Quenching of the Excited State of Hydrated Europium (III) Ions by Electron Transfer

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INTRODUCTION

A substantial fraction of current chemical literature deals with reactions involving light. It has been shown that many transition metal complexes can be used as light absorption sensitizers for chemical reactions involving electron transfer. Currently there is much interest in studying excited states of complexes as possible sensitizers for the photochemical conversion of solar energy. Other application of excited states include their use in synthetic chemistry and in solving biological problems.¹

Absorption of light results in the formation of an excited state (eq 1), where the electronically excited state is denoted by an asterisk.

The excited state of a complex is both a better oxidant and reductant than the ground state. Thus reactions thermodynamically forbidden for the ground state may be possible for the excited state. The conditions necessary to photoinduce electron transfer reactions include absorption of light to form an excited state of sufficient energy to make the excited state reaction thermodynamically allowed and an excited state life time long enough for bimolecular reactions to compete with excited state decay.

During the last several years there has been a growing interest in the photochemistry and photophysics of solvated Eu(III) ions and complexes owing to their potential use as probe ions in biological systems. The luminescence of Eu(III) and its complexes has been studied in detail.^{2,3} There has also been some interest in using the excited states of Eu(II) and Eu(III) in synthetic organic reactions.³

We are interested in quantifying the previously uninvestigated oxidation-reduction chemistry of the excited state of Eu(III) ions, $^*Eu_{aq}^{3+}$, in aqueous solutions. The excitation of Eu_{aq}^{3+} results in the population of the 5D_0 state, the relaxation of which back to the 7F ground state results in seven emission bands.² Monitoring the strong emission from the 5D_0 to 7F_2 transition at 616 nm provides a convenient method for following the reactions of $^*Eu^{3+}$ with quenchers. Whereas the ground state Eu_{aq}^{3+} is a poor oxidant, the excited state has a high potential (1.65 V vs. NHE for $^*Eu^{3+}/Eu^{2+}$) and might, in principle, react with electron donors by electron transfer.

The decay of the excited state in the absence of a quencher occurs by both radiative and nonradiative pathways. The latter include self-quenching and the quenching of the excited state by solvent molecules. Added solutes may quench the Eu(III) excited state by either energy transfer (eq 2) or by reductive electron transfer (eq 3).

Very little exploration of the excited state reactivity has been carried out, however, and little direct evidence exists for the quenching of $^*Eu^{3+}$ by reductive electron transfer.^{5,6} We provide such evidence in this report. Measurements of the quenching rates of $^*Eu^{3+}$ with most reductants are not easily made because, despite the strongly oxidizing potential, $^*Eu^{3+}$ reacts rather slowly. This phenomenon was examined in this study. For many experiments it proved desirable to use deuterium oxide rather than water as the solvent to increase the luminescence lifetime and intensity and thus facilitate the determination of slower quenching rates.

The electron transfer reactivity of $^*\text{Eu}^{3+}$ is compared with that of another oxidizing excited state, $^*\text{UO}_2^{2+}$.

EXPERIMENTAL

Solvents and Reagents

Europium trichloride hexahydrate was obtained commercially from Aldrich or prepared by dissolving Eu_2O_3 in HCl. Solutions of europium(III) were prepared by dissolving europium trichloride in distilled water or deuterium oxide and standardized spectrophotometrically at 393 nm ($\epsilon = 3 \text{ L mol}^{-1} \text{ cm}^{-1}$)³. Solutions of $\text{Eu}_{\text{aq}}^{2+}$ were prepared by reduction of $\text{Eu}_{\text{aq}}^{3+}$ with zinc amalgam under argon. Solutions of $\text{Fe}_{\text{aq}}^{2+}$ were prepared by dissolving hydrated ferrous chloride in D_2O under argon. The Fe^{2+} solutions were treated with zinc amalgam to reduce traces of Fe^{3+} and then standardized by titration with 1,10-phenanthroline. Stock solutions of VO^{2+} in dilute HCl were prepared by ion-exchanging the sulfate salt on a column of Dowex 50W-X8 and eluting with 2 M HCl. The concentration of VO^{2+} was determined spectrophotometrically at 760 nm ($\epsilon = 17.5 \text{ L mol}^{-1} \text{ cm}^{-1}$). Solutions of $\text{V}_{\text{aq}}^{2+}$ were prepared by the reduction of VO^{2+} with zinc amalgam under argon.⁷ Concentrations of the $\text{V}_{\text{aq}}^{2+}$ solutions were determined from the absorbance at 850 nm ($\epsilon = 3.22 \text{ L mol}^{-1} \text{ cm}^{-1}$). Solutions of $\text{Cr}_{\text{aq}}^{2+}$ were prepared by dissolving chromium metal in deaerated 6 M HCl⁸ and standardized spectrophotometrically at 713 nm ($\epsilon = 5.0 \text{ L mol}^{-1} \text{ cm}^{-1}$). Solutions of $\text{Ru}(\text{NH}_3)_6^{2+}$ were prepared by reducing $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ over zinc amalgam. All of the reaction solutions were purged with argon to prevent oxidation by oxygen.

