includes the estimate from the value of the scavenging ratio. An average of 3.0 kcal mol^{-1} would lie within both experimental error limits. We now, of course, have a kinetic estimate of the W–S bond energy as $\leq$3.9 kcal mol^{-1}.

We turn finally to the detailed nature of the primary photostep (2). This could consist of reaction 1 followed by rapid solvent coordination, but, if so, the $M(CO)_5$ species of reaction 1 cannot be the same as that of reaction 3, in view of the analysis around eq 8. A defensible possibility is that the former species is C_{4v} while the latter one is D_{3h}. Alternatively and perhaps indistinguishably, reaction 1 could be concerted. Yet another possibility, suggested by ligand field analysis of the d^6 case by Vanquickenborne and Ceulemans[28] (see also ref 29), is that the immediate product of reaction 1 is an excited-state C_{4v} species, which relaxes to ground-state C_{4v} and coordinates solvent. Our intermediate of reaction 3 would again be the D_{3h} species. The lifetime of an excited-state C_{4v} complex must be short, however, since we see no indication of its presence either in emission or in transient absorption. It seems more reasonable to expect the relatively long-lived intermediate to be D_{3h} rather than C_{4v} though one could interchange the C_{4v} and D_{3h} designations in the above discussion (see ref 30 and 31).

Acknowledgment. This investigation was supported in part by a contract with the U.S. Office of Naval Research.

Registry No. $W(CO)_6$, 14040-11-0; 4-acetylpyridine, 1122-54-9; methylcyclohexane, 108-87-2.

---

(28) Vanquickenborne, L. G.; Ceulemans, A. *Inorg. Chem.* **1978**, *17*, 2730.

(29) Petersen, J. D.; Jakse, F. P. *Inorg. Chem.* **1979**, *18*, 1818.

(30) Burdett, J. K.; Grzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147.

(31) Hay, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 2411.

Contribution from the Department of Chemistry,
The University of West Florida, Pensacola, Florida 32504

Energy Transfer between Uranyl(VI) and Europium(III) in Aqueous Perchlorate Solution

STEPHEN P. TANNER* and ADELIA R. VARGENAS

Received July 8, 1980

Fluorescence measurements on aqueous solutions containing uranyl(VI) and europium(III) perchlorates have shown that energy transfer from uranyl to europium is pH dependent. The uranyl species involved is not the UO_2^{2+} ion itself but one or more of the hydrolytic species. Emission spectra of the europium ion in the presence of uranyl indicate the formation of a complex between the lanthanide ion and the hydrolyzed uranyl species. The relative intensities of the europium emission lines, the energy-transfer efficiency, and the dependence of energy transfer on concentrations are all consistent with a mechanism which involves this complex.

Introduction

Fluorescence spectra and lifetime measurements are finding increasing use in probing the environment of lanthanide ions.[1-3] The variation in the relative intensities of the various emission lines and the fluorescence lifetimes of europium(III) in aqueous solution have provided information on the interaction between Eu^{3+} and ClO_4^- and NO_3^-.[2] An earlier fluorescence study in this laboratory[4] demonstrated that energy transfer between *o*-benzoyl benzoate and Eu^{3+} in ethanol/water solution involved the formation of a complex. Relative intensities of europium(III) emission lines and equilibrium constant determinations provided evidence for inner-sphere interaction. These results suggested that energy transfer from other potential donors to Eu(III) in solution may take place by a similar mechanism. The work reported in this paper involves energy transfer between the positively charged species uranyl(VI) and Eu(III).

The U(IV)–Eu(III) system has been studied previously in a variety of media.[5,6] There are, however, several factors which complicate the interpretation of the results. The anions present in solution, nitrate, formate, and acetate, form complexes with both Eu(III) and uranyl.[7-9] Also, the lack of information on the pH of the solutions leaves in doubt the nature of the uranyl species present. It was generally assumed that the UO_2^{2+} ion was the absorbing and donor species, yet in aqueous solution this ion exists in appreciable concentration only under relatively acidic conditions. At higher pH's dimeric and polymeric hydrolysis species are the dominant forms.[10,11] The work described in this paper was carried out in perchlorate solution to reduce complex formation, and the pH of the solutions was carefully measured. So that the fluorescence intensities could be enhanced, D_2O was used as solvent.[12]

