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# Photochemical Reactions of Pentakis(*N,N*-dimethylformamide)-dioxouranium(VI) Ions in Nonaqueous Solutions

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Photochemical reactions of $[UO_2(dmf)_5]^{2+}$ (dmf=*N,N*-dimethylformamide) ions were investigated in DMF and acetone solutions. The photolysis product of $[UO_2(dmf)_5]^{2+}$ at the initial stage was U(V), which was so stable in acid-free organic solvents in the dark that the absorption spectrum of U(V) was easily obtained in DMF. The molar extinction coefficient of U(V) was determined to be $45.5\pm1.5$ $M^{-1}$ $cm^{-1}$ (M=mol $dm^{-3}$) at 755 nm. The formation of U(V) seems to proceed through the intramolecular reaction ($k_i$) and the lower limit of $k_i$ was determined to be about $10^7$ $s^{-1}$ from the lifetime of excited uranyl ions by using a laser flash photolysis.

With respect to photochemical reactions of uranyl ions ($UO_2^{2+}$)[1] with organic substrates in aqueous acidic solutions, a large number of investigations were performed, especially with alcohols,[2–4] acetaldehyde,[5] and acetone.[6] In aqueous acidic solutions, the uranyl ion is reduced giving $UO_2^+$ as an intermediate, which immediately disproportionates to $U^{4+}$ and $UO_2^{2+}$.[7,8] On the other hand, a limited number of studies were carried out in nonaqueous solutions. It was reported that U(V) was formed on irradiation of $[UO_2(tbp)_2](NO_3)_2$ in TBP (tributyl phosphate)[9] and of $UO_2$(18-crown-6)$(ClO_4)_2$ in acetonitrile.[10] Cauzzo et al. studied the photochemical reaction mechanism of $UO_2(NO_3)_2\cdot$ 2TEP in TEP (triethyl phosphate),[11] and reported that U(V) formed was stable in the dark. The reaction of $[UO_2(hfac)_2]$thf (hfac=hexafluoroacetylacetonate, thf=tetrahydrofuran) was studied in hydrocarbon solvents, and the final product was considered to be $U^{4+}$, where the appearance of U(V) was proposed as an intermediate.[12] In order to elucidate photochemical reaction mechanisms of uranyl ions in nonaqueous solvents, the photochemical reactions of $[UO_2(dmf)_5](ClO_4)_2$ in DMF and acetone were studied, and a possible reaction mechanism including the formation of U(V) is proposed.

## Experimental

**Materials.** The $[UO_2(dmf)_5](ClO_4)_2$ complex was prepared by the same method as reported by Lincoln et al.[12] Dimethyl sulfoxide (DMSO) and DMF were distilled twice in vacuo and stored over 3A molecular sieves. Aceone was distilled after refluxing over potassium permanganate, followed by distillation with calcium chloride, then treated with phosphorus pentaoxide, and fractionally distilled. The distillate was stored over 4A molecular sieves. $^{13}$C-enriched DMF ($H^{13}CON(CH_3)_2$, Merck 90%) and acetone-$d_6$ ($CD_3COCD_3$, Merck 90%) were used without further purification. Preparation of $[U(dmso)_8](ClO_4)_4$ was performed by adding DMSO into aqueous $U^{4+}$ solution[14] which was prepared by electrolytic reduction of uranyl perchlorate solution. Brownish green crystals were filtered and washed with diethyl ether. All other chemicals were of analytical grade and used without further purification.

**Apparatus and Procedures.** Elemental analysis of the complexes was carried out by using a Shimadzu CHN-1A analyzer. Calcd for $[UO_2(dmf)_5](ClO_4)_2$: U, 28.53; C, 21.59; H, 4.22; N, 8.39. Found: U, 28.50; C, 20.98; H, 4.10; N, 8.39. Calcd for $[U(dmso)_8](ClO_4)_4$: U, 18.88 C, 15.24; H, 3.84. Found: U, 18.79; C, 15.67; H, 3.65. Luminescence spectra and intensities of excited uranyl ions were measured by using a JASCO FP-550A fluorescence spectrophotometer at room temperature. Uranyl ions were excited with light of 430 nm and the luminescence intensity was measured at 522 nm. Other spectrophotometric measurements were carried on a Shimadzu UV-210A spectrophotometer. The lifetimes of excited uranyl ions were measured by using a pulsed dye laser (420 nm) with a pulse width of 6.7 ns. Sample solutions for the measurement of quantum yields were degassed under vacuum and irradiated at 25±0.1 °C with a 500 W ultrahigh pressure mercury lamp (Ushio USH-500D) at various wavelengths by using a set of appropriate filters. Sample solutions for ESR measurements were degassed in vacuo and ESR spectra were recorded on a JEOL- JES-FX3 spectrometer. All the ESR measurements were carried out during the light irradiation.

