.3	−46.2±5.5	1.14
iii	6.61	11.2	13.3		43.7±1.1	−38.6±5.0	1.44
iv	2.73	2.87		15.2	k_1 pathway		
v	11.0	12.0		14.8	32.8±1.7	−92.0±5.9	0.190
vi	11.6	21.5		14.7	k_2 pathway		
vii	14.6	35.7		14.6	37.0±2.1	−49.6±8.8	5.66

a) Added as DMF. b) Calculated values from ΔH^{*} and ΔS^{*} at 25 °C.

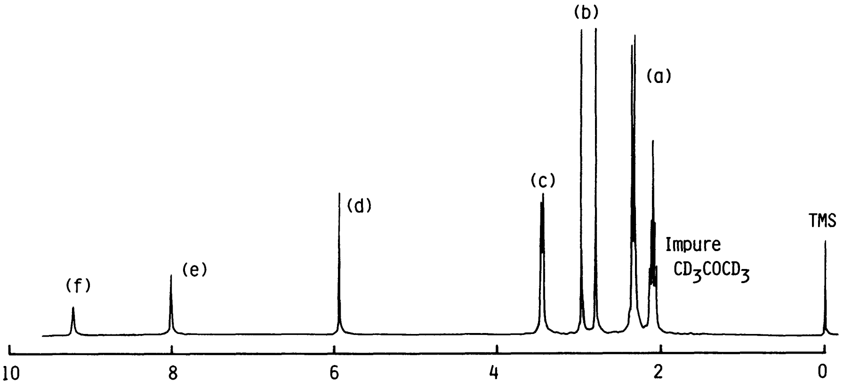

Fig. 1. The ^1H NMR spectrum of a solution containing of $[UO_2(acac)_2dmf]$ (0.0661 M), DMF (0.112 M), and CD_3COCD_3 (13.3 M) at −75 °C.

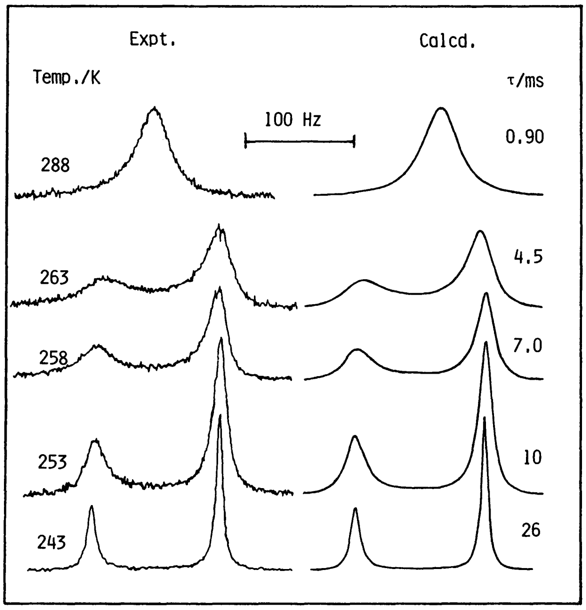

Fig. 2. Experimental (left side) and best-fit calculated lineshapes of a solution containing $[UO_2(acac)_2dmf]$ (0.0661 M), DMF (0.112 M), and CD_3COCD_3 (13.3 M). Temperatures and best-fit *t* values are shown at left and right sides of the figure, respectively.

that two acac ions and one DMF molecule coordinate to a uranyl ion. The singlet signal of the 3-H protons means that two coordinated acac ions are bidentate ligands. Therefore, the structure of $[UO_2(acac)_2dmf]$ is presumed to be pentagonal bipyramidal, which is the same as those of $[UO_2(acac)_2dmso]$ and $[UO_2(acac)_2 \cdot H_2O]$.[6,10] This structure is supported by the separation of the methyl protons of the coordinated acac, because in such a structure the two methyl groups of the coordinated acac are in different magnetic environments, *i.e.* the nearest group to and the farthest group from the coordinated dmf.