The laboratory-distilled water was purified by use of a Millipore-Q purification system. 1-Propanol (Fisher) was distilled once prior to use. Deuterium oxide (Aldrich), biacetyl (Aldrich), N,N,N',N'-tetramethyl-1,4-phenylenediamine

(TMPD, Aldrich), N,N'-diphenyl-1,4-phenylenediamine (DPPD, Aldrich), and hydroquinone were all used as purchased. Ferrocene and decamethylferrocene (Aldrich) were both purified by vacuum sublimation prior to use.

Solutions of TMPD and DPPD were prepared by dissolving each compound in solvent purged with argon. These solutions were protected from light and used within 24 hours.

Kinetics

The laser flash photolysis system used for this study was a flash-lamp pumped dye laser (Phase-R model DL-1100) with a laser pulse width of $\sim 0.6 \mu\text{s}$. The excitation of Eu^{3+} was achieved using LD-473 and LD-460 dyes; Coumarin 423 was used for the excitation of biacetyl. This arrangement is similar to one described in the literature⁹. The single-shot laser pulse impinges on a square 1-cm fluorescence cell. The $^*\text{Eu}^{3+}$ luminescence was monitored at 616 nm with a Hamamatsu R 928 photomultiplier tube positioned at 90° to the exciting pulse. The voltage vs. time data were collected, digitalized, and displayed on a Nicolet model 2090-3A digitizing oscilloscope. The data were transferred to an IBM PS/2 model computer storage and data analysis. The data gave good fits to first-order kinetics. A nonlinear least-squares program was used to calculate the rate constant. For two reactions, those with TMPD and DPPD, it was possible also to monitor formation of a strongly-absorbing product at 565 nm ($\text{TMPD}^{\bullet+}$, $\epsilon = 12,500 \text{ L mol}^{-1} \text{ cm}^{-1}$)¹⁰ and 441 nm ($\text{DPPD}^{\bullet+}$, $\epsilon = 9,400 \text{ L mol}^{-1} \text{ cm}^{-1}$) using a 50-W quartz-halogen analyzing lamp.. The molar absorptivity of $\text{DPPD}^{\bullet+}$ in neutral solution was determined spectrophotometrically in 1:1 D_2O / 1-propanol. The $\text{DPPD}^{\bullet+}$ was generated in solution by oxidation of DPPD with O_2 catalyzed by cupric acetate.

The absorption data were also fit to first-order kinetics, eq 3, since as shown below $[^*Eu^{3+}]_0 \ll [Q]$ in every case.

$$Abs_t = Abs_{\infty} + (Abs_0 - Abs_{\infty})e^{-k_{\psi}t} \quad (4)$$

The solutions for the kinetic experiments were made up anaerobically in 1-cm fluorescence cells. Large concentrations of Eu_{aq}^{3+} (~ 0.1 M) had to be used because of its weak light absorption and the low quantum yield of the excited state. The concentration of $^*Eu^{3+}$ formed by laser excitation of 0.1 M Eu^{3+} , calculated from absorbance changes observed in the reaction of TMPD and $^*Eu^{3+}$, was 0.4 mM. Barium chloride was used to buffer the ionic strength of the reaction solutions when necessary. The reactions with all quenchers were carried out under pseudo-first-order conditions such that $[^*Eu^{3+}] \ll [Q]$ in reactions solutions. Reproducible rate constants were obtained for single laser flash experiments carried out on independently prepared solutions and for multiple laser flashes to the same solution. Very little of either Eu^{3+} or Q is consumed in a given flash, or series of flashes, at these concentrations.