## Results

**Absorption Spectra of Uranium Species and a Luminescence Spectrum of the Excited Uranyl Ion.** Absorption spectra of $[UO_2(dmf)_5]^{2+}$ in DMF and acetone, and a luminescence spectrum of the excited uranyl ion in acetone are illustrated in Fig. 1. The molar extinction coefficient ($\varepsilon_{VI}$) of the uranyl ion in

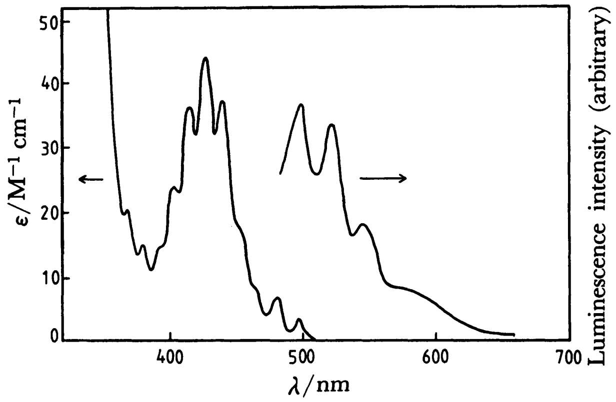

Fig. 1. Absorption spectrum of $[UO_2(dmf)_5](ClO_4)_2$ in DMF and acetone, and its luminescence spectrum in acetone.

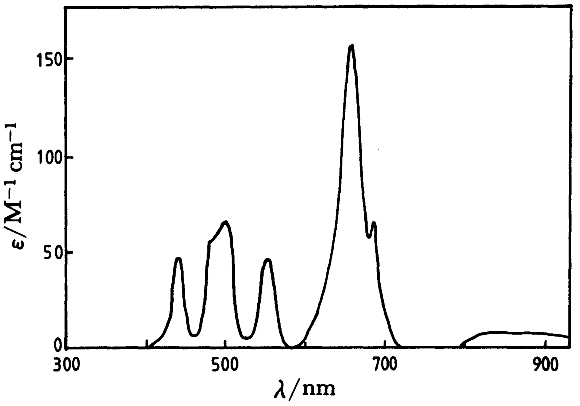

Fig. 2. Absorption spectrum of the DMF solution containing $[UO_2(dmf)_5](ClO_4)_2$ and $HClO_4$ after long-time irradiation.

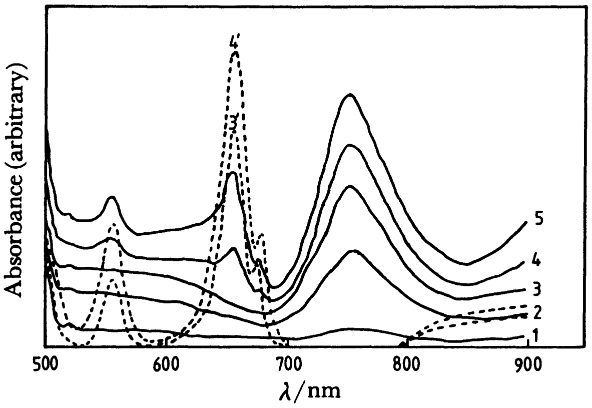

Fig. 3. Spectral changes of 0.1 M $[UO_2(dmf)_5]^{2+}$ in DMF irradiated with 365 nm light. (1): 2 min, (2): 13 min, (3): 23 min, (4): 30 min, (5): 40 min. Spectra 3′ and 4′ were obtained on addition of $HClO_4$ to solutions 3 and 4, respectively.