In CD_2Cl_2, similar phenomena were also observed in the ^1H NMR spectra. The IR spectra of $[UO_2(acac)_2dmf]$ measured in CD_2Cl_2 showed that the C–O stretching for the coordinated dmf was observed at 1652 cm^{-1}, which was 27 cm^{-1} lower than that observed in pure DMF (1675 cm^{-1}). It has been known that the C–O stretching, so-called Amide I, will shift to a lower side when DMF coordinated through oxygen.[11,12] Hence, the observed band of C–O stretching indicates that dmf in $[UO_2(acac)_2dmf]$ is coordinated through oxygen. In addition, only one band corresponding to the carbonyl vibration of coordinated acac was observed at 1574 cm^{-1}. This result indicates that acac ions in $[UO_2(acac)_2dmf]$ are coordinated as the bidentate, since the frequency less than 1600 cm^{-1} is characteristic of the carbonyl vibration of chelated metal β-diketonato complexes.[13] On the basis of these results, it is concluded that $[UO_2(acac)_2dmf]$ has a pentagonal bipyramidal structure in CD_3COCD_3 and CD_2Cl_2.

dmf Exchange in $[UO_2(acac)_2dmf]$. The formyl proton signals of the coordinated and free DMF were measured at various temperatures. Results are shown in Fig. 2. This figure shows that DMF molecule exchanges between the coordinated and free sites. The best-fit life times (τ values) were determined by using a computer program for the two-site exchange[14] and are shown at the right side in Fig. 2 together with the corresponding line shapes. From these τ values, the first-order rate constants, k_{ex}, were calculated by the following equations, where τ and P with the subscripts f and c are the life times and mole fractions of the free and coordinated sites, respectively.

$$\tau = P_f\tau_c = P_c\tau_f \tag{1}$$

$$k_{ex} = 1/\tau_c = \text{rate}/[UO_2(acac)_2dmf] = (kT/h)\exp(-\Delta H^{\ast}/RT)\exp(\Delta S^{\ast}/R), \tag{2}$$

The same measurements were carried out for the solutions with different compositions listed in Table 1. In Fig. 3, the values of k_{ex} are plotted semilogarithmically against the reciprocal temperature. The activation parameters obtained from Fig. 3 are listed in Table 1. As can be seen in Fig. 3 and Table 1, the exchange rate of dmf in CD_3COCD_3 is independent of [DMF], while that in CD_2Cl_2 is dependent on [DMF]. Plots of k_{ex} values against [DMF] are linear in CD_2Cl_2(Fig. 4) and result in the following equation.

$$k_{ex} = k_1 + k_2[DMF] \tag{3}$$

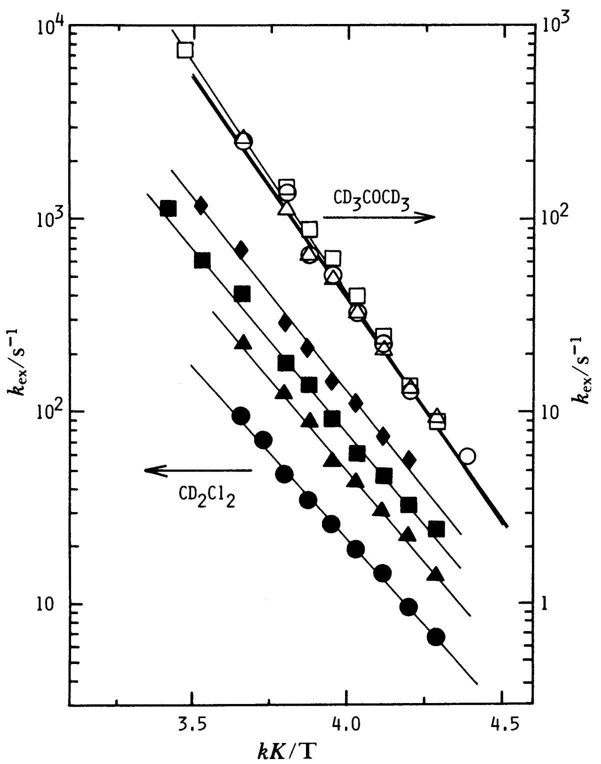

Fig. 3. Semilogarithmic plots of k_{ex} against the reciprocal temperature for the exchange of dmf in $[UO_2(acac)_2dmf]$ in CD_3COCD_3 and CD_2Cl_2. The symbols of ○, △, □, ●, ▲, ■, and ◆, correspond to i, ii, iii, iv, v, vi, and vii solutions in Table 1.

