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A Nuclear Magnetic Resonance Study of the Kinetics of Ligand-Exchange Reactions in Uranyl Complexes. 4. Intramolecular-Exchange Reaction of Methyl Groups of Acetylacetonate in $UO_2(acac)_2L$ with L = $Me_2S{=}O$, $Me_2N{=}COH$, and $Et_2N{=}COH$

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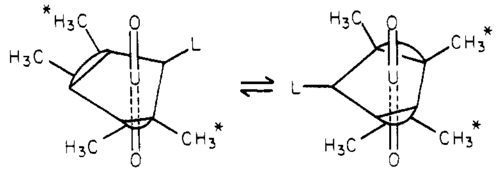
Kinetics of the intramolecular exchange of methyl groups of the coordinated acac in $UO_2(acac)_2L$ (acac = acetylacetonate; L = Me_2SO, DMF, DEF) have been studied in various solvents (CD_3COCD_3, CD_2Cl_2, CD_3NO_2, *o*-$C_6H_4Cl_2$) by means of NMR. The rate constants of the intramolecular-exchange reactions, k_{intra}, are well correlated with those of intermolecular-exchange reactions of L between the inner and outer coordination spheres of $UO_2(acac)_2L$, k_{inter}. It was found that the values of activation enthalpies for the intra- and intermolecular reactions resembled each other, and k_{intra} was always approximately the half of k_{inter} in all experiments studied. The exchange process including the dissociation of L as the rate-determining step was proposed to be the most reasonable mechanism.

Kinetics of ligand-exchange reactions for various uranyl complexes with unidentate ligands have been studied by NMR.[1-10] However, little information is available concerning the kinetics of the uranyl chelate complexes.[11-15] In an earlier paper[16] dealing with the kinetics of Me_2SO exchange in $UO_2(acac)_2Me_2SO$ (Me_2SO = dimethyl sulfoxide) by using NMR, it was found that the ^1H NMR signal of the coordinated acac methyl protons was present as a doublet at low temperatures, while as a singlet at high temperatures. This can be explained by considering the following intramolecular exchange in the equatorial plane of pentagonal-bipyramidal complexes, where an asterisk is used to denote the exchanging groups.



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In this paper we report the kinetics of the above intramolecular exchange for various $UO_2(acac)_2L$ complexes (L = Me_2SO, *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF) by means of NMR.

Experimental Section

Synthesis of Complexes. The $UO_2(acac)_2L$ (L = Me_2SO, DMF, DEF) complexes were prepared by dissolving $UO_2(acac)_2H_2O$ in warm solvents. The $UO_2(acac)_2H_2O$ complex was prepared by the procedure of Comyns et al.[17] Solutions containing uranyl complexes were cooled, and the resultant orange crystals were filtered and dried under vacuum for 1 day. Anal. Calcd. for $UO_2(acac)_2Me_2SO$: C, 26.38; H, 3.69. Found: C, 26.49; H, 3.66. Calcd for $UO_2(acac)_2DMF$: C, 28.84; H, 4.28; N, 2.59. Found: C, 28.79; H, 3.89; N, 2.46. Calcd for $UO_2(acac)_2DEF$: C, 31.64; H, 4.78; N, 2.46. Found: C, 31.43; H, 4.41; N, 2.58. Elemental analyses of the complexes were carried out in the Institute of Physical and Chemical Research.

Other Materials. Acetone-d_6 (CD_3COCD_3, Merck 99.8%), dichloromethane-d_2 (CD_2Cl_2, Merck 99%), nitromethane-d_3 (CD_3NO_2, Merck 99%), and *o*-dichlorobenzene (*o*-$C_6H_4Cl_2$, Wako Pure Chemical Ind. Ltd.) were used as solvents (S). The solvents CD_3COCD_3, CD_3NO_2, and CD_2Cl_2 were dried over 3A and 4A molecular sieves (Wako Pure Chemical Ind. Ltd.), and *o*-$C_6H_4Cl_2$ was distilled twice in vacuo and stored over 3A molecular sieves.