DMF and acetone at 426 nm was 44.4 $M^{-1}cm^{-1}$. The luminescence of the excited uranyl ion was not observed in DMF at room temperature, but observed in acetone. Figure 2 shows an absorption spectrum which was obtained after long-time irradiation of the DMF solution containing $[UO_2(dmf)_5](ClO_4)_2$ and a small amount of perchloric acid. This spectrum is well-consistent with that of the U(IV)-DMF complex ($\varepsilon_{IV}$=155.7±1.5 $M^{-1}cm^{-1}$ at 657 nm) which was prepared by dissolving $[U(dmso)_8](ClO_4)_4$ into DMF or by dissolving $U^{4+}$ into DMF ($H_2O$: DMF=1:99).[15] Therefore, the spectrum was identified as that of the U(IV)-DMF complex. Figure 3 shows changes in absorption spectrum of 0.1 M $[UO_2(dmf)_5](ClO_4)_2$ in DMF irradiated with 365 nm light. The appearance of a different absorption peak at 755 nm indicates the formation of a new complex (A), and then the absorption spectrum after further irradiation shows the formation of another compound ($U^{IV}$) which has two peaks at 558 and 657 nm. These two peaks are consistent with those of the U(IV)-DMF complex, but the peak heights are quite different. Addition of perchloric acid to the complex A solution under nitrogen atmosphere caused the rapid disappearance of complex A and the formation of U(VI)- and U(IV)-DMF complexes. Therefore, complex A was identified as the U(V)-DMF complex which disproportionated as follows:[7,8)]

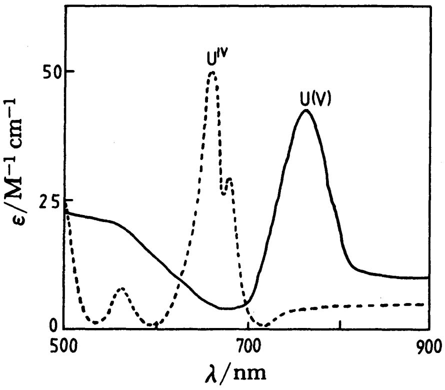

Fig. 4. Absorption spectra of U(V) and $U^{IV}$ in DMF.

$$2UO_2^+ + 4H^+ \longrightarrow UO_2^{2+} + U^{4+} + 2H_2O \qquad (1)$$

The concentration of U(V) was determined spectrophotometrically in the following way. An appropriate quantity of perchloric acid was added to the U(V) solution and the concentration of the resulting U(IV) was used for the determination of the U(V) concentration using the relation of 2[U(IV)]=[U(V)]. The molar extinction coefficient of U(V) at 755 nm was determined to be 45.5±1.5 $M^{-1}cm^{-1}$. The spectrum of U(V) was obtained as follows. The molar extinction coefficient of U(V) at wavelength $\lambda$, $\varepsilon_V(\lambda)$, can be evaluated by

$$\varepsilon_V(\lambda) = \varepsilon_{VI}(\lambda) + \frac{\Delta A(\lambda,t)}{\Delta C_V(t)}, \qquad (2)$$

where $\Delta A(\lambda, t)$ is the absorbance change of the solution at the wavelength of $\lambda$ after irradiation time $t$, and $\Delta C_V(t)$ is the concentration change of U(V) after $t$. The U(V) spectrum obtained is shown in Fig. 4.

The spectrum of $U^{IV}$, which is discussed later, was obtained by adding perchloric acid to the solution containing U(V) and $U^{IV}$, and using Eq. 3.

$$\varepsilon^{IV}(\lambda) = \varepsilon_{VI}(\lambda) + \frac{\Delta A(\lambda,t)+\{\varepsilon_{VI}(\lambda)-\varepsilon_V(\lambda)\}\Delta C_V(t)}{\Delta C^{IV}(t)}, \qquad (3)$$

where $\varepsilon^{IV}(\lambda)$ and $\Delta C^{IV}$ denote the molar extinction coefficient at $\lambda$ and the concentration change of $U^{IV}$, respectively. The absorption spectrum of $U^{IV}$ is also shown in Fig. 4.