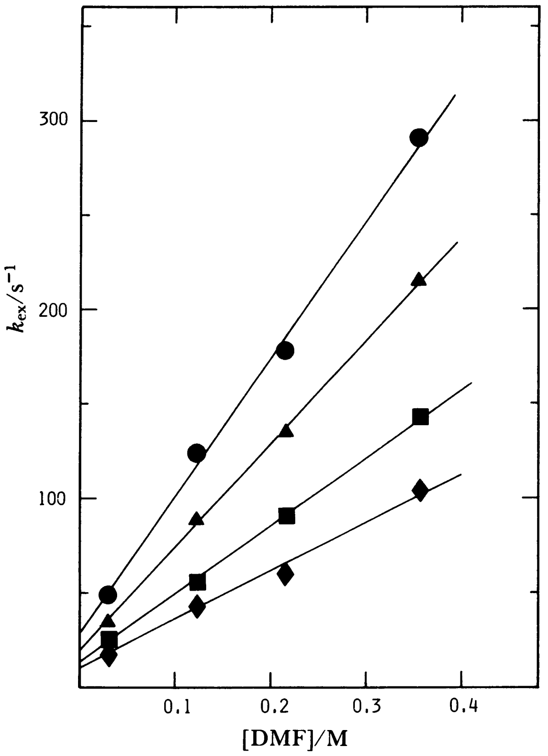

Fig. 4. plots of k_{ex} *vs.* [DMF] for the exchange of dmf in $[UO_2(acac)_2dmf]$ in CD_2Cl_2. ●: −10 °C; ▲: −15 °C; ■: −20 °C; ◆: −25 °C.

The values of k_1 and k_2 were obtained from the intercepts and the slopes of the plots in Fig. 4 by means of the least-squares method, and are listed in Table 2. The activation parameters for these pathways are given in Table 1.

Exchange Mechanism. The exchange rate of dmf in $[UO_2(acac)_2 \cdot dmf]$ in CD_3COCD_3 is independent of the free DMF concentration. This result suggests that the dmf exchange in CD_3COCD_3 proceeds through either the D or I mechanism.[7] In the D mechanism, the exchange processes are expressed as

$$\begin{aligned} &UO_2(acac)_2dmf + DMF^* \xrightarrow[\text{slow}]{k_d} \\ &\quad UO_2(acac)_2 + DMF + DMF^* \xrightarrow[\text{fast}]{} \\ &\qquad UO_2(acac)_2dmf^* + DMF, \end{aligned} \tag{4}$$

where an asterisk is used to denote the exchanging species. In this mechanism, the rate-determining step is the dissociation of the coordinated dmf from $[UO_2(acac)_2dmf]$. Thus, k_{ex} is given by

$$k_{ex} = k_d \tag{5}$$

Table 2. The values of k_1 and k_2 at various temperatures for the exchange of dmf in $[UO_2(acac)_2dmf]$ in CD_2Cl_2

Temp	k_1	k_2
°C	$10\,s^{-1}$	$10^2\,M^{-1}\,s^{-1}$
−10	2.82±0.72	7.26±0.33
−15	2.01±0.24	5.45±0.11
−20	1.44±0.13	3.56±0.58
−25	1.08±0.38	2.54±0.18

In the I mechanism, the exchange processes are represented as follows.

$$\begin{aligned} &UO_2(acac)_2dmf + DMF^* \underset{\text{fast}}{\overset{K_{os}}{\rightleftharpoons}} UO_2(acac)_2dmf \cdots DMF^* \\ &\quad \xrightarrow[\text{slow}]{k_I} UO_2(acac)_2dmf^* \cdots DMF \\ &\quad \longrightarrow UO_2(acac)_2dmf^* + DMF, \end{aligned} \tag{6}$$

where K_{os} is the formation constant of the outer-sphere complex, $UO_2(acac)_2dmf \cdots DMF^*$, and k_I is the rate constant for the interchange of dmf molecule between the first and second coordination spheres. In this mechanism, k_{ex} is given by Eq. (7).

$$k_{ex} = k_I K_{os}[DMF]/(1+K_{os}[DMF]) \tag{7}$$

If $K_{os}[DMF] \gg 1$, Eq. (7) can be simplified as

$$k_{ex} = k_I. \tag{8}$$

Equations (5) and (8) are compatible with the experimental results. However, the I mechanism seems to be unlikely for the following reasons. In the I mechanism, the condition of $K_{os}[DMF] \gg 1$ must be satisfied over the DMF concentration range (0.0383—

