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

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Abstract

The exchange reaction of acac(acetylacetonate) in $UO_2(acac)_2dmf$ (dmf = *N*,*N*-dimethylformamide) in *o*-dichlorobenzene has been studied by the NMR line-broadening method. The exchange rate depends on the concentration of the enol isomer of acetylacetone in its low region, and approaches the limiting value in its high region. It is proposed that the exchange reaction proceeds through the mechanism in which the dissociation of one end of the chelated acac is the rate-determining step. The kinetic parameters for this step are as follows: k (25 °C) = 5.03×10^{-3} s^{-1}, $\Delta H^{\ddagger} = 91.6 \pm 3.8$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 17.2 \pm 10.5$ JK^{-1} mol^{-1}. The exchange rate becomes slower by the addition of free DMF. This may be due to the competition of DMF with the enol isomer of acetylacetone in attacking a four-coordinated intermediate in the equatorial plane.

Introduction

In view of the separation of uranium isotopes by using IR lasers, the structure and photochemical reactivity of uranyl β-diketonato complexes, UO_2(β-diketonato)$_2$L (L = adduct ligands), in solid or gas state have been extensively studied [1–10]. However, only limited data are available with respect to the properties of UO_2(β-diketonato)$_2$L in solution [11–16]. Recently, we reported the kinetic study of the exchange reaction of acac in $UO_2(acac)_2dmso$ (dmso = dimethyl sulfoxide) in o-$C_6H_4Cl_2$ and proposed the mechanism in which the dissociation of one end of the coordinated acac is the rate-determining step, followed by the attack of the enol isomer of free acetylacetone on the four-coordinated intermediate in the equatorial plane [15]. There is also, however, a possibility that the acac exchange proceeds through an outer-sphere complex. In order to examine whether or not the proposed mechanism for the acac exchange in $UO_2(acac)_2dmso$ is also applicable to the exchange of β-diketonate in other uranyl β-diketonato complexes, the acac exchange in $UO_2(acac)_2dmf$ was studied by the NMR line-broadening method. If the acac exchange in $UO_2(acac)_2dmf$ proceeds via the formation of the outer-sphere complex, it is expected that the outer-sphere complex formation constant becomes comparable to that obtained from the outer-sphere complex formation mechanism in the acac exchange in $UO_2(acac)_2dmso$.

Experimental

The $UO_2(acac)_2dmf$ complex was prepared by the same method as described in a previous paper [14]. Acetylacetone (Hacac) and *o*-dichlorobenzene (Wako Pure Chemical Ind., Ltd) were purified by using the same method as reported in a previous paper [15]. ^1H NMR spectra were measured by using a Jeol JNM-MH-100 NMR spectrometer equipped with a JNM-VT-3B temperature controller. Measurements of ultraviolet and visible spectra were carried out using a Jasco UVIDEC-505 spectrophotometer. The exchange reaction of acac in $UO_2(acac)_2dmf$ was followed by measuring the changes in line-shape of methyl proton signals of the coordinated acac and free Hacac at desired temperatures. The kinetic analyses were carried out using a computer program based on the modified Bloch equation for the two-site exchange as described previously [14, 17].

Results and Discussion

Structure of $UO_2(acac)_2dmf$ in the Mixture of o-$C_6H_4Cl_2$ and Hacac

In previous papers [14, 16], we reported that the $UO_2(acac)_2dmf$ in CD_3COCD_3 and CD_2Cl_2 has a pentagonal-bipyramidal structure. It was confirmed from the NMR, UV and visible spectra that the structure of $UO_2(acac)_2dmf$ in the mixture of o-$C_6H_4Cl_2$

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and Hacac is the same as that in the solid state, because the area ratios of the methyl proton signals of the coordinated acac to the coordinated dmf remained constant in the NMR spectra of $UO_2(acac)_2dmf$ in such mixtures, and the UV and visible spectra for solutions were also self-consistent.