Preparation of Samples. Sample solutions were prepared by weighing the complexes, L, and solvents in a 1-cm^3 volumetric flask and were placed in an NMR sample tube and sealed. All samples were prepared in a glovebox filled with dried nitrogen. Exposure to light was minimized in order to avoid the photochemical redox reactions of uranyl complexes.[18]

Measurements of NMR Spectra and Kinetic Analysis. The measurement of the ^1H NMR spectra was carried out at 100 MHz on a JEOL JNM-MH 100 NMR spectrometer equipped with a JEOL JNM-VT-3B temperature controller. Temperatures were determined by the chemical shift difference between the methyl proton and the hydroxyl proton signals of methanol.

Kinetic analysis was carried out by using a computer program for the modified Bloch equation based on the two-site exchange[19] (eq 2),

$$G = \frac{-i\gamma H_1 M_0[P_a + P_b + \tau(P_a\alpha_b + P_b\alpha_a)]}{P_a\alpha_a + P_b\alpha_b + \alpha_a\alpha_b\tau} \qquad (2)$$

where $\tau = P_a\tau_b = P_b\tau_a$, $\alpha_a = 1/T_{2a} - i(\omega_{0a} - \omega)$, and $\alpha_b = 1/T_{2b} - i(\omega_{0b} - \omega)$. The values of P_a and P_b are the mole fractions of the sites a and b, τ_a and τ_b are the mean lifetimes of each site, and the values of $1/T_2$ and ω_0 with subscripts a and b refer to the line widths and the chemical shifts of two sites in the absence of chemical exchange, respectively. The theoretical spectra were calculated from eq 2 by using P_a, P_b, T_{2a}, T_{2b}, ω_{0a}, ω_{0b}, and the appropriate τ values and compared with the experimental spectra. All computations were carried out with a Hitach M-200H computer.

Results and Discussion

The ^1H NMR spectra of $UO_2(acac)_2Me_2SO$ in *o*-$C_6H_4Cl_2$ at −20 and 30 °C are shown in Figure 1, in which signals a and c are those of the methyl protons and C3 protons of the coordinated acac, respectively, and signal b is the methyl proton signal of the coordinated Me_2SO. Spectrum Ia represents the expanded signal a. It is found that the methyl

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Table I. Dependence of k_{intra} on the Concentration of $UO_2(acac)_2L$ (L = Me_2SO, DMF, DEF)[a]

complex	[complex]/ 10^{-2} mol kg^{-1}	k_{intra}/s^{-1} 10 °C	0 °C	−10 °C	−20 °C
$UO_2(acac)_2Me_2SO$	1.74	18.0 ± 1.5	9.36 ± 0.48	5.00 ± 0.92	2.20 ± 0.52
	3.11	20.8 ± 1.0	8.84 ± 0.72	4.41 ± 1.08	1.76 ± 0.19
$UO_2(acac)_2DMF$	1.76	25.8 ± 2.1	12.8 ± 0.5	6.09 ± 0.64	3.75 ± 0.48
	3.64	22.8 ± 1.1	14.5 ± 1.7	6.70 ± 0.22	3.26 ± 0.15
$UO_2(acac)_2DEF$	1.83	20.9 ± 2.9	12.1 ± 1.8	5.31 ± 0.61	4.63 ± 1.15
	4.72	22.5 ± 2.5	11.5 ± 0.4	6.85 ± 0.29	3.14 ± 0.19

[a] In CD_2Cl_2 solvent.

Table II. Kinetic Parameters for the Exchange of Methyl Groups of acac in $UO_2(acac)_2L$ (L = Me_2SO, DMF, DEF)

complex	[complex]/ 10^{-2} mol kg^{-1}	solvent	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$k_{\text{intra}}(25\ °C)^a$/ 10 s^{-1}
$UO_2(acac)_2Me_2SO$	3.11	CD_2Cl_2	42.4 ± 2.9	−70.1 ± 10.9	5.45
	5.74	CD_3COCD_3	46.6 ± 1.7	−47.5 ± 6.7	15.2
	3.49	o-$C_6H_4Cl_2$	49.6 ± 0.8	−44.9 ± 2.5	6.32
	4.17	CD_3NO_2	45.8 ± 1.3	−60.5 ± 5.0	4.49
$UO_2(acac)_2DMF$	3.64	CD_2Cl_2	35.3 ± 1.3	−94.5 ± 4.2	5.19
	5.98	CD_3COCD_3	39.1 ± 1.5	−63.4 ± 3.4	47.0
$UO_2(acac)_2DEF$	4.72	CD_2Cl_2	34.0 ± 1.3	−100 ± 5	4.26

[a] Calculated values from $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at 25 °C.