0.112 M) employed in this study. This indicates that K_{os} should be at least larger than 50 M^{-1}. However, such a value of K_{os} is too large considering that the reactants [$UO_2(acac)_2dmf$] and DMF are both uncharged. On the other hand, the four-coordinated intermediate in the equatorial plane should be formed in the D mechanism. This is supported by the fact that some uranyl complexes, *e.g.* $[UO_2(H_2O)_4]^{2+}$,[15,16] $[UO_2(hmpa)_4]^{2+}$[17] (hmpa=hexamethylphosphoric triamide), exist in solution as a tetragonal bipyramidal structure.

In CD_2Cl_2, the dmf exchange occurs through two pathways as seen in Fig. 4. The k_1 pathway, where the exchange rate is independent of the free DMF concentration, is considered to be the same D mechanism as the dmf exchange in CD_3COCD_3. The k_2 pathway exhibits a first-order dependence with respect to the free DMF concentration and seems to proceed through either the I or A mechanism.[7] In the A mechanism, the dmf exchange processes are expressed as

$$UO_2(acac)_2dmf + DMF^* \xrightarrow[\text{slow}]{k_a} UO_2(acac)_2dmf{\cdot}dmf^* \xrightarrow[\text{fast}]{} UO_2(acac)_2dmf^* + DMF, \qquad (9)$$

where the rate-determining step is the coordination of DMF to [$UO_2(acac)_2dmf$], followed by the formation of six-coordinated intermediate in the equatorial plane. Hence, if the dmf exchange in CD_2Cl_2 proceeds through the D and A mechanisms, k_{ex} is given by Eq. (10).

$$k_{ex} = k_d + k_a[DMF] \qquad (10)$$

On the other hand, if the dmf exchange proceeds through the D and I mechanisms, k_{ex} is given by Eq. (11).

$$k_{ex} = \frac{k_d + k_I K_{os}[DMF]}{1 + K_{os}[DMF]} \qquad (11)$$

When $K_{os}[DMF] \ll 1$, Eq. (11) becomes Eq. (12).

$$k_{ex} = k_d + k_I K_{os}[DMF] \qquad (12)$$

Both of Eqs. (10) and (12) are compatible with Eq. (3). Although it has been known that the uranyl ion forms six-coordinated complexes in the equatorial plane with small ligands,[18] the A mechanism for the k_2 pathway seems to be unlikely, because the coordinated acac is a bulky chelating ligand and may make it difficult to form a six-coordinated intermediate in the equatorial plane of [$UO_2(acac)_2dmf$]. On the other hand, if the k_2 pathway proceeds through the I mechanism, the condition of $K_{os}[DMF] \ll 1$ has to be satisfied. This condition seems to be fulfilled in the present exchange reaction, since both of [$UO_2(acac)_2dmf$] and DMF are uncharged and hence the K_{os} vlaue is expected to be relatively small. In fact, the corresponding K_{os} value to the dmso exchange in[$UO_2(acac)_2dmso$] in CD_2Cl_2 is *ca.* 5 M^{-1}.[6] Taking into account Gutmann's donor number[19] that the basicity of DMF is smaller than that of DMSO, the K_{os} value for tbe present exchange reaction is supposed to be smaller than 5 M^{-1} and satisfies the condition mentioned above in the DMF concentration range 0.0287 to 0.357 M (Table 1). Therefore, it is suggested that the dmf exchange in [$UO_2(acac)_2dmf$] in CD_2Cl_2 proceeds through both the D and I mechanisms.