Exchange Reaction of acac in $UO_2(acac)_2dmf$

Figure 1 shows the changes in line-shape of methyl proton signals of the coordinated acac (c) and free Hacac with changing temperature. It is apparent from Fig. 1 that the exchange reaction occurs between the coordinated acac and the enol isomer (a) of Hacac, because the line-width and chemical shift of the enol methyl proton signal change with increasing temperature, while such a phenomenon was not observed in the keto methyl proton signal (b). The best-fit lifetimes (τ-values) at each temperature are shown at the right side of Fig. 1 together with the corresponding calculated line-shapes. The first-order exchange rate constant, k_{ex}, was calculated from the following equations,

$$\tau = \tau_c p_f = \tau_f p_c \quad (1)$$

$$k_{ex} = 1/\tau_c = \text{rate}/2[UO_2(acac)_2dmf], \quad (2)$$

where τ and p with subscripts c and f are the mean lifetimes and mole fractions of the coordinated and free sites, respectively. Measurements of k_{ex} were performed for the solutions listed in Table I. Figure 2 shows the plots of k_{ex} *versus* [enol] for solutions (i–vi) and indicates that k_{ex} approaches limiting values as [enol] increases. The plots of k_{ex} *versus* [DMF] for solutions (iii, vii–ix) in Fig. 3 show that the exchange rate of acac becomes slower by the addition of free DMF. These phenomena are very similar to those observed in the acac exchange in $UO_2(acac)_2$-dmso [15].

Possible Mechanism

The similarity of the present exchange to the acac exchange in $UO_2(acac)_2$dmso suggests that the mechanisms proposed for the acac exchange in $UO_2(acac)_2$dmso are also applicable to the present reaction. The proposed mechanisms are shown in Scheme 1, where an asterisk is used to denote the exchanging species. In mechanism 1 (**I** → **II** → **IV** → **IV′** → **I′**), the rate-determining step is the pathway **I** → **II**, and the added DMF competes with free Hacac in attacking the vacant site of intermediate **II**. In mechanism 2 (**I** → **III** → **IV** → **IV′** → **I′**), **III** is the outer-sphere complex, and K_{os} is the outer-sphere complex formation constant. In this mechanism, the retardation effect of added DMF is due to the formation of the outer-sphere complex, **III′**. From mechanisms 1 and 2, the first-order exchange rate constant (k_{ex}) is given by eqns. 3 and 4, respectively.

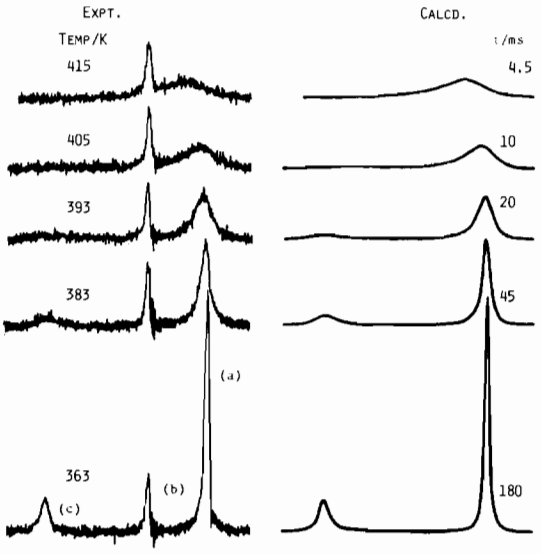


Fig. 1. Experimental (left side) and best-fit calculated NMR signals of the methyl protons of coordinated acac and free Hacac in a solution consisting of $UO_2(acac)_2dmf$ (3.68×10^{-2} M, M = mol dm^{-3}), Hacac (0.313 M), and o-$C_6H_4Cl_2$ (8.38 M).

TABLE I. Solution Composition for the Exchange of acac in $UO_2(acac)_2dmf$

Solution	$[UO_2(acac)_2dmf]$ (10^{-2} M)	[Hacac] (M)	[DMF] (10^{-2} M)	[o-$C_6H_4Cl_2$] (M)
i	3.77	0.0499		8.98
ii	3.64	0.0899		8.85
iii	3.73	0.122		8.75
iv	3.70	0.189		8.57
v	3.88	0.236		8.47
vi	3.68	0.313		8.38
vii	3.73	0.122	1.64	8.71
viii	3.82	0.123	2.74	8.68
ix	3.73	0.123	4.93	8.63