Experimental Section

Preparation of Solutions. Europium perchlorate solutions were prepared by dissolving 99.99% Eu_2O_3 (Michigan Chemical Co.) in excess perchloric acid. Excess acid was removed by evaporating almost to dryness and then redissolving in distilled H_2O. The process was repeated several times until the acid concentration was reduced. Finally, $Eu(ClO_4)_3$ was dissolved in D_2O and evaporated almost to dryness before being dissolved in D_2O and brought up to a known volume. The concentration was checked by passing samples through a cation-exchange column and titrating the liberated acid.

Uranyl perchlorate solutions were prepared by ion exchange of uranyl acetate solutions. An exchange column of Dowex 1 × 10 anion-exchange resin was converted to the perchlorate form by passing

---

(1) Giuliani, J. F.; Donohue, T. *Inorg. Chem.* **1978**, *17*, 1090.

(2) Bünzli, J. C. G.; Yersin, J. R. *Inorg. Chem.* **1979**, *18*, 605.

(3) Horrocks, W. D., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334.

(4) Tanner, S. P.; Thomas, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 706.

(5) Kropp, J. L. *J. Chem. Phys.* **1967**, *46*, 843.

(6) Joshi, B. D.; Dalvi, A. G. I.; Bangia, T. R. *J. Lumin.* **1975**, *10*, 261.

(7) Ahrland, S. *Acta Chem. Scand.* **1951**, *5*, 199.

(8) Ramamoorthy, S.; Santappa, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 411.

(9) Day, R. A., Jr.; Wilhite, R. N.; Hamilton, F. D. *J. Am. Chem. Soc.* **1955**, *77*, 3180.

(10) Rush, R. M.; Johnson, J. S.; Kraus, K. A. *Inorg. Chem.* **1962**, *1*, 378.

(11) Rush, R. M.; Johnson, J. S. *J. Phys. Chem.* **1963**, *67*, 821.

(12) Kropp, J. L.; Windsor, M. W. *J. Chem. Phys.* **1965**, *42*, 1599.

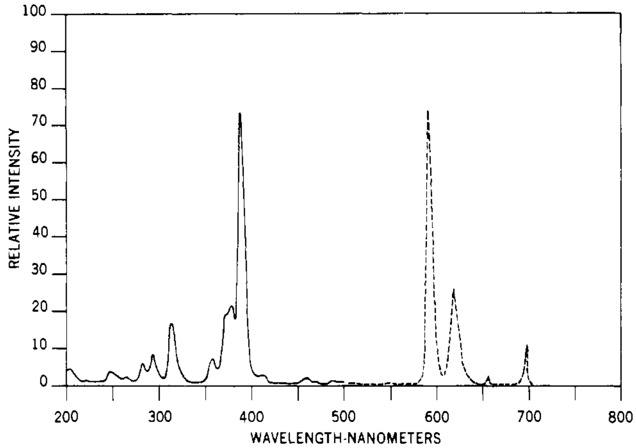

Figure 1. Excitation and emission spectra of 0.1 M europium(III) perchlorate in D_2O: $\lambda_{ex} = 392$ nm, $\lambda_{em} = 590$ nm (ex = excitation, em = emission).

4 M $HClO_4$ through the chloride form until all the chloride was exchanged. After being washed with distilled water, the column was finally washed and filled with D_2O. A solution of known concentration of ACS-grade uranyl acetate in D_2O was passed through the column, which was washed carefully with D_2O, and the eluant was brought to a known volume. Sodium (ethylenediaminetetraacetato)europate(III) was prepared by the literature procedure[13] and recrystallized from D_2O.

Spectral and pH Measurements. Fluorescence spectra were measured on an Aminco-Bowman spectrophotofluorometer with a photomultiplier tube with an S-20 response. The slits for both excitation and emission were set such that further reduction did not improve the resolution of the europium excitation or emission spectra. Absorption spectra were measured on a Cary 15 recording spectrophotometer, and pH measurements were made on a Corning Model 112 pH meter standardized with a phthalate buffer. So that precipitation of $KClO_4$ at the calomel electrode junction could be avoided, a sodium sulfate salt bridge was used. The pH's of the solutions were adjusted by adding perchloric acid (concentrated $HClO_4$ diluted with D_2O) and a solution of solid NaOH dissolved in D_2O. The small fraction of protons in these solutions did not significantly change the solvent composition of the final solutions. Except where noted, all measurements were made at room temperature.