**ESR Spectrum.** Figure 5 shows the ESR spectrum of photolysis products of $[UO_2(dmf)_5](ClO_4)_2$ in the rigid DMF matrix at −170 °C, where ESR measurements were carried out during the light irradiation. The ESR measurement was also carried out for $[UO_2$-

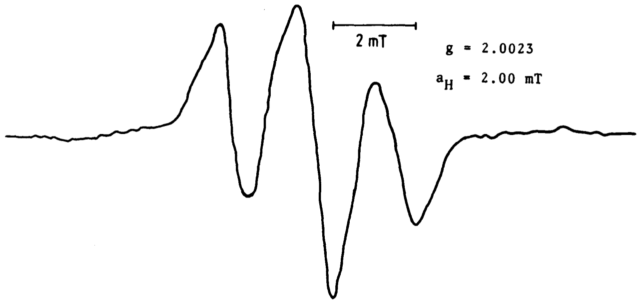

Fig. 5. ESR spectrum of the sample containing $[UO_2(dmf)_5]^{2+}$ in DMF during the irradiation at 365 nm and −170 °C. Symbols $g$ and $a_H$ are the $g$-factor (reference: $Mn^{2+}$) and hyperfine coupling constant, respectively.

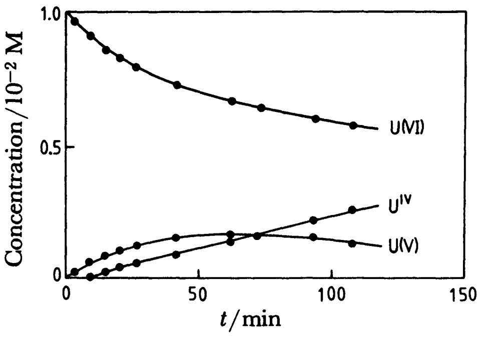

Fig. 6. Changes in the concentrations of reactant and products on irradiation of $[UO_2(dmf)_5]^{2+}$ in DMF with light of 313 nm. $[UO_2(dmf)_5^{2+}]=0.01$ M, T=25 °C.

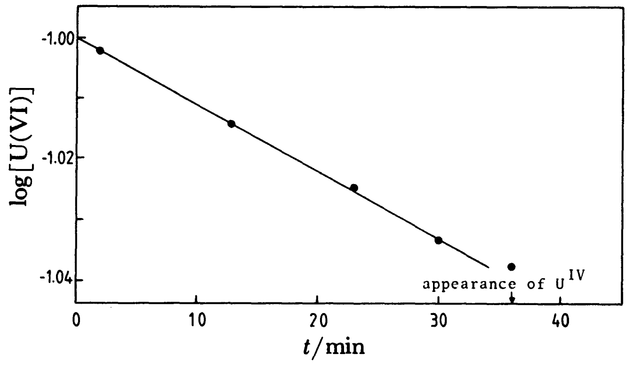

Fig. 7. Plot of log [U(VI)] vs. irradiation time. $[UO_2(dmf)_5^{2+}]=0.10$ M, $\lambda_{irr}$(wavelength of irradiating light)= 365 nm, $T$=25 °C.

Table 1. Dependence of the Quantum Yield of U(V) on the Absorbed Light Intensity[a]

| $I_a$ <br> $10^{-7}$ einstein $min^{-1}$ | | $\Phi_V$ |
|---|---|---|
| 0.56 | | 0.31 |
| 1.55 | | 0.31 |
| 1.62 | | 0.34 |
| 3.66 | | 0.31 |
| 4.62 | | 0.32 |
| 4.65 | | 0.29 |
| 4.99 | | 0.32 |
| 5.13 | | 0.31 |
| | average | 0.31±0.01 |

a) $[UO_2(dmf)_5^{2+}]=0.020$ M, $\lambda_{irr}=365$ nm, $T$=25 °C.

Table 2. Dependence of the Quantum Yield of U(V) on the Initial Concentration of U(VI)

| $[UO_2(dmf)_5^{2+}]$ <br> M | $\Phi_V$ |
|---|---|
| 0.010 | 0.31±0.01[a] |
| 0.020 | 0.31±0.01[b] |
| 0.100 | 0.30±0.03[b] |
| 0.202 | 0.32±0.01[b] |

a) $\lambda_{irr}=436$ nm, $T$=25 °C. b) $\lambda_{irr}=365$ nm, $T$=25 °C.