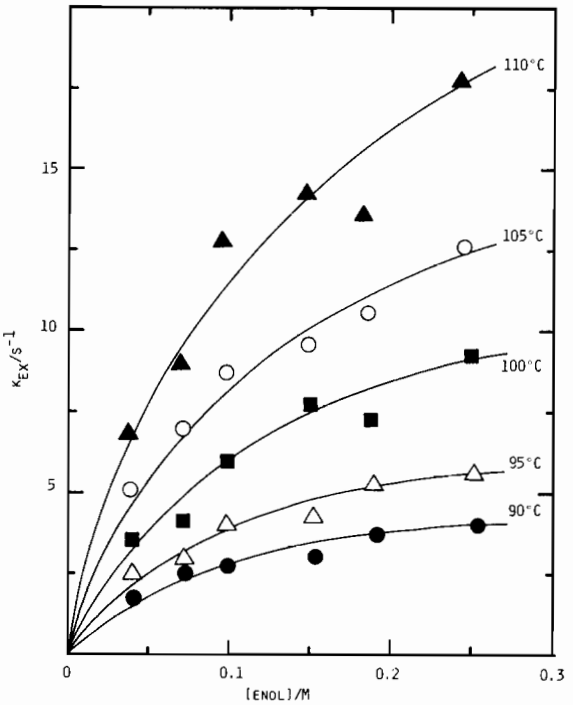


Fig. 2. Plots of k_{ex} *vs.* [enol] for the exchange of acac in $UO_2(acac)_2dmf$: •, 90 °C; △, 95 °C; ▪, 100 °C; ○, 105 °C; ▲, 110 °C.

$$k_{ex} = \frac{k_1 k_2 [enol]}{k_{-1} + k_2 [enol] + k_3 [DMF]} \quad (3)$$

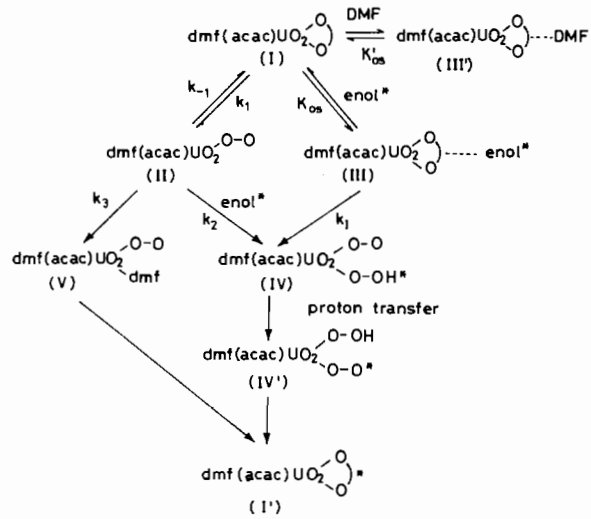
$$k_{ex} = \frac{k_I K_{os} [enol]}{1 + K_{os} [enol] + K'_{os} [DMF]} \quad (4)$$

Equations 3 and 4 are modified as follows.

$$\frac{1}{k_{ex}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2 [enol]} + \frac{k_3 [DMF]}{k_1 k_2 [enol]} \quad (3')$$

$$\frac{1}{k_{ex}} = \frac{1}{k_I} + \frac{1}{k_I K_{os} [enol]} + \frac{K'_{os} [DMF]}{k_I K_{os} [enol]} \quad (4')$$

If mechanism 1 or 2 is reasonable as the mechanism for the present exchange reaction, it is expected that the plots of $1/k_{ex}$ *versus* $1/[enol]$ in the absence of free DMF and those of $1/k_{ex}$ *versus* [DMF] at constant [enol] should yield straight lines. Figures 4 and 5 show these plots, and it seems that both the mechanisms are acceptable. The values of intercepts (A) and slopes (B) in Figs. 4 and 5 and the kinetic parameters derived from these values are summarized in Tables II and III. The values of K_{os} and K'_{os} in Tables II and III are much larger than those for acac exchange in $UO_2(acac)_2dmso$ ($K_{os} = 0.24$ M^{-1} and $K'_{os} = 17.8$ M^{-1} at 100 °C). If the acac exchange in $UO_2(acac)_2L$ (L = dmso or dmf) proceeds through mechanism 2, the K_{os} values for both acac exchange



Scheme 1.