Results and Discussion

The excitation and emission spectra (Figure 1) of the europium ion in aqueous perchlorate are unchanged over the pH range of 0–6. The corresponding spectra of uranyl perchlorate vary considerably with pH as the relative concentrations of the different hydrolic species change. The spectra are shown in Figure 2. The intensity of the emission increases by a factor of approximately 20 as the pH increases from 0.64 to 4.0, while the vibrational fine structure becomes less resolved. The change in the fluorescence spectrum with pH is similar to that of the absorption spectrum which also shows a lower resolution and an increase in intensity as the pH increases.[14]

Excitation and emission spectra of solutions containing both uranyl and europium perchlorate are given in Figure 3. At the higher pH's, it is evident that energy transfer from uranyl to Eu^{3+} takes place efficiently. The excitation spectrum for the $^5D_0 \rightarrow {}^7F_1$ Eu^{3+} emission line at 590 nm is very similar to that for uranyl emission except for the sharp peak at 392 nm which is due to direct excitation of Eu^{3+}. As the pH is lowered to 2.84, the excitation spectrum of the Eu^{3+} emission is little different from that expected for direct excitation. With the excitation wavelength at 347 nm, the intensity of the europium emission is lower by a factor of about 100 compared to that in a similar solution at pH 3.87. In 0.1 M acid solution, there is no evidence that energy transfer takes place, and the excitation and emission spectra are almost identical with those shown in Figure 1.

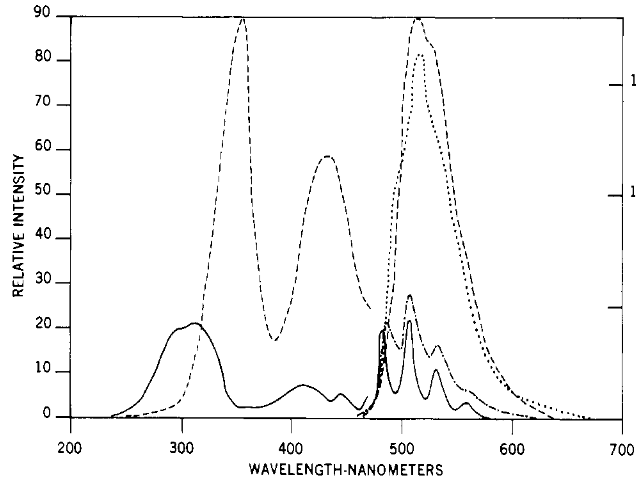

Figure 2. Excitation and emission spectra of 0.05 M uranyl(VI) perchlorate in D_2O: ---, pH 4.01 (left-hand scale); ···, pH 3.32 (right-hand scale); –·–, pH 2.56 (right-hand scale); —, pH 0.64 (right-hand scale).