$(dmf)_5](ClO_4)_2$ dissolved in $H^{13}CON(CH_3)_2$ at −170 °C, which shows the same ESR spectrum given in Fig. 5, and the radical species was assigned to $HCON(CH_3)CH_2\cdot$.[16,17] In addition, $[UO_2(dmf)_5](ClO_4)_2$ in the rigid acetone-$d_6$ matrix yielded the same radical.

**Changes in Concentration of Uranium Species.** Figure 6 shows the changes in concentration of $U^{IV}$, U(V) and U(VI) resulted from the irradiation of 0.01 M $[UO_2(dmf)_5](ClO_4)_2$ in DMF at 313 nm. The U(VI) concentration was estimated by subtracting ([U(V)]+[$U^{IV}$]) from the initial concentration of U(VI). The U(V) concentration has a maximum, and $U^{IV}$ appears somewhat later during the irradiation, and gradually increases. These changes occur irrespective of $\lambda$ of the light and the initial concentration of U(VI). The ratio of the maximum U(V) concentration to the initial U(VI) concentration is about 0.16—0.19 in the initial U(VI) concentration range of $2\times10^{-3}$—$2\times10^{-1}$ M. The plot of log[U(VI)] vs. irradiation time before the appearance of $U^{IV}$ gives a first-order decay as shown in Fig. 7.

**Quantum Yields.** The quantum yield of U(V), $\Phi_V$, was measured to elucidate the photochemical reaction mechanism of $[UO_2(dmf)_5](ClO_4)_2$ in DMF and acetone. Table 1 shows the dependence of quantum yields on the absorbed light intensities, and indicates that the quantum yield does not depend on the absorbed light intensity. The quantum yield is also independent of the initial U(VI) concentration (Table 2). Additional experiments were carried out to investigate the depencence of the quantum yield on the DMF concentration, where the solution of $[UO_2(dmf)_5](ClO_4)_2$ dissolved in the mixture of acetone and DMF was used. As a milky precipitate which was readily soluble in perchloric acid was observed with irradiation and was supposed to be hydrolysis products or polymers of U(IV), perchloric acid was added to the solution in these experiments prior to irradiation. In the acetone-DMF mixture, where the concentration of DMF was over three times higher than that of the uranyl ion, the number of coordinated DMF molecules was determined to be five by the NMR method at −50 °C. As the

Table 3. Quantum Yield of U(IV) as a Function of DMF Concentration[a)]

| [DMF] / M | $\Phi_{IV}$ |
|---|---|
| 0.126 | 0.11±0.01 |
| 0.319 | 0.10±0.00 |
| 0.642 | 0.12±0.01 |
| 1.261 | 0.12±0.00 |

a) $[UO_2(dmf)_5^{2+}]=0.010\,M$, $[H^+]=0.023\,M$, $\lambda_{irr}=365$ nm, $T=25\,°C$.

Table 4. Quantum Yield of U(V) as a Function of Wavelength of Irradiating Light[a)]

| $\lambda_{irr}$ / nm | $\Phi_V$ |
|---|---|
| 313 | 0.26±0.01 |
| 334 | 0.28±0.02 |
| 365 | 0.31±0.01 |
| 436 | 0.31±0.01 |

a) $[UO_2(dmf)_5^{2+}]=0.010\,M$, $T=25\,°C$.

donicity of DMF is larger than those of acetone and water on the basis of Gutmann's donor number,[18,19)] the first-coordination sphere of the uranyl ion might be fully occupied by DMF even at 25 °C. The results are given as the quantum yield of U(IV) in Table 3. As the quantum yield of U(IV) in the photochemical reaction of the uranyl ion in acetone is less than $10^{-3}$ in this acid concentration range (ca. 0.02 M),[6)] the chemical path of the excited uranyl ion with acetone can be neglected. As is seen in Table 3, the quantum yield was independent of the DMF concentration. Table 4 shows the dependence of the quantum yield of U(V) on the wavelength of light.

**Luminescence Lifetime.** Measurements of the luminescence lifetime of 0.01 M $[UO_2(dmf)_5](ClO_4)_2$ in acetone containing 0.18 M DMF were not successful because the decay of luminescence was faster than the time resolution of the instrument (50 ns), and hence the lifetime of the excited uranyl complex was estimated to be less than 50 ns.