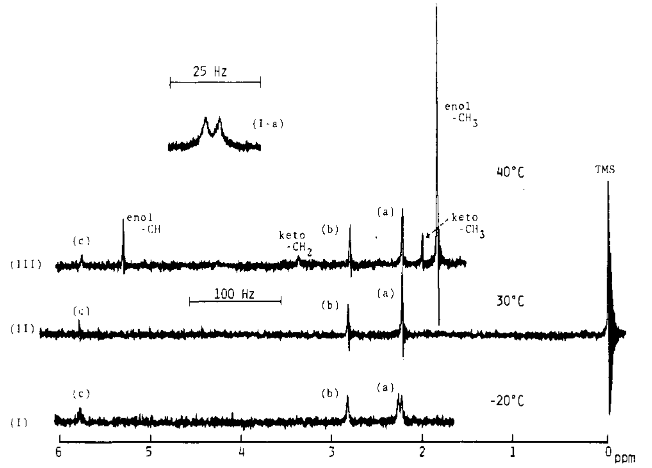

Figure 1. ^1H NMR spectra of $UO_2(acac)_2Me_2SO$ in o-$C_6H_4Cl_2$ at −20 and 30 °C and of a solution consisting of $UO_2(acac)_2Me_2SO$, Hacac, and o-$C_6H_4Cl_2$ at 40 °C.

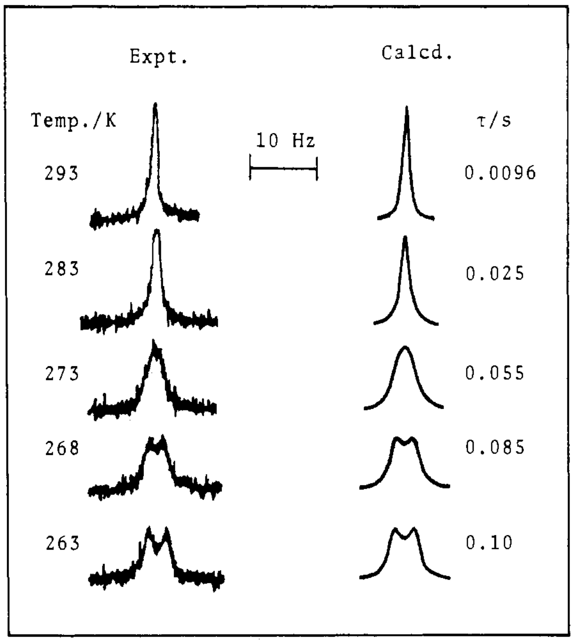

Figure 2. Experimental (left side) and best fit calculated ^1H NMR line shapes of $UO_2(acac)_2Me_2SO$ (0.0349 mol/kg) in o-$C_6H_4Cl_2$. Temperatures and best fit τ values are shown at left and right sides of the figure, respectively.

proton signal of the coordinated acac has two equivalent peaks at −20 °C, while the corresponding peak becomes a singlet at 30 °C. The area ratio of signals a to b to c was 6:3:1, where the signal of c was used as a standard. This area ratio and the chemical shifts of signals a, b, and c were not changed with temperature. These facts suggest that over the present temperature region the complex is present in the pentagonal-bipyramidal structure in o-$C_6H_4Cl_2$ similar to those in CD_3COCD_3 and CD_2Cl_2.[16] The coalescence of the methyl proton signal suggests that the exchange reaction takes place between the two methyl groups of the coordinated acac, i.e. the nearest group to and the farthest group from the coordinated Me_2SO. Similar phenomena were observed in the ^1H NMR spectra of $UO_2(acac)_2Me_2SO$ in CD_3COCD_3, CD_2Cl_2, and CD_3NO_2. The line shapes of the methyl proton signal from the coordinated acac at various temperatures are shown in Figure 2. The result indicates the typical two-site exchange between two methyl groups as described by reaction 1. The best fit τ values at each temperature were obtained by using the method described in the Experimental Section. The calculated line shapes and the corresponding τ values are also shown in Figure 2. Similar treatments were made in various solvents, CD_3COCD_3, CD_2Cl_2, and CD_3NO_2. Since the exchange occurs between the two kinds of methyl groups of the coordinated acac, the following equations should be applied: $\tau_a = \tau_b$ and P_a and $P_b = 0.5$. Hence, the first-order exchange rate constant, k_{intra}, is given by eq 3. The k_{intra} values were calculated from