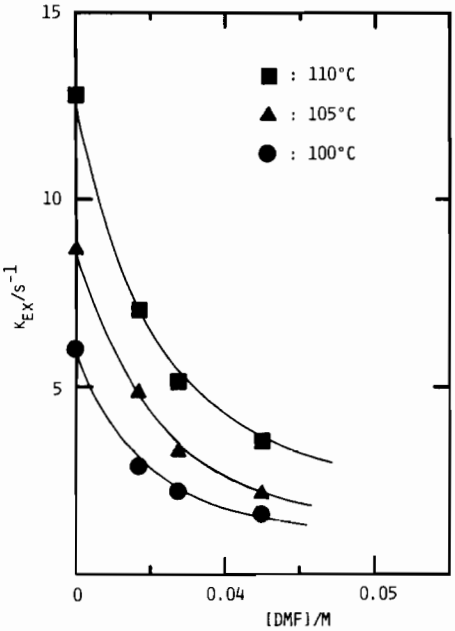


Fig. 3. Plots of k_{ex} *vs.* [DMF] for the effect of added DMF on the exchange of acac in $UO_2(acac)_2dmf$: •, 100 °C; ▲, 105 °C; ▪, 110 °C.

reactions should be nearly consistent with each other, because both complexes are similar in structure. Furthermore, the K'_{os} value for acac exchange in $UO_2(acac)_2dmf$ is expected to be smaller than that in $UO_2(acac)_2dmso$, since the basicity of DMF is smaller than that of DMSO on the basis of Gutmann's donor number (*DN*) ($DN_{DMF} = 26$ 6 and $DN_{DMSO} = 29.8$) [18]. From the values of K_{os} and K'_{os}, it seems that mechanism 1 is more acceptable than mechanism 2.

The kinetic parameters based on mechanism 1 for the acac exchange reactions in $UO_2(acac)_2L$

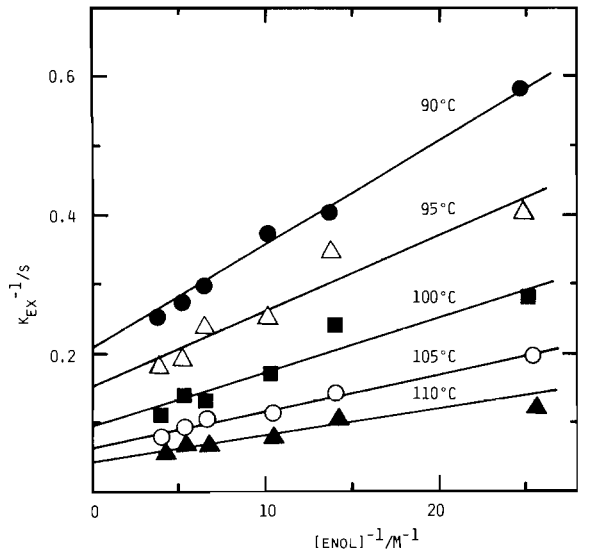


Fig. 4. Plots of $1/k_{ex}$ *vs.* 1/[enol] for the exchange of acac in $UO_2(acac)_2$dmf: •, 90 °C; △, 95 °C; ▪, 100 °C; ○, 105 °C; ▲, 110 °C.

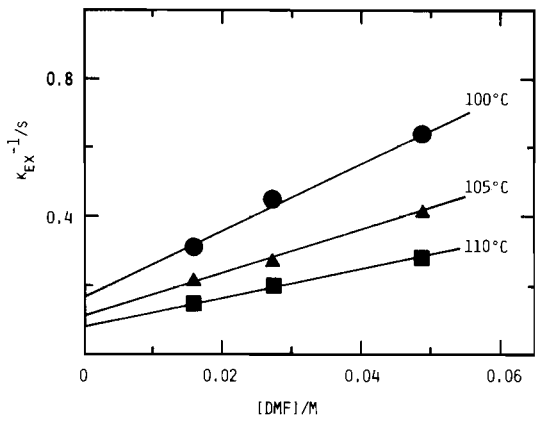


Fig. 5. Plots of $1/k_{ex}$ *vs.* [DMF] for the effect of added DMF on the exchange of acac in $UO_2(acac)_2$dmf: •, 100 °C; ▲, 105 °C; ▪, 110 °C.