## Discussion

The absorption spectrum of U(V) obtained in this work is very similar to those produced by electrolysis of U(VI) in DMSO,[20)] and by reduction of U(VI) with Eu(II) in aqueous solution.[21)] However, it is very different in shape and peak position from the spectrum of U(V) in triethyl phosphate.[11)] The U(V) formed by photolysis of $[UO_2(dmf)_5](ClO_4)_2$ in DMF is very stable in oxygen- and acid-free solution in the dark, and did not disproportionate. Therefore, it is considered that $U^{IV}$ is produced by the light absorption of U(V). As no change occurs when U(V) is irradiated with light of $\lambda>520$ nm, U(V) presumably absorbs light of the charge-transfer band with short wavelength and is reduced to $U^{IV}$. The molar extinction coefficient of $U^{IV}$ at 657 nm was 50.0 $M^{-1}cm^{-1}$ when $U^{IV}$ is assumed to be a single species. The absorption spectrum of $U^{IV}$ is very similar to that of U(IV) except for its value of the molar extinction coefficient, which is about one third of U(IV). Long irradiation of the sample solution caused a remarkable increase in base line of the absorption spectrum, especially at a short-wavelength region. This might be due to the light scattering from colloidal particles. Cauzzo et al. suggested that U(V) was in a $UO_2^+$ form and $U^{IV}$ was in a $UO_2$ form in TEP.[11)] Gritzner and Selbin reported that a brown colloidal precipitate was $UO_2$ in DMSO.[20)] The $U^{IV}$ formed in DMF seems similar to those so far reported. Unfortunately, the colloidal precipitate could not be isolated by centrifugation.

**Mechanism.** The primary photochemical reactions can be expressed as follows:

$$UO_2L_5^{2+} \xrightarrow{h\nu} (UO_2L_5^{2+})^*, \tag{4}$$

$$(UO_2L_5^{2+})^* \longrightarrow UO_2L_4^+ + \cdot L + H^+, \tag{5}$$

or

$$(UO_2L_5^{2+})^* + L \longrightarrow UO_2L_5^+ + \cdot L + H^+, \tag{6}$$

where L and ·L represent DMF and $HCON(CH_3)CH_2\cdot$, respectively. Figure 7 supports the reaction path of Eqs. 5 or 6, and means that the following reaction path, if any, in which the excited uranyl ion reacts with a product (P), can be ignored.

$$(UO_2L_5^{2+})^* + P \longrightarrow UO_2L_n^+ + P' \tag{7}$$

As the quantum yield of U(V) is independent of the absorbed light intensity, it is reasonable to assume that U(V) is formed from $(UO_2L_5^{2+})^*$, which is represented by Eqs. 5 or 6. In addition, the following reaction seems to be negligible because the quantum yield of U(V) is less than unity.

$$UO_2L_5^{2+} + \cdot L \longrightarrow UO_2L_5^+ + \cdot L^+ \tag{8}$$

The ·L radical may disappear by radical recombination or self-decomposition.

On the assumption that the formation of U(V) occurs from $(UO_2L_5^{2+})^*$, and from the fact that the quantum yield is less than unity, one would expect that the deactivation path expressed by Eq. 9 would be operative.

$$(UO_2L_5^{2+})^* \xrightarrow{k_d} UO_2L_5^{2+} \tag{9}$$

This path may include the recombination in the solvent "cage".

$$(UO_2L_5^{2+})^* \xrightarrow{k_r} (UO_2L_4^+\cdots \cdot L\cdots H^+) \longrightarrow UO_2L_5^{2+} \tag{10}$$

The results in Table 2 suggest that the self-quenching of $(UO_2L_5^{2+})^*$, which was observed in TEP,[11] is negligible.

$$(UO_2L_5^{2+})^* + UO_2L_5^{2+} \longrightarrow 2UO_2L_5^{2+} \tag{11}$$

It is of great interest to clarify which path (Eqs. 5 or 6) being operative. As seen in Table 3, the quantum yield of U(IV) is independent of the DMF concentration, and the ESR spectrum of $[UO_2(dmf)_5](ClO_4)_2$ in acetone-$d_6$ irradiated at −170 °C gives the signal of $HCON(CH_3)CH_2\cdot$. These results might indicate that the uranyl ion directly reacts with the coordinated dmf, i.e. the photochemical reaction occurs by intramolecular reaction (Eq. 5). Miyake et al.[22] observed the ESR spectrum of U(V) in both photo- and electrolytic-reduction processes of $[UO_2(dmf)_5]^{2+}$ in DMF and found the stronger bond between uranium and oxygen in the equatorial plane than in the axial direction. This fact also supports the formation mechanism of U(V) by the intramolecular reaction.