$$k_{\text{intra}} = 1/(2\tau) = (kT/h)\exp(-\Delta H^{\ddagger}/RT)\exp(\Delta S^{\ddagger}/R) \tag{3}$$

the best fit τ values by using eq 3. The exchange rates were measured for different complex concentrations in CD_2Cl_2 (Table I). Results indicate that the exchange rate is first order with respect to the complex concentration. The logarithms of k_{intra} obtained in each solvent were plotted against the reciprocal temperature as shown in Figure 3. The activation parameters were obtained from these plots by using the least-squares method and are listed in Table II.

In order to examine the effect of the coordinated ligands, L, similar measurements were performed for the complexes $UO_2(acac)_2DMF$ and $UO_2(acac)_2DEF$ in CD_2Cl_2. The ^1H NMR spectra of these complexes are shown in Figures 4 and 5. In Figure 4, doublet a and singlet c are the signals of the

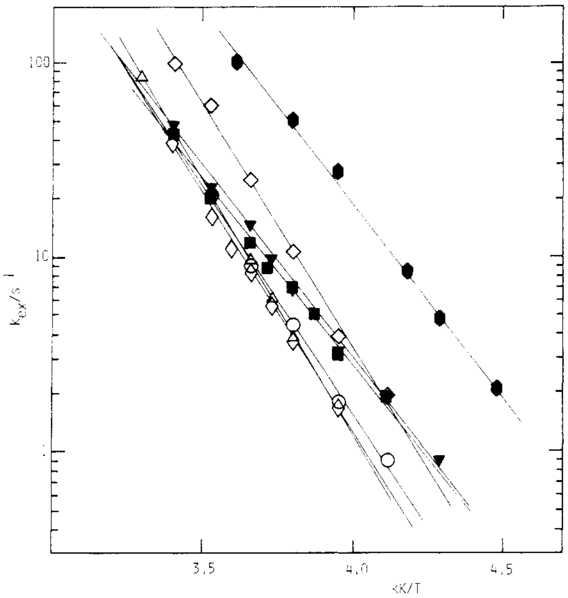

Figure 3. Semilogarithmic plots of k_{intra} against the reciprocal temperature for the exchange of methyl groups of acac in $UO_2(acac)_2L$ (L = Me_2SO, DMF, DEF): ○, $UO_2(acac)_2Me_2SO$ in CD_2Cl_2; △, $UO_2(acac)_2Me_2SO$ in o-$C_6H_4Cl_2$; ◇, $UO_2(acac)_2Me_2SO$ in CD_3COCD_3; ◆, $UO_2(acac)_2Me_2SO$ in CD_3NO_2; ▲, $UO_2(acac)_2DMF$ in CD_2Cl_2; ●, $UO_2(acac)_2DMF$ in CD_3COCD_3; ■, $UO_2(acac)_2DEF$ in CD_2Cl_2.

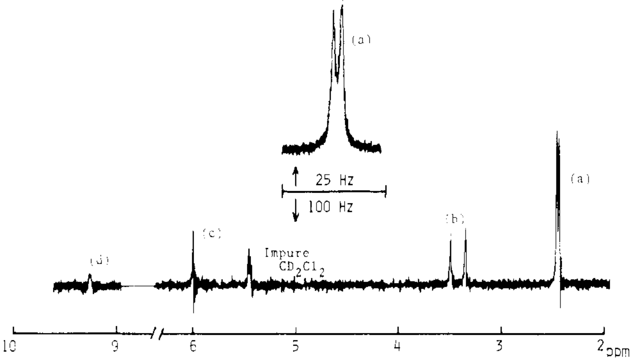

Figure 4. ^1H NMR spectrum of $UO_2(acac)_2DMF$ in CD_2Cl_2 at −40 °C.