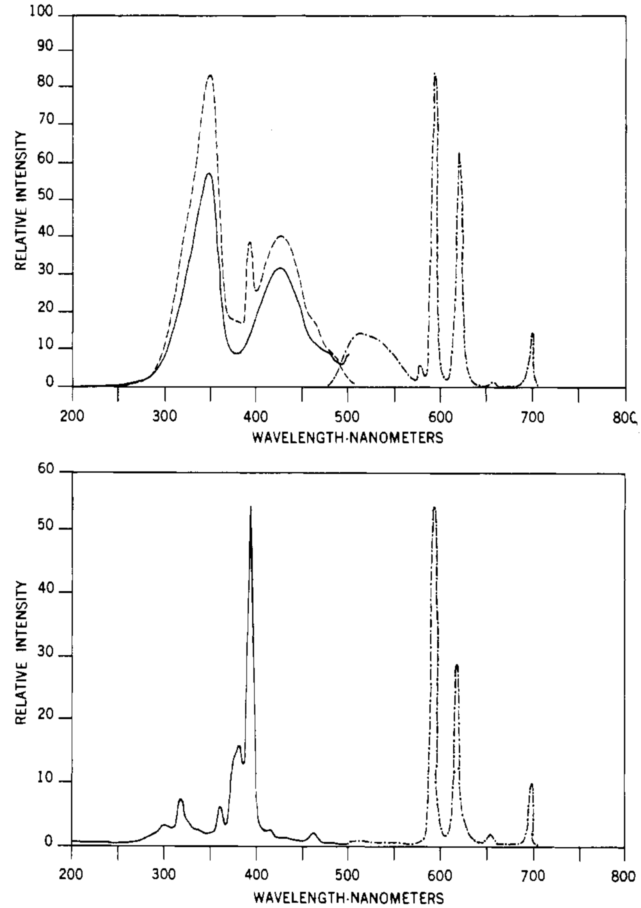

Figure 3. Excitation and emission spectra of D_2O solutions of 0.05 M uranyl perchlorate and 0.05 M europium perchlorate. Top (pH 3.87): –·–, emission spectrum with $\lambda_{ex} = 347$ nm; ---, excitation spectrum of $\lambda_{em} = 590$ nm; —, excitation spectrum of $\lambda_{em} = 515$ nm (not on same scale). Bottom (pH 2.84): –·–, emission spectrum with $\lambda_{ex} = 392$ nm; —, excitation spectrum of $\lambda_{em} = 590$ nm.

The dependence of the energy transfer on the pH of the solution indicates that the nature of the uranyl species is important. The hydrolysis of UO_2^{2+} has been studied extensively by a variety of procedures. The major species proposed are

---

(13) Moeller, T.; Moss, F. A. J.; Marshall, R. H. *J. Am. Chem. Soc.* **1955**, *77*, 3182.

(14) Bell, J. T.; Biggers, R. E. *J. Mol. Spectrosc.* **1967**, *22*, 262.

Table I. Emission Intensities[a] (Arbitrary Units)

$[Eu^{3+}]$, M	$I_{UO_2^{2+}}$ (515 nm)	$I_{Eu^{3+}}$[b] (590 nm)	$I_{Eu^{3+}}$[b] (615 nm)	I_{590}/I_{615}
0.00	13.3			
0.010	12.9	3.6	3.3	1.09
0.020	11.9	5.4	5.0	1.08
0.040	10.2	10.3	8.9	1.16
0.060	9.4	13.7	11.2	1.22
0.080	8.8	15.4	12.2	1.26
0.100	8.0	15.9	12.0	1.33

[a] $[UO_2^{2+}] = 0.050$ M, pH 3.75, $\lambda_{ex} = 347$ nm. [b] Corrected for emission due to UO_2^{2+}.

UO_2^{2+}, $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$. On the basis of published values of stability constants,[10] the concentrations of these species at pH 3.87 and 2.84 in solutions containing a total uranyl concentration of 0.05 M, corresponding to solutions used for the fluorescence measurements are as follows: pH 3.87, $[UO_2^{2+}] = 1.6 \times 10^{-2}$, $[UO_2(OH)^+] = 2 \times 10^{-3}$, $[(UO_2)_2(OH)_2^{2+}] = 1.4 \times 10^{-2}$, $[(UO_2)_3(OH)_5^+] = 2 \times 10^{-3}$; pH 2.84, $[UO_2^{2+}] = 4.8 \times 10^{-2}$, $[(UO_2)(OH)^+] = 5 \times 10^{-4}$, $[(UO_2)_2(OH)_2^{2+}] = 1.0 \times 10^{-3}$, $[(UO_2)_3(OH)_5^+] = 4 \times 10^{-7}$.

At lower pH's the concentrations of the hydrolic species are further suppressed. It is evident that UO_2^{2+} is a minor contributor in the energy-transfer process. The species taking part could be $(UO_2)_2(OH)_2^{2+}$, or several hydrolytic species may be involved.

