Deactivation Mechanism of Excited Uranium(VI) Complexes in Aqueous Solutions

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The rate of luminescence decay of various uranium(VI) complexes has been measured by a nitrogen laser photolysis method in aqueous solutions. It was found that the luminescence consisted of a short- and a long-lived component in aqueous solutions at pH > 3. These components were assigned as the emissions from excited aqua and hydrolysed ions, $*UO_2^{2^+}$ and $*(UO_2)_2(OH)_2^{2^+}$, for which the decay constants were defined as k_1 and k_2 , respectively. k_1 and k_2 were unaffected by either the concentration of U^{VI} ion or the pH. The quenching rate constant, k_q , of various U^{VI} complexes (fluoro, sulphato, phosphato complexes as well as aqua ones) was determined in aqueous solutions with various quenching anions, CI^- , Br^- , I^- and NCS⁻. The values of k_q were well correlated with the redox potentials of quenching anions. The mechanism of the quenching reaction was interpreted on the basis of a linear free-energy relationship.

The reactivities of excited U^{VI} ions have been studied extensively.¹⁻²¹ Matsushima et al. studied the quenching rate constants of uranyl luminescence with halogen and halogen-like anions from Stern-Volmer plots, and found that the quenching rate constants were related to the oxidation potentials of quenchers.¹ Ikeda and co-workers determined the quenching rate constants from direct lifetime measurements of uranyl luminescence and concluded that an electrontransfer process played an important role for the quenching.4,5 They also found that the luminescence lifetime increased with the addition of fluoride, phosphate and sulphate ions. On the other hand, interest has been expressed in the non-exponential decay of uranyl luminescence in aqueous solutions. Marcantonatos explained that the short- and longlived luminescences were attributed to emissions from the excited uranyl aqua ion and from an exciplex which was formed by the interaction of the excited uranyl ion with the ground-state uranyl ion.⁷⁻¹⁰ A similar dual luminescence was also reported by Formosinho and co-workers in a series of papers.¹¹⁻¹⁶ They interpreted this phenomenon in terms of a mechanism involving a reversible crossing process between two different excited uranyl states.

In spite of the high number of earlier studies, the deactivation mechanism of the excited uranyl ion remains uncertain. This paper presents the results of the detailed analysis of uranyl luminescence decay in aqueous solutions for a better understanding of the deactivation mechanism.

Experimental

A stock solution of uranyl perchlorate was prepared by the following procedure. Uranyl nitrate, which was recrystallized twice from distilled water, was dissolved in distilled water and mixed with hydrogen peroxide. The resulting precipitate was filtered after washing several times with distilled water and dried by heating for 4 h at 200 °C and another 8 h at 400 °C. Uranyl trioxide formed by this procedure gave uranyl perchlorate by reacting with 70% perchloric acid. Sodium perchlorate was prepared by recrystallizing reagent-grade sodium perchlorate (Wako Pure Chemical Ind., Ltd.) from distilled water. All other chemicals were reagent grade (Wako). A Toa IM-20E pH meter was used for pH measurements by using standard buffer solutions at pH > 2. However, for pH < 2, the pH meter readings were calibrated to give $-\log[H^+]$, where H^+ represented hydrogen-ion concentration, by using standard $HClO_4$ solutions. Decay rates of uranyl luminescence were measured using a nitrogen laser (Molectron UV-22), photomultiplier (Hamamatsu Photonics R1509), and digital memory (Iwatsu DM-2350), which was connected to a personal computer (NEC PC-9801). A Hitachi model 850 fluorescence spectrophotometer was used to record luminescence spectra. The ionic strength was kept at 3.0 mol dm⁻³ by using sodium perchlorate.

Results

Luminescence in Aqueous Solutions

Fig. 1 shows the emission spectra of uranyl ions in aqueous solution measured at various pHs from 2.0 to 3.6. The intensity of the spectra increases markedly with increasing pH and the major peaks shift to higher wavelengths especially for a pH > 3.0; no appreciable change was observed at pH < 2.0. This spectral change correlates well with the formation of hydrolysed species, $(UO_2)_2(OH)_2^{2+}$, which will be abbreviated as (2,2) hereafter.²² Therefore, it is reasonable to conclude that the spectrum at pH = 2.0 corresponds to the spectrum of aqua ion UO_2^{2+} and the spectrum at pH = 3.6 is mainly attributed to that of (2,2). The spectrum at 3.0 represents a combination of these two components. Fig. 2 and 3 show time-resolved luminescence spectra at pH = 1.9 and 3.0, respectively. In fig. 2, the intensity decreases simply with increasing time, while in fig. 3, the major peaks shift to higher wavelength and the spectrum tends to be similar to the emission spectrum at pH 3.0 in fig. 1. The results clearly indicate that the luminescence at pH 3.0 consists of two components with different lifetimes, where the short-lived component corresponds to the emission from the excited aqua ion, $*UO_2^{2+}$. and the long-lived one to the emission from the excited hydrolysed species *(2,2), resulting in the dual exponential decay of uranyl luminescence. As expected from these results, a single exponential decay was observed in highly acidic solutions, i.e. at pH 1.2 (fig. 4).