methyl protons and C3 protons of the coordinated acac, respectively. Signals b and d are assigned to be the methyl protons and the formyl protons of the coordinated DMF, respectively. The area ratio of signals a to b to c was 6:3:1 and indicates that the structure of $UO_2(acac)_2DMF$ must be pentagonal bipyramidal, similar to those of $UO_2(acac)_2H_2O$[20] and $UO_2(acac)_2Me_2SO$.[16] In Figure 5, signals b and d are the methyl protons and C3 protons of the coordinated acac, respectively, and signals a, c, and e are the methyl and methylene protons of the ethyl groups and the formyl protons of the coordinated DEF, respectively. The area ratio of signals b to d to e was 12:2:1 and also indicates the structure of $UO_2(acac)_2DEF$ to be pentagonal bipyramidal. The methyl proton signals of the coordinated acac of $UO_2(acac)_2DMF$ and $UO_2(acac)_2DEF$ were observed at various temperatures and complex concentrations in CD_2Cl_2. The spectra, similar to those shown in Figure 2, were observed in these complexes. Rate constants are independent of the concentration of complex as shown in Table I. For $UO_2(acac)_2DMF$, the exchange reaction of the methyl groups was also measured in CD_3COCD_3. The activation parameters were obtained from the plots

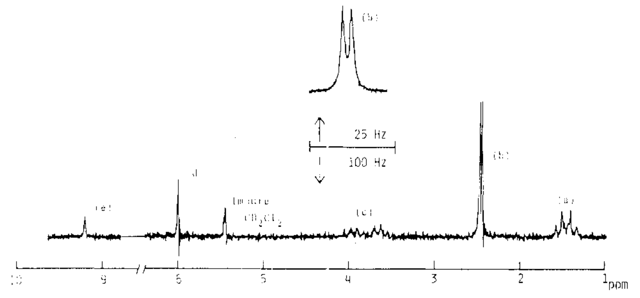

Figure 5. ^1H NMR spectrum of $UO_2(acac)_2DEF$ in CD_2Cl_2 at −60 °C.

of log k_{intra} vs. $1/T$ in Figure 3 and are listed in Table II.

The possibility of the reaction passing through the binuclear complex can be ruled out from the results in Table I. Hence, the following four mechanisms are postulated as possible mechanisms for the exchange of methyl groups of the coordinated acac: (i) complete dissociation of one of the two coordinated acac; (ii) ring opening of one of the two coordinated acac, which gives a four-coordinated intermediate in the equatorial plane; (iii) a twist mechanism in which the methyl groups exchange without the dissociation of coordinated ligands; (iv) dissociation of L, which gives a four-coordinated intermediate in the equatorial plane, followed by fast displacement.

Part III in Figure 1 shows the ^1H NMR spectrum of the o-$C_6H_4Cl_2$ solution containing free acetylacetone (Hacac) and $UO_2(acac)_2Me_2SO$ at 40 °C. Symbols a, b, and c correspond to those in spectra I and II in Figure 1. The methyl proton signal of the coordinated acac (a) is a singlet because of the relatively fast exchange between two different magnetic environments as shown in reaction 1. However, the methyl proton signals of keto and enol isomers of free Hacac are observed at higher field than that of the coordinated acac. This indicates that the exchange rate between the coordinated acac and free Hacac is much slower than that of reaction 1. If reaction 1 proceeds through mechanism i, the methyl proton signals of the coordinted acac and free Hacac should coalesce. Similar phenomena were also observed for the other solutions listed in Table II. Therefore, mechanism i is eliminated.

Mechanism ii also can be ruled out for the following reason. The rate constant for the dissociation of one end of the coordinated acac in $UO_2(acac)_2Me_2SO$ was estimated to be 2.0 s^{-1} at 25 °C from the study of the exchange reaction of acac between the coordinated and free sites in o-$C_6H_4Cl_2$.[21] This value is much smaller than the rate constant for reaction 1, 63.5 s^{-1}, under the same conditions.

Mechanism iii seems to be most unlikely. Since the axial O=U=O bond is extremely strong and inert,[22,23] it should be most difficult for the complex to form the twist structure without changing the axial conformation.