RESULTS

The measured lifetimes of $^*\text{Eu}^{3+}$ in H_2O and D_2O agree with those reported in the literature.¹ They are 0.10 ms ($k_0 = 9.8 \times 10^3 \text{ s}^{-1}$) in water and 2.4 ms ($k_0 = 4.1 \times 10^2 \text{ s}^{-1}$) in D_2O .

Quenching with metal complexes

In the presence of prospective quenchers the $^*\text{Eu}_{\text{aq}}^{3+}$ luminescence decayed more rapidly than in the absence of added reagents. Typical $^*\text{Eu}^{3+}$ emission traces in the absence of an added quencher and the presence of a quencher are shown in Figures 1 and 2 respectively. The pseudo-first-order rate constants, k_{q} of eq 4, vary linearly with concentration of the quencher as shown in Figure 3. The slope of each such plot gives the rate constant for the quenching of $^*\text{Eu}^{3+}$.

The reactions employing selected metal ions as quenchers were carried out in D_2O and/or H_2O at a constant ionic strength of 1.0 M, controlled by the addition of barium chloride. This choice was made because the charge type matches that of the MX_2 quenchers, thereby providing a more constant ionic environment. Typical reactions were studied at 5-10 mM HCl. The concentration ranges employed were typically 5-100 mM for $\text{M}_{\text{aq}}^{n+}$, and 0.3-3 mM for $\text{Ru}(\text{NH}_3)_6^{2+}$, $\text{Fe}(\text{C}_5\text{H}_5)_2$, and $\text{Fe}(\text{C}_5\text{Me}_5)_2$. The rate constants for inorganic and organic quenchers are given in Table 1. Concentrations of quenchers and observed rate constants for all reactions are given in the Appendix.

As expected from the relatively high reduction potential of the $\text{Fe}_{\text{aq}}^{3+}/\text{Fe}_{\text{aq}}^{2+}$ couple, the rate constant for the quenching of $^*\text{Eu}^{3+}$ by $\text{Fe}_{\text{aq}}^{2+}$,

Figure 1. Luminescence from $^*Eu_{aq}^{3+}$ in 0.5 mM HCl, ionic strength of 1.

Figure 2. Luminescence from $^*Eu_{aq}^{3+}$ in the presence of 0.08 M Eu_{aq}^{2+} and 0.5mM HCl, ionic strength of 1.

Figure 3. A plot of the pseudo-first-order rate constants against concentrations of iron reagents for the quenching of $^*Eu^{3+}$ by $Fe(C_5Me_5)_2$ (circles) and $Fe(C_5H_5)_2$ (triangles). The data points shown are average values from quadruplicate laser flash experiments.

Table 1. Rate Constants for the Quenching of $^*Eu^{3+}$ by Electron Donors in Aqueous Solution at 23 °C

Quencher	Solvent ^a	E° V / NHE	<i>k</i> / L mol ⁻¹ s ⁻¹
Cr(H ₂ O) ₆ ²⁺	D ₂ O	-0.42	(2.41 ± 0.02)10 ⁵
Eu _{aq} ²⁺	H ₂ O	-0.38	(2.33 ± 0.06)10 ⁵
V(H ₂ O) ₆ ²⁺	D ₂ O	-0.26	(2.32 ± 0.02)10 ⁵
Hydroquinone	D ₂ O	0.023	(1.53 ± 0.05)10 ³
Ru(NH ₃) ₆ ²⁺	H ₂ O	0.062	(2.14 ± 0.05)10 ⁷
Fe(C ₅ Me ₅) ₂	1:1 H ₂ O/1-Propanol	0.12	(1.87 ± 0.03)10 ⁷
TMPD	D ₂ O	0.27	(9.2 ± 0.4)10 ⁵
DPPD	1:1 D ₂ O/1-Propanol	0.35	(2.72 ± 0.09)10 ⁵
Fe(C ₅ H ₅) ₂	1:1 H ₂ O/1-Propanol	0.51	(6.6 ± 0.1)10 ⁶
Fe(H ₂ O) ₆ ²⁺	D ₂ O	0.77	(5.1 ± 0.3)10 ³

^a Reactions with Cr(H₂O)₆²⁺, Eu_{aq}²⁺, and Ru(NH₃)₆²⁺ were carried out in 0.5-1 mM HCl, the reaction with V(H₂O)₆²⁺ in 0.1 M HCl, and the reaction with Fe(H₂O)₆²⁺ in 10 mM HCl. All other reactions were carried out in neutral solutions.