The decay of uranyl luminescence in aqueous solutions is analysed by the following equation with respect to the luminescence intensity:

$$I = I_{01} \exp(-k_1 t) + I_{02} \exp(-k_2 t)$$
(1)

where I_{01} and I_{02} refer to luminescence intensities at time = 0, and k_1 and k_2 are the decay constants of $*UO_2^{2^+}$ and *(2,2), respectively. The values of k_1 and k_2 were determined





Fig. 1. Emission spectra of uranyl ion in acidic perchlorate solutions as a function of pH. $[UO_2^{2^+}]_t = 0.01 \text{ mol } dm^{-3}$, ionic strength = 3.0 and 25 °C.

by means of non-linear least-squares method. Experiments were carried out under various conditions and typical data are listed in table 1 together with those reported in earlier papers. k_1 and k_2 were determined in the pH range 3.0-3.5 and both were independent of pH, their average values being $(5.8 \pm 0.3) \times 10^5$ and $(1.3 \pm 0.2) \times 10^5$ s⁻¹, respectively. These values were not affected by the change in total uranyl



Fig. 2. Time-resolved emission spectra of uranyl ion at pH = 1.9, $[UO_2^{2^+}]_i = 0.01$ mol dm⁻³, ionic strength = 3.0, and at 25 °C.



Fig. 3. Time-resolved emission spectra of uranyl ion at pH = 3.0, $[UO_2^{2^+}]_1 = 0.01 \text{ mol } dm^{-3}$, ionic strength = 3.0, and at 25 °C.

concentrations $[UO_2^{2^+}]_t$ from 0.008 to 0.02 mol dm⁻³. k_1 remained constant with $[UO_2^{2^+}]_t$ at low pH, *i.e.* $k_1 = (5.4 \pm 0.3) \times 10^5 \text{ s}^{-1}$ under the following conditions: 1.0×10^{-2} mol dm⁻³ < $[UO_2^{2^+}]_t < 3.5 \times 10^{-2}$ mol dm⁻³ at pH 1.2 and 25 °C, where k_1 was determined from a single exponential decay curve. Little effect of ionic strength on k_1 and k_2 was observed.

The decay constants for $(UO_2^{2^+})$ and (2,2) in the presence of quenchers, k_1 and k_2 , respectively, are related to the following equation:

$$k_i = k_{0i} + k_{qi}[Q] \tag{2}$$

where *i* can be 1 or 2, [Q] is the concentration of quenchers, and k_{0i} is the decay constant in the absence of quenchers. In fig. 5 and 6, $k_i - k_{0i}$ are plotted against [Q]. The linear plots give k_{qi} , which are listed in table 2 together with the k_{q1} values of Ikeda and co-workers.⁴

Luminescence of Uranyl Complexes

The decay constants of uranyl luminescence in a variety of solutions including fluoride, sulphate and phosphate ions were determined in the absence (k_0) and the presence (k_i) of

Table 1. Luminescence decay constants k_1 and k_2 in aqueous solutions at 25 °C

$[UO_2^{2^+}]_{l/mol dm^{-3}}$	pН	ionic strength	$k_1/10^5 \mathrm{s}^{-1}$	$k_2/10^5 \text{ s}^{-1}$	ref.
0.01	1.0	1.0	4.2	_	5
0.08	1.9	0.3	7.7	1.9	7
0.01	3.0	_	7.4	1.2	11
0.2	0.7		4.5		20
0.01	3.0	3.0	5.8	1.3	this work
0.01	2.0	3.0	5.4		this work
0.01	1.0	3.0	5.2	—	this work