As is shown in Fig. 1, the uranyl ion has a triplet state ($T_1$) around 426 nm and a charge transfer band (CT) at shorter wavelengths. The wavelength dependence of the quantum yield of U(V) indicates that the excitation to the triplet state of the uranyl ion gives better yield than that to the charge transfer band. This implies that the photochemical reaction occurs from the triplet state of the excited uranyl ion.

Since the recombination in the solvent cage usually decreases as the irradiation wavelength becomes shorter, it is expected that the quantum yield of U(V) increases. The results in Table 4 are not in accord with this expectation, and consequently suggest no appreciable recombination in the solvent cage.

The decrease in quantum yield at the charge transfer band suggests the presence of a nonradiative deactivation from the charge-transfer band, which results in a lowering of the quantum yield of intersystem crossing from CT to $T_1$.

From the above discussion, the photochemical reaction mechanism is described as follows:

$$UO_2(dmf)_5^{2+} \xrightarrow{h\nu} (UO_2(dmf)_5^{2+})^*, \tag{4'}$$

$$(UO_2(dmf)_5^{2+})^* \xrightarrow{k_1} UO_2(dmf)_4^{+} + HCON(CH_3)CH_2\cdot + H^+, \tag{5'}$$

$$\longrightarrow UO_2(dmf)_n^{+} + P,$$

$$(UO_2(dmf)_5^{2+})^* \xrightarrow{k_d} UO_2(dmf)_5^{2+}, \tag{9'}$$

where n is the number of coordinated dmf. The average value of the quantum yields in Table 1 and the relation, $\Phi_V = k_i/(k_i+k_d)$, give the value of $k_d/k_i = 2.2$. The energy level diagram is shown in Fig. 8, where ISC denotes the intersystem crossing ($\Phi < 1$) and $k_{dCT}$ is the deactivation rate constant from CT. In the photochemical reaction of $UO_2(NO_3)_2\cdot 2TEP$ in TEP, the ratio of the maximum concentration of U(V) to the initial concentration of U(VI) decreased as the initial U(VI) concentration increased, and it was suggested that the photoexcited U(V) disproportionated to give $U^{IV}$ and U(VI)[11]. However, the ratio is about constant at any initial concentration of U(VI) in DMF, and no disproportionation was observed.

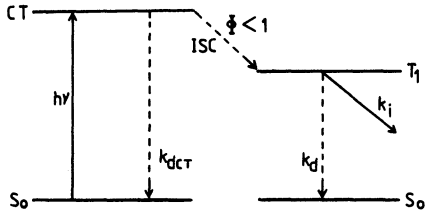

Fig. 8. Energy level diagram.

The photochemical reaction mechanism of $[UO_2(dmf)_5](ClO_4)_2$ in acetone is essentially the same as that in DMF except for the presence of the following luminescence path.

$$(UO_2(dmf)_5^{2+})^* \xrightarrow{k_1} UO_2(dmf)_5^{2+} + h\nu' \tag{12}$$

This might lead to the result that the quantum yield of U(V) in DMF is larger than that in acetone containing perchloric acid as is shown in Table 3, where $2\Phi_{IV}$ corresponds to $\Phi_V$. Since the lifetime of the excited uranyl complex ion was less than 50 ns as described above, the lower limit of the $k_i$ value is estimated to be $\approx 10^7\ s^{-1}$.

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1) For the sake of simplicity, the symbols of U(IV), U(V), and U(VI) are used for $U^{4+}$, $UO_2^+$, and $UO_2^{2+}$ respectively, unless otherwise noted, and $U^{IV}$ represents unidentified chemical species with 4+ oxidation state.

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