$5.1 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$, was the lowest in the series of metal ions studied. The variation of $[\text{H}^+]$ in the range of 0.01-0.06 M had no effect on the kinetics.

The reactions with $\text{Cr}_{\text{aq}}^{2+}$, $\text{Eu}_{\text{aq}}^{2+}$, and $\text{V}_{\text{aq}}^{2+}$ all have similar rate constants, $(2.3\text{-}2.4) \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$. The reactions with $\text{V}_{\text{aq}}^{2+}$ were done at 0.1 M HCl to prevent formation of the strongly absorbing VOV^{4+} .

The most reactive electron-transfer quenchers in this work are $\text{Ru}(\text{NH}_3)_6^{2+}$, decamethylferrocene and ferrocene.

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in the range of 0.8 to 2.5 mM does not quench $^*\text{Eu}^{3+}$. Figure 4 compares the nonreactivity of $\text{Co}(\text{NH}_3)_6^{3+}$ with the redox active $\text{Ru}(\text{NH}_3)_6^{2+}$ complex. Likewise the use of MnCl_2 at 50 to 100 mM levels did not quench $^*\text{Eu}^{3+}$, yielding $k < 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ for this reaction.

Quenching with organic compounds

Of the several organic quenchers one might consider, we tried hydroquinone, *o*-cresol, TMPD, DPPD, *N,N,N',N'*-tetramethylbenzidine, and *a,a,a',a'*-tetramethyl-1,4-benzenedimethanol. Of these organic substrates, only hydroquinone, TMPD, and DPPD acted as quenchers for $^*\text{Eu}^{3+}$.

Experiments involving TMPD in D_2O provided direct evidence that the quenching of $^*\text{Eu}^{3+}$ occurs by electron transfer. The pseudo-first-order rate constants were obtained by following both the luminescence decay of $^*\text{Eu}^{3+}$ and the absorbance increase due to the buildup of $\text{TMPD}^{\bullet+}$. The values of k_y at 5.0 mM TMPD are 4600 s^{-1} and 4900 s^{-1} for the absorption and emission measurements, respectively. From the absorbance change at 565 nm ($\epsilon_{\text{TMPD}^{\bullet+}} = 12,500 \text{ L mol}^{-1} \text{ cm}^{-1}$), we calculate the initial concentration of $^*\text{Eu}^{3+}$ to be 0.4 mM, assuming that the formation of $\text{TMPD}^{\bullet+}$ occurs with a 1:1 stoichiometry. The low concentration of

Figure 4. A plot of the pseudo-first-order rate constants against concentrations for the quenching of $^*Eu^{3+}$ by $Ru(NH_3)_6^{2+}$ (circles) and $Co(NH_3)_6^{3+}$ (triangles). The data points shown are average values from quadruplicate laser flash experiments.

$^*Eu^{3+}$ that was formed by the laser excitation of Eu^{3+} complicated the detection of reaction products, except for those with high extinction coefficients. The reaction of $^*Eu^{3+}$ with DPPD was also followed by monitoring the absorbance of the radical product $DPPD^{\bullet+}$ and the luminescence of $^*Eu^{3+}$. The pseudo-first-order rate constants at 2.5 mM DPPD are $(2.2 \pm 0.3) \times 10^3 \text{ s}^{-1}$ and $(3.1 \pm 0.4) \times 10^3 \text{ s}^{-1}$ for emission and absorption measurements respectively. The two rate constants are in agreement with each other given the small size of the absorbance changes for absorption experiments (0.002 to 0.003 absorbance units) and the precision of the experimental kinetic data.

Photosensitization

Concern over the low concentration of the excited state prompted us to look for alternative ways of generating $^*Eu^{3+}$. Since Eu(III) absorbs light at 460 nm, where the excited state of biacetyl has an emission band, we inferred that energy transfer from excited biacetyl to Eu(III) might form $^*Eu^{3+}$. Indeed, we found that the energy transfer from excited biacetyl to Eu^{3+} is an effective way of producing $^*Eu^{3+}$. An excitation wavelength of 423 nm, the lowest one accessible with our laser, was chosen for these experiments. The formation of $^*Eu^{3+}$ was indicated by the luminescence at the characteristic 616 nm wavelength. The lifetime of this luminescence matched the lifetimes we had obtained for $^*Eu^{3+}$ formed by direct excitation at 460 and 473 nm.