20.0

J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86



Fig. 4. Luminescence decay in an acidic solution. (a) Luminescence intensity, *I*, versus time, the solid line being a non-linear least-squares fit of experimental data to a single exponential function, and the errors are shown in (b); (c) a plot of ln *I versus* time. The experiment was carried out at 25 °C and under the conditions pH = 1.2, $[UO_2^{2^+}]_t = 0.01 \text{ mol dm}^{-3}$, ionic strength = 3.0.

quenchers. The values of k_0 are summarized in table 3 together with data reported in earlier papers. From the stability constants²³ reported the major uranyl species are considered to be $UO_2F_4^{2-}$, UO_2SO_4 and $UO_2(H_2PO_4)_2$ under

the present conditions. The quenching rate constants (k_q) for these complexes are listed in table 4. As fig. 7 shows, the k_q values for $UO_2^{2^+}$, (2,2) and $UO_2F_4^{2^-}$ correlated well with the redox potentials of quenching anions E_0 ($X_2 + 2e^- \rightleftharpoons 2X^-$).



Fig. 5. Plots of $k_1 - k_{01}$ versus the concentration of various quenchers under the conditions: pH = 1.2, $[UO_2^{2^+}]_1 = 0.01 \text{ mol } dm^{-3}$, ionic strength = 3.0, temp. = 25 °C. (×) 1⁻, (\Box) SCN⁻, (Δ) Br⁻, (\bigcirc) Cl⁻.



Fig. 6. Plots of $k_2 - k_{02}$ versus the concentrations of various quenchers under the conditions: pH = 3.4, $[UO_2^{2^+}]_t = 0.01 \text{ mol } dm^{-3}$, ionic strength = 3.0 and temp. = 25 °C. (×) I⁻, (□) SCN⁻, (△) Br⁻, (○) Cl⁻.

Table 2. Quenching rate constants for $UO_2^{2+}(k_{q1})$ and for $UO_2(OH)_2^{2+}(k_{q2})$ with anions (X⁻)

quencher	conditions	$k_{q1}/10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_{q2}/10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	ref.
Cl-	$HClO_4$, 1 mol dm ⁻³	1.7		4
	pH 3.4, NaClO ₄ , 3 mol dm ^{-3}	1.8	0.22	this work
Br ⁻	$HClO_4$, 1 mol dm ⁻³	4.8	_	4
	pH 3.4, NaClO ₄ , 3 mol dm ^{-3}	4.1	2.2	this work
I -	$HClO_4$, 1 mol dm ⁻³	6.9		4
	pH 3.4, NaClO ₄ , 3 mol dm ^{-3}	6.2	5.8	this work
SCN ⁻	pH 3.4, NaClO ₄ , 3 mol dm ^{-3}	4.8	4.1	this work

 $[UO_2^{2^+}]_t = 0.01 \text{ mol } dm^{-3} \text{ and } 25 \,^{\circ}\text{C}.$

J. CHE	M. SOC.	FARADAY	TRANS.,	1990,	VOL.	86
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Table 3. Luminescence decay constant k_0 in the presence of fluoride, phosphate and sulphate ions at 25 °C

ref.	$k_0/10^3 \text{ s}^{-1}$	ionic strength	pH	$[UO_2^{2+}]/mol dm^{-3}$	amount of salt/mol dm ⁻³
			NaF		
5	6.7	1.0	1.0	0.01	1.0
20	11.5		$[HClO_{4}] = 0.22 \text{ mol } dm^{-3}$	0.2	1.9
this work	5.6	3.0	2.0	0.01	0.12
			H ₁ PO ₄		
5	5.3		3 4	0.01	1.0
5	5.3		$[HClO_{4}] = 1 \text{ mol } dm^{-3}$	0.01	1.0
this work	6.9	1.0	$[HClO_{4}] = 0.1 \text{ mol } dm^{-3}$	0.01	1.2
21	33		- +3	0.02	2.0
20	12.3			0.2	
			Na ₂ SO ₄		
5	270		1.0	0.01	0.02
5	88		1.0	0.01	0.5
this work	210	3.0	1.0	0.01	0.02
			H₂SO₄		
20	70.9		- +		0.2

Discussion

The biexponential decay of uranyl luminescence has been discussed extensively by Marcantonatos *et al.*,^{8,9} and Formosinho *et al.*¹¹⁻¹⁶ Marcantonatos interpreted the dual



Fig. 7. Plots of log k_q versus the oxidation potential (E₀) of quenchers for various uranyl complexes: (\bigcirc) UO₂(aq)²⁺; (\triangle) (UO₂)₂(OH)²⁺₂; (\square) UO₂F²⁻₄.

luminescence of the uranyl ion in terms of a mechanism involving an exciplex, which was formed by the following reaction:

$$*UO_2^{2^+} + H_2O \rightleftharpoons *UO_2H^{2^+} + OH$$

*UO₂H²⁺ + UO₂²⁺ ⇒ *U₂O₄H⁴⁺.