It has been suggested[24,25] that if the intramolecular exchange reaction takes place through mechanism ii or iii, the activation free energy decreases with increasing dielectric constant of the solvent owing to a lowering of the activation enthalpy as a result of greater charge separation and greater solvation in the transition state. In the present study, the free energy of activation decreases in the order $CD_3NO_2 \approx CD_2Cl_2 \approx o$-$C_6H_4Cl_2 > CD_3COCD_3$ (see Table II). This is different from the order expected from the dielectric constant, $CD_2Cl_2 >$

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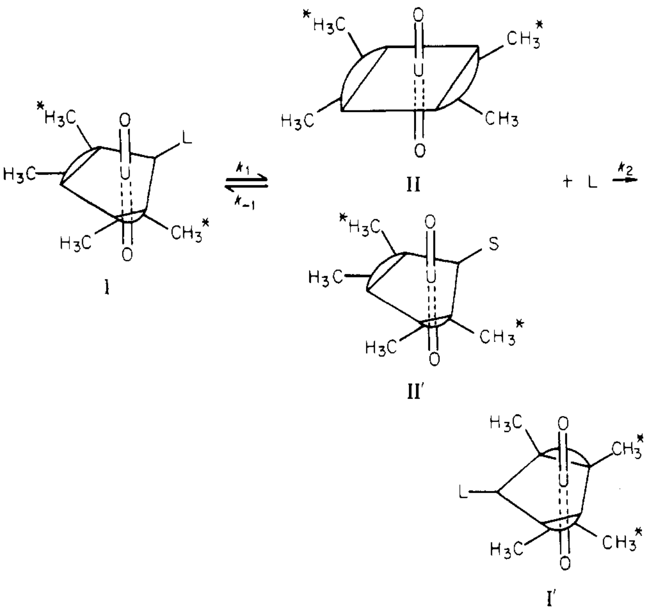
Table III. Kinetic Parameters for the Exchange of Methyl Groups of acac and of L in $UO_2(acac)_2L$ (L = Me_2SO, DMF)

complex	solvent	reaction[a]	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	k(−10 °C)/s^{-1}	ref
$UO_2(acac)_2Me_2SO$	CD_3COCD_3	intra	46.6 ± 1.7	−47.5 ± 6.7	10.6 ± 1.5	this work
		inter	45.8 ± 0.8	−46.6 ± 2.9	19.0 ± 1.2	16
	CD_2Cl_2	intra	42.4 ± 2.9	−70.1 ± 10.9	4.41 ± 1.08	this work
		inter	47.9 ± 5.2	−46.6 ± 11.2	8.45 ± 0.41	16
$UO_2(acac)_2DMF$	CD_3COCD_3	intra	39.1 ± 1.5	−63.4 ± 3.4	50.3 ± 2.7	this work
		inter	42.0 ± 1.3	−46.2 ± 5.5	106 ± 13	21
	CD_2Cl_2	intra	35.3 ± 1.3	−94.5 ± 4.2	6.70 ± 0.22	this work
		inter	32.8 ± 1.7	−92.0 ± 5.9	28.2 ± 7.2	21

[a] Intra: intramolecular exchange of methyl groups of the coordinated acac. Inter: exchange reaction of L in $UO_2(acac)_2L$ (L = Me_2SO, DMF).

Scheme I



o-$C_6H_4Cl_2$ > CD_3COCD_3 > CD_3NO_2. This result may also be used to support the idea that mechanisms ii and iii are not applicable to reaction 1.

It has been reported that if the free L is present in solutions containing $UO_2(acac)_2L$, the intermolecular exchange reaction takes place between coordinated and free L.[2,16]

$$UO_2(acac)_2L + L^* \xrightleftharpoons{k_{inter}} UO_2(acac)_2L^* + L \qquad (4)$$

Reaction 4 proceeds primarily through the D mechanism,[26] where the rate-determining step is the dissociation of L. This fact strongly suggests the possibility of mechanism iv. The assumption of mechanism iv results in the reactions of Scheme I.