We measured the triplet lifetime of biacetyl in water to be 0.05 ms, shorter than the reported 0.23 ms.¹¹ This suggests an impurity may be present. The shorter than expected lifetime does not, however, interfere with the use of biacetyl in the experiment with Eu^{3+} . Quenching of the excited biacetyl by Eu_{aq}^{3+} was observed by following the decay of the biacetyl phosphorescence at 460 nm; the second-order

rate constant was $k_4 = (2.07 \pm 0.05) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$. The concentration of Cl^- was kept constant in these experiments and the rate constant for the quenching of $^*\text{BA}$ by Cl^- appeared as the intercept in plot of the k_{ψ} vs. $[\text{Eu}_{\text{aq}}^{3+}]$.¹²

The $^*\text{Eu}^{3+}$, formed by energy transfer from biacetyl, was then examined by measuring the quenching rate with $\text{Ru}(\text{NH}_3)_6^{2+}$. We obtained a value of $1.2 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$, which differs by a factor of ~ 2 from the value we observed for $^*\text{Eu}^{3+}$ that was formed directly by laser excitation. This deviation may be attributed to a possible effect of 0.01 M biacetyl on this system. Because of this interference, the $^*\text{Eu}^{3+}$ used in all the other reactions in this study was generated by direct excitation, and not by energy transfer from biacetyl. We also measured the rate at which $\text{Ru}(\text{NH}_3)_6^{2+}$ quenches $^*\text{BA}$, and obtained a rate constant of $5.6 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$.

Back electron transfer

The quenching by electron transfer is in general followed by back electron transfer, eq 6.

In the laser flash photolysis experiments there was no evidence for back electron transfer in any of the systems explored in this work. This was traced to the very low rates of these reactions. By use of conventional spectrophotometry we determined the rate constant for the reaction between Eu^{2+} and $\text{TMPD}^{\bullet+}$, $k_5 = 2 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$. In the quenching reactions only $0.4 \times 10^{-6} \text{ M}$ Eu^{2+} and $0.4 \times 10^{-6} \text{ M}$ Q^+ were formed. At these concentrations the back electron transfer reaction of Eu^{2+} and $\text{TMPD}^{\bullet+}$ will have a half life of 600 s, which is much too slow to observe with our laser system.

For the quenching of $^*Eu^{3+}$ by Fe^{2+} , it is known that the back reaction of Fe(III) and Eu(II) has an inverse H^+ dependence and a direct Cl^- dependence. In quenching experiments with Fe^{2+} the Cl^- concentration was high, such that Fe(III) formed in quenching reactions will be present as $FeCl^{2+}$. The second-order rate constant for the reaction of Eu^{2+} and $FeCl^{2+}$ is $2 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$.¹³ Again, flash photolysis experiments with Fe^{2+} and Eu^{3+} yield $0.4 \times 10^{-6} \text{ M}$ of each product and the calculated half life for the back reaction is 0.6 s. We also tried unsuccessfully to trap the Fe(III) formed in the forward reaction with NaSCN and with $Co(tim)^{2+}$.

DISCUSSION

The quenching of $^*\text{Eu}^{3+}$ by metal ions appears to occur by electron transfer. Even though we were unable to observe directly the buildup of M^{3+} , we noted that no quenching takes place when the redox-inactive $\text{M}_{\text{aq}}^{2+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ were used. Since both of these complexes could, but do not, react by energy transfer, we conclude that $^*\text{Eu}^{3+}$ is not a strong energy transfer reagent.

Also, there is a rough correspondence between the quenching rate constants for this set of reactions and their thermodynamic driving forces for electron transfer, once other factors are allowed for. The similarity of the quenching constants of $\text{Eu}_{\text{aq}}^{2+}$ and $\text{Cr}_{\text{aq}}^{2+}$, for example, is anticipated for electron transfer reactions, given their similar redox potentials and similar (and very slow) $\text{M}_{\text{aq}}^{3+}/\text{M}_{\text{aq}}^{2+}$ electron exchange rate constants. The rather large¹⁴ electron-exchange rate constant for $\text{Ru}(\text{NH}_3)_6^{3+}/\text{Ru}(\text{NH}_3)_6^{2+}$ makes $\text{Ru}(\text{NH}_3)_6^{2+}$ one of the most effective quenchers of $^*\text{Eu}^{3+}$. More will be said later on this subject.