This mechanism was based on the experimental results as follows: (1) the emission spectrum obtained with different time windows exhibited a bathochromic shift (ca. 60 cm⁻¹ at wavelengths < 520 nm and 200 cm⁻¹ at ca. 520 nm); (2) the luminescence decay was biexponential in high concentrations of uranyl ion $([UO_2^{2+}] = 0.06-0.1 \text{ mol } dm^{-3})$, but monoexponential at low concentration $([UO_2^{2^+}] = 0.003 \text{ mol})$ dm^{-3}). This biexponential decay was observed at low pH (1.2), where the formation of hydrolysed species in the ground-state was excluded. Our experimental results are basically similar to those of Marcantonatos. The bathochromic shift is seen in the resolved emission spectra (fig. 3), but this shift is *ca.* 300 cm⁻¹ over the entire range. The biexponential behaviour was also marked at higher uranyl ion concentrations. However, the data at low pH differ significantly from those of Marcantonatos. Fig. 4 clearly shows that the decay is mono-exponential at pH 1.2 unlike the result of Marcantonatos obtained under the same conditions. In fact, the biexponential decay was not observed at pH < 2.0 in the present experiments. Formosinho et al. proposed a model involving a reversible crossing between two excited states, excited aqua ion, *U, and another excited state, *X, as follows:

Table 4. Quenening face constants κ_n of various drany complexe	Table 4.	Quenching rate constants k_a	of various urany	complexes
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1			$k_q/10^9 \text{ dm}^3$	$mol^{-1} s^{-1}$		
(complex)	$[UO_2^{2^+}]/mol dm^{-3}$	C1-	Br ⁻	Ι-	SCN ⁻	ref.
NaF 0.12 mol dm ⁻³ + NaClO ₄ 1 mol dm ⁻³ $[UO_2F_2^2]$	0.01	0.018	0.89	3.0	1.9	this work
$H_{1}PO_{1}$ mol dm ⁻³	0.01	0.08	0.85	2.1	_	4
$H_{3}^{3}PO_{4}^{7}$ 1.2 mol dm ⁻³ + NaClO ₄ 1 mol dm ⁻³ [UO ₂ (H ₂ PO ₄) ₂]	0.01	0.045	0.85	2.0	1.6	this work
$Na_2SO_4 0.02 \text{ mol } dm^{-3}$ + $NaClO_4 1 \text{ mol } dm^{-3}$ $[UO_2SO_4]$	0.01	0.38	2.5	4.6	3.8	this work

59

J. CHEM. SOC. FARADAY TRANS., 1990, VOL. 86

$$\stackrel{*\mathrm{U}}{\longleftarrow} \stackrel{k_{\mathrm{i}}}{\underset{k_{\mathrm{u}}}{\longleftarrow}} \stackrel{*\mathrm{X}}{\underset{k_{\mathrm{u}}}{\longleftarrow}} \stackrel{*\mathrm{X}}{\underset{k_{\mathrm{u}}}{\longleftarrow}}$$

Although this is a unique model and the mathematical treatment certainly leads to a biexponential function with time, the existence of *X, which undergoes the same slow reversible crossing with time as that of the decay rate of *U, has not been confirmed. Furthermore, we cannot obtain the same results in fundamental data with respect to the dependences of k_1 and k_2 on pH and uranyl concentrations.

We have concluded that the dual luminescence is attributed to the emission from the excited aqua ion $*UO_2^{2+}$ and excited hydrolysed species *(2,2). In our recent ¹⁷O NMR studies on the uranyl ion, the ¹⁷O resonance of uranyl oxygen atoms, which was a single Lorentzian curve in strongly acidic solutions, revealed two distinct peaks at a $pH > 3.^{22,24}$ These two peaks were assigned to UO_2^{2+} and (2,2), respectively, and the rate constants for the change between these species were determined to be 59.3 and 93.8 s^{-1} at a pH 3.15 for the forward and reverse processes, respectively. Since the above exchange is much slower than the luminescence decay, the species UO_2^{2+} and (2,2) can be considered to exist independently within the timescale of uranyl luminescence. The relatively slower decay of the luminescence of (2,2) compared with that of aqua ion could result from the slow exchange rate between these excited states * UO_2^{2+} and *(2,2). This is justified by the fact the decay of the luminescence of $UO_2F_4^{2-}$ is nearly 100 times slower than that of an aqua ion (table 3), indicating that the ligand exchange in $*UO_2F_4^{2-}$ should be slow compared with the timescale of its luminescence decay.