Changes in the relative intensities of the emission lines of Eu(III) on addition of uranyl provide evidence for interaction between the two species. In the absence of uranyl, the relative intensities of the principle emission lines of Eu^{3+} at 590 nm ($^5D_0 \rightarrow {}^7F_1$) and 615 nm ($^5D_0 \rightarrow {}^7F_2$) are unchanged over the pH range of 0–6.8. With uranyl present the intensity of the $^5D_0 \rightarrow {}^7F_2$ emission line increases relative to that of $^5D_0 \rightarrow {}^7F_1$. This increase becomes more pronounced as the pH of the solutions is raised and the energy-transfer efficiency increases. Thus it appears that energy transfer between uranyl and europium involves the formation of a complex between the europium ion and hydrolytic uranyl species. In acid solution the relative intensities of the two Eu^{3+} emission lines are essentially unchanged by the addition of uranyl. As noted earlier, no energy transfer can be detected under acidic conditions.

Energy transfer takes place efficiently in Eu^{III}/U^{VI} solutions frozen to liquid-nitrogen temperatures. This contrasts with the behavior observed for Tb^{III}/Eu^{III}/malic acid systems for which dynamic collision mechanisms[17] are proposed. For a complex formation mechanism the continued existence of the complex in the glassy state facilitates energy transfer.

Solutions containing uranyl and the europium(III) EDTA complex, in D_2O and at pH 3.75, were also investigated. In these systems energy transfer between uranyl and Eu(III) is negligible. Since a precipitate forms after a few hours and on exposure to light, all solutions were freshly prepared and were exposed to the excitation source for the minimum time. The absence of energy transfer to Eu(III) complexed by EDTA lends further support to the suggestion that close interaction between Eu(III) and the excited uranyl species is required.

A series of measurements was made on solutions at pH 3.75 in which the uranyl concentration was held constant while the $[Eu^{III}]$ was varied from 0.01 to 0.10 M. (See Table I.) As the ratio of [uranyl]/[europium] changes, the relative intensities of the europium emission lines also change, in a manner consistent with association between the hydrolyzed uranyl species and europium(III). The relative intensity is the same whether the excitation wavelength is set at 347 nm for maximum energy transfer or at $\lambda = 392$ for maximum direct excitation of europium and depends only on the [uranyl]/[europium] ratio and the pH. This is expected since for Eu(III) the rate of ligand exchange[15,16] is several orders of magnitude greater than the rate of luminescence decay.[3]

As in the earlier work of Kropp,[5] the quenching of the uranyl emission by europium satisfies the Stern–Volmer equation $I_0/I = 1 + K[Eu^{3+}]$, where K is interpreted as $k_q\tau_0$, k_q being the quenching rate constant and τ_0 the lifetime of the excited uranyl. Under the conditions of these experiments, $K = 7 \pm 1$ M^{-1}. It was shown previously[4] that an equation similar to the Stern–Volmer equation would apply to energy transfer through complex formation where K is related to the stability constant. The buildup of fluorescence of Eu(III) at constant uranyl concentration fits the equation $1/I = (1/G)(1 + 1/K[Eu^{3+}])$, which can also result from either a collision or complex formation mechanism. The interpretation of the constants K and G depends on the mechanism.[4,5] The value of K was determined to be 12 ± 4 M^{-1}.

Summary

Energy transfer between uranyl and europium(III) in aqueous perchlorate solution does not involve the UO_2^{2+} ion itself but an hydrolytic species. On the basis of the dependence of energy transfer on the pH of the solution, the uranyl species most likely to be involved is $(UO_2)_2(OH)_2^{2+}$. There is evidence from the europium emission that a complex is formed between uranyl and europium.

The concentration dependence of the quenching of uranyl and sensitization of Eu(III) is consistent with either a collision mechanism or a static mechanism of energy transfer. There is evidence that the transfer process, at least in part, takes place through the formation of a complex.

Registry No. $Eu(ClO_4)_3$, 13537-22-9; $UO_2(ClO_4)_2$, 13093-00-0.

---

(15) Eigen, M. *Pure Appl. Chem.* **1963**, *6*, 105.
(16) Garnsey, R.; Ebdon, D. W. *J. Am. Chem. Soc.* **1969**, *91*, 50.
(17) Salama, S.; Richardson, F. S. *Inorg. Chem.* **1980**, *19*, 629.