TABLE III. VAlues of k_3/k_2 and K'_{os} at Various Temperatures

Temperature (°C)	A[a] (10^{-2} s)	B[b] (M^{-1} s)	k_3/k_2	K'_{os} (M^{-1})
100	17.9 ± 1.2	9.56 ± 0.41	10.6	113
105	11.2 ± 0.6	6.14 ± 0.20	9.92	108
110	7.82 ± 0.36	4.14 ± 0.12	8.99	98.9

[a] $A = \dfrac{k_{-1} + k_2[\text{enol}]}{k_1 k_2[\text{enol}]}$ or $\dfrac{1 + K_{os}[\text{enol}]}{k_1 K_{os}[\text{enol}]}$.

[b] $B = \dfrac{k_3}{k_1 k_2[\text{enol}]}$ or $\dfrac{K'_{os}}{k_I K_{os}[\text{enol}]}$.

(L = dmso or dmf) are shown in Table IV. Although the dependences of the exchange rate of acac on [enol] and [DMSO] or [DMF] are similar to each other, the kinetic parameters are quite different, as seen in Table IV. The difference in basicity of the coordinated dmso and dmf may furnish a probable explanation for the kinetic difference. The DMSO molecule has higher electron donicity than the DMF molecule on the basis of *DN*. Therefore, the electron density of the uranyl ion in $UO_2(acac)_2$dmso is higher than that in $UO_2(acac)_2$dmf. This favors a greater weakening of the bond-strength between the uranyl ion and acac in $UO_2(acac)_2$dmso than that in $UO_2(acac)_2$dmf, and results in a faster acac exchange in $UO_2(acac)_2$dmso than that in $UO_2(acac)_2$dmf. However, the differences in kinetic parameters seem to be too large as compared with the difference in basicity of DMSO and DMF.

Even though the real reason for differences between the acac exchange reactions in $UO_2(acac)_2$dmso and $UO_2(acac)_2$dmf is not yet given, the present result lends further support for the view that the intramolecular exchange reaction of methyl groups of the coordinated acac in $UO_2(acac)_2$dmf

TABLE II. Values of k_1, k_I, k_2/k_{-1}, and K_{os} at Various Temperatures and Kinetic Parameters for the k_1 or k_I Pathway

Temperature (°C)	A[a] (10^{-2} s)	B[b] (10^{-3} M s)	k_1 or k_I (s^{-1})	k_2/k_{-1} or K_{os} (M^{-1})
90	20.6 ± 1.7	15.1 ± 1.3	4.85 ± 0.37	13.7 ± 0.7
95	14.9 ± 2.2	10.9 ± 1.7	6.71 ± 0.86	13.7 ± 1.2
100	8.83 ± 1.66	8.22 ± 1.27	11.3 ± 1.8	10.7 ± 1.5
105	6.00 ± 0.65	5.49 ± 0.49	16.7 ± 1.6	10.9 ± 0.9
110	4.41 ± 0.59	4.03 ± 0.44	22.7 ± 2.7	11.0 ± 1.1
		k_1 or k_I (25 °C) = 5.03×10^{-3} s^{-1}		
		$\Delta H^{\ddagger}$ = 91.6 ± 3.8 kJ mol^{-1}		
		$\Delta S^{\ddagger}$ = 17.2 ± 10.5 JK^{-1} mol^{-1}		

[a] $A = 1/k_1$ or $1/k_I$. [b] $B = k_{-1}/(k_1 k_2)$ or $1/(k_I K_{os})$.

TABLE IV. Kinetic Parameters for the Exchange of acac in $UO_2(acac)_2L$ (L = dmso and dmf)

Complex	k_1[a] (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})	k_2/k_{-1}[a] (M^{-1})	k_3/k_2[a]
$UO_2(acac)_2$dmso	530	66.4 ± 8.4	−17.1 ± 26.8	0.24	74.0
$UO_2(acac)_2$dmf	11.3	91.6 ± 3.8	17.2 ± 10.5	10.7	10.6

[a]Temperature = 100 °C.

does not proceed through the dissociation of one end of the coordinated acac in $UO_2(acac)_2$dmf, since the k_{ex} value (5.03×10^{-3} s^{-1} at 25 °C) is much smaller than the rate constant of the intramolecular exchange of methyl groups (51.9 s^{-1} at 25 °C) [14].

Acknowledgements

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