The quenching of uranyl luminescence is of particular interest and many studies have been performed. The quenching rate constants reported by Ikeda and co-workers⁴ agree with the present results (tables 2 and 3) and their proposed mechanism involving electron transfer between excited uranyl ions and quenchers seems to be reasonable. For a deeper understanding of quenching reactions, the analysis of experimental results was performed in more detail. Fig. 8 represents plots of log k_q obtained for the various complexes versus log k_0 . As seen in fig. 8, the plots are linear for each

Fig. 8. Plots of $\log k_q$ versus uranyl complexes. k_q was determined for the following quenchers: (\times) I⁻, (\Box) SCN⁻, (\triangle) Br⁻, (\bigcirc) Cl⁻. A, $UO_2^{2^+}$; B, UO_2SO_4 ; C, $(UO_2)_2(OH)_2^{2^+}$; D, $UO_2(H_2PO_4)_2$; E, $UO_2F_4^{2^-}$.

quencher and all lines join at one point. This is explained well in terms of a linear free-energy relationship.²⁵ In the absence of quenchers, the decay of excited uranyl complexes $UO_2(L)$, where L denotes a ligand such as H_2O or F^- , can be described by

*UO₂(L)
$$\stackrel{\kappa_0}{\longrightarrow}$$
 UO₂(L) (3)

and the corresponding energy diagram is shown below.



The linear free-energy relationship leads to the equation:

$$\Delta G_0^*(\mathbf{L}) = \Delta G_{\mathbf{E}}^* + a \Delta G(\mathbf{L}) \tag{4}$$

where $\Delta G_0^*(L)$ is the free energy of activation of reaction (3), ΔG_E^* is the free energy of activation for an excited complex, *UO₂(E), which is in the hypothetically highest energy state), $\Delta G(L)$ is the difference of free energies between *UO₂(L) and *UO₂(E), and *a* is a constant. In solutions containing quenching anions X⁻, the reaction can be expressed by

*UO₂(L) + X⁻
$$\xrightarrow{k_q}$$
 UO₂(L) + X⁻ (5)

leading to the equation:

$$\Delta G_{\mathbf{q}}^{*}(\mathbf{L}) = \Delta G_{\mathbf{q}}^{*} + b_{\mathbf{x}} \Delta G(\mathbf{L})$$
(6)

where $\Delta G_q^*(L)$ is the free energy of activation of reaction (5), ΔG_q^* the free energy of activation for the quenching reaction of *UO₂(E) and b_x refers to a constant, which differs as a function of quenchers. Elimination of $\Delta G(L)$ from eqn (4) and (6) gives the following equation

$$\Delta G_{\mathbf{q}}^{*}(\mathbf{L}) = (b_{\mathbf{x}}/a)\Delta G_{\mathbf{0}}^{*}(\mathbf{L}) + \text{constant}$$
(7)
constant = $\Delta G_{\mathbf{q}}^{*} - (b_{\mathbf{x}}/a)\Delta G_{\mathbf{E}}^{*}.$

Eqn (7) is consistent with

$$\ln k_a = (b_r/a)\ln k_0 + \text{constant}$$
(8)

which is demonstrated in fig. 8. The point in this figure where all the lines cross (we call this point an isoquenching point) gives the maximum decay constant, which might be attributed to the decay of *UO₂(E), where a = b = 0, and ΔG_a^* and ΔG_a^* would have minimum values.

The question arises as to how the excited uranyl ion is deactivated in the absence of quenchers. Formosinho and Miguel suggested that the reversible crossing¹³ was attributed to water exchange²⁶ in excited uranyl ions. The water exchange might possibly deactivate the excited uranyl ion. As a matter of fact, the coordination of a stable ligand such as F^- prohibits the approach of water molecules to the first coordination sphere. However, a chemical process between $*UO_2^{2^+}$ and H_2O cannot be ruled out in view of the fact that



ozone, whose oxidation potential (2.07 V) is smaller than the estimated value (2.5 V) for $*UO_2^{2^+}$, reacts with H_2O or OH^- forming a variety of radicals.²⁷

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