In Scheme I, the k_1 pathway is the rate-determining step, and II and II' are the possible intermediates. Intermediate II is formed by the complete D mechanism. The existence of II' is postulated by the fact that the rates of reaction 4 differ in various solvents because of the solvent effect for the intermediate.[16]

On the basis of Scheme I, the observed first-order rate constant for reaction 1, k_{intra}, is given by eq 5. In the case

$$k_{intra} = k_1k_2/(k_{-1} + k_2) \qquad (5)$$

where the complete D mechanism passes through intermediate II, k_{-1} should be statistically equal to k_2. Then, eq 5 is simplified to eq 6. It should be noted that the ligand exchange

$$k_{intra} = k_1/2 \qquad (6)$$

in reaction 4 proceeds through the dissociation of L as the rate-determining step, and hence k_1 is directly related to k_{inter} in ractioin 4, i.e. $k_1 = k_{inter}$. If intermediate II' is assumed, k_{intra} should deviate from $k_{inter}/2$ depending on the ratio of k_2/k_{-1} but never exceed k_{inter}.

The results listed in Table III show that k_{intra} is approximately equal to $k_{inter}/2$. This is the most reasonable result expected from Scheme I and suggests a stronger possibility for intermediate II rather than II'. However, intermedite II' will not be excluded, until more data in other solvents have been collected. Furthermore, ΔH^* values for k_{intra} and k_{inter} are very close to each other when compared for the same system. Since reactions 1 and 4 proceed through the same rate-determining k_1 step, ΔH^* values should become similar for both reactions. These facts strongly support mechanism iv described in Scheme I.

In Table II, ΔH^* values of k_{intra} change with different coordinated ligands (Me_2SO, DMF, DEF). Such a change in ΔH^* is relatively large compared with those observed in the reactions of $UO_2(acac)_2Me_2SO$ in various solvents, CD_2Cl_2, CD_3COCD_3, CD_3NO_2, and o-$C_6H_4Cl_2$. This is readily explained by considering Scheme I. Since the rate-determining step is the dissociation of L in mechanism iv, the bond strength between UO_2^{2+} and L should be directly related to the energy of the bond breaking of L. Therefore, it is reasonable that the ΔH^* values change with various coordinated ligands, L.

The large negative values of ΔS^* might be responsible for the solvent effect as suggested by Bennetto and Caldin.[27,28] They indicated that even in dissociation reactions ΔS^* may possess negative values as a result of the contribution of the solvent rearrangement around the metal complexes.

Vasilescu and Oncescu[12] have reported the configurational rearrangement of the bis(benzoylacetonato)dioxoouranium(VI) complex and proposed that this reaction proceeds through the one-end dissociation of the ligand in the equatorial plane. It is not surprising that their experimental results led to a conclusion different from the present study, because the structure of the complex used in their experiments is tetragonal bipyramidal, which differs from the common pentagonal-bipyramidal structure for uranyl complexes.

Kramer et al.[13] have reported the exchange reaction between nonequivalent fluoromethyl groups in $UO_2(hfac)_2THF$ (hfac = hexafluoroacetylacetonate, THF = tetrahydrofuran). They proposed a base migration mechanism in which the THF molecule migrates from one side to the opposite side via an intermediate capped octahedral structure.

However, Glavincevski and Brownstein[29] studied recently the same exchange reaction reported by Kramer et al. and denied Kramer's mechanism. They proposed that the exchange between the nonequivalent fluoromethyl groups of the coordinated hfac in $UO_2(hfac)_2THF$ proceeds through two mechanisms, i.e. the intermolecular displacement of THF and the rotation of the hfac ring. Although the intermolecular

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displacement mechanism was not discussed in detail, this mechanism seems to be similar to mechanism iv.

Furthermore, Delpuech et al.[30] studied two kinds of exchange reactions in $[UO_2(nipa)_2EtOH]^{2+}$ (nipa = nonamethylimidodiphosphoramide, EtOH = ethanol), i.e. the intermolecular exchange between the coordinated ethanol and free ethanol and the intramolecular exchange between the nonequivalent phosphorus atoms of the coordinated nipa. They found that the intermolecular exchange occurs more rapidly than the intramolecular exchange and the activation entropies for both reactions have negative values. These results are consistent with our results. They suggested that the intermolecular exchange proceeds through the I mechanism and the intramolecular exchange proceeds through the mechanism in which the rate-determining step is the dissociation of the coordinated ethanol or the ring opening of one of the two coordinated nipa. The former and the latter mechanisms for the intramolecular exchange correspond to mechanisms iv and ii, respectively. These facts lend support to the conclusion that mechanism iv is the most reasonable mechanism for the present exchange reactions.