The difference in mechanisms observed in two solvents CD_3COCD_3 and CD_2Cl_2, which was also observed in the dmso exchange in [$UO_2(acac)_2dmso$] and [$UO_2(dbm)_2dmso$] in the same two solvents,[6] may primarily be due to the difference in basicity and dielectric constant of these solvents. Acetone has a relatively large basicity compared with dichloromethane and tends to preferentially solvate to the second coordination sphere of [$UO_2(acac)_2dmf$] under the present experimental conditions. This preferential solvation may block the access of DMF molecule to the outer-sphere of [$UO_2(acac)_2dmf$]. Moreover, the dielectric constant of acetone (20.7) is fairly larger than that of dichloromethane(8.93). These factors may lead to the smaller K_{os} value in CD_3COCD_3 than that in CD_2Cl_2. This is consistent with the results that the dmf exchange in CD_3COCD_3 proceeds through only the D mechanism, while that in CD_2Cl_2 proceeds through both the D and I mechanisms. In spite of the result that the dmf exchange in [$UO_2(acac)_2dmf$] proceeds through the D and I mechanisms, activation entropies have large negative values. This may be attributed to the contribution of solvent rearrangement around the complex as proposed by Benneto and Caldin.[20]

It is of interest to compare the dmf exchange in [$UO_2(acac)_2dmf$] with that in $[UO_2(dmf)_5]^{2+}$ and the dmso exchange in [$UO_2(acac)_2dmso$], whose kinetic parameters are summarized in Table 3. It was not clear which mechanism (I_d or I_a) is reasonable for the dmf exchange in $[UO_2(dmf)_5]^{2+}$. The fact that the dmf ex-

Table 3. Kinetic parameters for this work and related reactions[a)]

Reaction	Mechanism	ΔH^{*}	ΔS^{*}	Rate constant(25 °C)[b)]	Ref.
		kJ mol^{-1}	JK^{-1} mol^{-1}	s^{-1}	
$[UO_2(dmf)_5]^{2+}$+DMF	D	42.0±2.1	−15.1±3.3	4.70×10^4	9
	I	48.3±0.9	38.6±2.6	2.34×10^6	9
[$UO_2(acac)_2dmf$]+DMF	D	32.8±1.7	−92.0±5.9	1.90×10^2	This work
	I	37.0±2.1[c)]	−49.6±8.8[c)]	$5.66\times10^3/M^{-1}$ [c)]	This work
[$UO_2(acac)_2dmso$]+DMSO	D	47.9±5.2	−46.6±11.2	1.02×10^2	6
	I	35.4±12.4	−69.7±20.5	1.01×10^3	6

a) In CD_2Cl_2 solvent. b) Calculated values from ΔH^{*} and ΔS^{*} at 25 °C. c) The values of kinetic parameters for $k_I K_{os}$.

change rate in $[UO_2(acac)_2dmf]$ becomes slower than that in $[UO_2(dmf)_5]^{2+}$ suggests that the dmf exchange in $[UO_2(dmf)_5]^{2+}$ proceeds through the I_a mechanism, since if the exchange occurs associatively, the exchange rate is expected to be reduced with crowding at the reaction site. In the ligand(L) exchange in $[UO_2(acac)_2L]$ (L=dmso or dmf) proceeding through the D mechanism, the rate constant for the dmf exchange is larger than that for the dmso exchange. This may be due to the fact that the basicity of DMF is smaller than that of DMSO, and hence the bond-strength between UO_2^{2+} and dmf in $[UO_2(acac)_2dmf]$ is expected to be weaker than that between UO_2^{2+} and dmso in $[UO_2(acac)_2dmso]$, because the rate-determining step is the dissociation of dmf or dmso in the D mechanism. This is supported by the result that the ΔH^{*} value for the dmf exchange is smaller than that for the dmso exchange. Since the kinetic parameters in the I mechanism for the dmf exchange in $[UO_2(acac)_2dmf]$ are obtained for $k_I K_{os}$, it is difficult to compare directly with the kinetic parameters for the dmso exchange in $[UO_2(acac)_2dmso]$. The K_{os} value is considered to be smaller than that for the dmso exchange in $[UO_2(acac)_2dmso]$ (*ca.* $5\,M^{-1}$). Therefore,the k_I value for the dmf exchange in $[UO_2(acac)_2dmf]$ should be larger than $1.01\times10^3\,s^{-1}$ (Table 3) for the dmso exchange in $[UO_2(acac)_2\cdot dmso]$. This suggests that the I mechanism for the exchange of L in $[UO_2(acac)_2L]$ (L=dmso or dmf) is not I_a but I_d on the basis of the same reasons as described above. It might be concluded that the D mechanism is the major process for the exchange of L in $[UO_2(\beta\text{-diketonato})_2L]$ complexes because of the steric hindrance.

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