We note that $\text{Fe}(\text{C}_5\text{Me}_5)_2$ quenches $^*\text{Eu}^{3+}$ three times faster than $\text{Fe}(\text{C}_5\text{H}_5)_2$ does. This is consistent with electron transfer quenching, because $\text{Fe}(\text{C}_5\text{Me}_5)_2$ is a stronger reductant than $\text{Fe}(\text{C}_5\text{H}_5)_2$. Similarly hydroquinone is reactive as a quencher, while a weaker reductant *o*-cresol is not. Also, TMPD is more reactive than DPPD as a result of the more reducing potential of TMPD.

The application of the Marcus equation, eq 7, to a situation in which the driving force is very high yet the reactions are most likely highly nonadiabatic is problematic at best. The reactions of $\text{Eu}_{\text{aq}}^{3+}$ clearly fall into this category.

Nonetheless, some qualitative conclusions can be drawn on the basis of this approach.

$$k_{AB}^2 = k_{AA}k_{BB}K_{AB}f \quad (7)$$

The rate constants for quenching of $^*Eu^{3+}$ by Eu^{2+} and Cr^{2+} are in agreement with each other. Given that the driving force happens to be nearly the same and both electron self-exchange rate constants are similar, this result could have been anticipated.

As expected, Fe^{2+} reacts much more slowly than Cr^{2+} and Eu^{2+} . Whereas Cr^{2+} reacts *ca.* 50 times more rapidly than Fe^{2+} , the Marcus correlation, eq 6 would have had it reacting approximately 14,000 times faster. A comparison of Eu^{2+} and Fe^{2+} yields similar results. When using the Marcus cross-relation for reactions with large driving forces, such as reactions with Cr^{2+} and Eu^{2+} , it is not unusual to find such deviations. The important qualitative observation is the much smaller reactivity of Fe^{2+} compared to Eu^{2+} and Cr^{2+} , as expected.

Although the reduction potential for the $^*Eu^{3+}/Eu^{2+}$ couple is 1.65 V, only the strongest reductants reacted at measurable rates with $^*Eu^{3+}$. Weaker organic reductants N,N,N',N' -tetramethylbenzidine, a,a,a',a' -tetramethyl-1,4-benzenedimethanol, and *o*-cresol did not quench $^*Eu^{3+}$. The low redox reactivity of $^*Eu^{3+}$ parallels certain features of Eu^{2+} . For example, the low electron exchange rate for $Eu_{aq}^{3+}/Eu_{aq}^{2+}$ ($2 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$)¹⁵ provides a rationale for the relatively small rate constants for reactions in which Eu_{aq}^{2+} is oxidized by outer-sphere electron transfer, even when the driving force is substantial. It would thus appear that the involvement of *f* orbitals in electron transfer is partly responsible for the slow reactions of both $^*Eu^{3+}$ and Eu^{2+} . In the terminology of the Marcus relation, the low reactivity of $^*Eu^{3+}$ allows us to conclude that the rate constant for

the $^*\text{Eu}_{\text{aq}}^{3+}/\text{Eu}_{\text{aq}}^{2+}$ electron-exchange reaction is, like that for the ground state, rather small.

From the data for quenching of $^*\text{Eu}^{3+}$ with Eu^{2+} and Cr^{2+} , and the electron exchange rates for the $\text{Eu}^{3+}/\text{Eu}^{2+}$ and $\text{Cr}^{3+}/\text{Cr}^{2+}$, couples we are able to calculate an electron-exchange rate constant for $^*\text{Eu}_{\text{aq}}^{3+}/\text{Eu}_{\text{aq}}^{2+}$ of $\sim 10^{-12} \text{ L mol}^{-1} \text{ s}^{-1}$, the average value of two calculations. The numerical value is not to be taken seriously; but the conclusion stands that the electron exchange occurs very slowly. It is further interesting that the reaction of $^*\text{Eu}^{3+}$ and Fe^{2+} is pH-independent in the same range of $[\text{H}_3\text{O}^+]$ where the $\text{Eu}^{2+}\text{-Fe}^{3+}$ reaction shows a strong inverse acid dependence, the major term in the rate law having a term proportional to $[\text{H}_3\text{O}^+]^1$. The excited state reaction is thus seen to be outer-sphere electron transfer and the ground state reaction proceeds through an OH⁻-bridged transition state. That is to say, quenching and back electron transfer have been independently shown to adopt different mechanisms. These of course are not the microscopic reverse of one another.