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Registry No. $UO_2(acac)_2Me_2SO$, 71357-22-7; $UO_2(acac)_2DMF$, 89145-11-9; $UO_2(acac)_2DEF$, 89145-12-0; Hacac, 123-54-6.

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Photolysis of the Tantalum Cluster $Ta_6Br_{12}^{2+}$ in Aqueous Acidic Solution

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Irradiation of $[Ta_6Br_{12}]^{2+}$ in deaerated hydrochloric acid solution led to the photooxidation of the cluster ion and the formation of hydrogen according to $[Ta_6Br_{12}]^{2+} + H^+ \rightarrow [Ta_6Br_{12}]^{3+} + {}^1/_2H_2$. Quantum yields increased with increasing acidity of the solution and with decreasing wavelength of excitation, varying from 3×10^{-4} at 640 nm to 10^{-2} at 254 nm in 1 M HCl. Evidence is presented that the evolution of hydrogen does not involve the intermediate formation of hydrogen atoms. It is assumed that the key step involves a two-electron transfer from $[Ta_6Br_{12}]^{2+}$ to a water molecule in the solvent cage, yielding $[Ta_6Br_{12}]^{4+}$ and H^-, which is scavenged by H^+, generating H_2.

Introduction

In contrast to the case for mononuclear[1-3] and binuclear[3,4] metal complexes not much is known about the photochemistry of polynuclear compounds.[3] In particular, extended metal cluster complexes deserve attention with regard to excited-state properties. In analogy to the situation for large aromatic molecules, the excited states are not likely to be much distorted. While small clusters such as $Fe_3(CO)_{12}$[5] may undergo a photocleavage of metal–metal bonds, the structure of larger clusters such as $[Mo_6Cl_{14}]^{2-}$[6] is not affected photochemically. In contrast, larger clusters may easily undergo bimolecular photoredox reactions accepting or donating electrons. Since clusters frequently have available several oxidation states at small differences of redox potentials, they may participate in multielectron-transfer processes. In addition, redox reactions of larger clusters are generally not associated with the decomposition of these compounds due to the delocalization of the redox orbitals over the whole cluster structure. These considerations suggest that clusters are attractive candidates for reversible multielectron photoredox reactions, which are interesting with regard to processes such as the light-induced splitting of water.[7] We started to explore cluster complexes and report our observations on the photochemistry of $[Ta_6Br_{12}]^{2+}$. The present study is also of interest with regard to the photochemistry of the early transition metals in general. The investigation of light-induced reactions of these metals has been largely restricted to organometallic compounds.[3]

Experimental Section

The compound $[Ta_6Br_{12}]Br_2 \cdot 8H_2O$ was prepared by a published procedure.[8] Its electronic absorption spectrum agreed well with that reported previously.[9]

The light sources were an Osram HBO 100 W/2, an Osram XBO 450 W/4, and a Hanovia Xe/Hg 977 B-1 (1000-W) lamp. The Schott interference filters PIL 254 and 366 were used for the selection of the mercury lines at 254 and 366 nm. Irradiations at 640 nm were achieved with a Schoeffel GM 250-1 monochromator. Solutions of the complex were deaerated by argon and photolyzed in 1-cm spectrophotometer cells at room temperature. For quantum-yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer, which was calibrated and equipped with an RkP-345 detector.

Progress of the photooxidation was monitored by UV–visible spectral measurements with a Varian-Techtron Super Scan 3 recording spectrophotometer and a Zeiss PMQ II spectrometer for measurements at selected wavelengths. The product of the photooxidation $[Ta_6B_{12}]^{3+}$ was identified by its absorption spectrum.[9] The change of absorbance at 640 nm was used to calculate the amount of photooxidation. At 640 nm the molar extinction coefficients are $\epsilon = 6600$ for $[Ta_6Br_{12}]^{2+}$ and $\epsilon = 600$ for $[Ta_6Br_{12}]^{3+}$.

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