Figure 3 presents a comparison of the reactivity of $^*\text{Eu}_{\text{aq}}^{3+}$ with that of $^*\text{UO}_2^{2+}$. The data used for this plot are given in Table 2. The values tabulated are for reactions that are believed to occur by electron-transfer. A linear correlation is expected for a log-log plot of this type, which compares the rate constants for the reduction of two excited states by identical quenchers. The straight line correlation provides more evidence for the electron transfer quenching of $^*\text{Eu}^{3+}$ by electron transfer. Equation 7 describes the equation for the line shown in Figure 5.

$$\log k_{\text{Eu}} = -8.6 + 1.6 \log k_{\text{U}} \quad (8)$$

Figure 5. Correlation of the kinetic data for the reduction of $^*Eu^{3+}$ and $^*UO_2^{2+}$ by Fe^{2+} (1), aniline (2), diphenylamine (3), and $Fe(C_5H_5)_2$ (4).

Table 2: Rate Constants for the Electron-Transfer Quenching of $^*Eu_{aq}^{3+}$ and $^*UO_2^{2+}$

Quencher	$k_q (^*Eu^{3+}) / L \text{ mol}^{-1} \text{ s}^{-1}$	$k_q (^*UO_2^{2+}) / L \text{ mol}^{-1} \text{ s}^{-1}$
Fe^{2+}	5.1×10^3	4.0×10^7
$Fe(C_5H_5)_2$	6.6×10^7	1.6×10^{10}
Aniline	5.0×10^4	8.7×10^8
Diphenylamine	4.2×10^5	1.1×10^9

The greater reactivity of $^*\text{UO}_2^{2+}$ reflects not only the greater reduction potential ($E = 2.6 \text{ V}$), but probably also the fact that the electron accepting $6d$ orbital is more easily accessible than the $4f$ orbital of $^*\text{Eu}^{3+}$.

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APPENDIX

Table A 1. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ with $\text{Cr}_{\text{aq}}^{2+}$ ^a

$[\text{Cr}^{2+}]/10^{-2} \text{ M}$	$k_{\text{obs}}/10^3 \text{ s}^{-1}$
0.000	0.397
0.683	1.69
1.71	4.24
2.73	6.04
5.13	12.1
6.83	16.3
8.54	21.1
10.3	25.0

^a In 1 mM HCl

Table A2. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ with $\text{Eu}_{\text{aq}}^{2+}$ ^a

$[\text{Eu}_{\text{aq}}^{2+}]/10^{-2} \text{ M}$	$k_{\text{obs}}/10^3 \text{ s}^{-1}$
0.000	5.19
1.00	6.65
1.67	7.78
3.33	11.5
4.00	13.2
5.00	15.0
6.67	18.6
8.33	22.5
10.0	29.5

^a In 0.5 mM HCl

Table A3. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ with $\text{V}_{\text{aq}}^{2+}$ ^a

$[\text{V}^{2+}]/10^{-2} \text{ M}$	$k_{\text{obs}}/10^3 \text{ s}^{-1}$
0.000	2.46
0.333	3.23
0.833	4.34
1.67	6.00
2.50	7.93
3.33	9.89
4.16	12.1
5.00	14.2

^a In 0.1 M HCl

Table A4. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ with hydroquinone^a

[hydroquinone]/10 ⁻¹ M	k _{obs} / 10 ² s ⁻¹
0.000	3.49
0.167	3.71
0.417	4.51
1.08	5.03
1.25	5.39
1.67	6.00
2.08	7.08
2.50	7.18

^a In neutral solution

Table A5. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ with $\text{Ru}(\text{NH}_3)_6^{2+}$ ^a

$[\text{Ru}(\text{NH}_3)_6^{2+}]/10^{-3} \text{ M}$	$k_{\text{obs}}/10^4 \text{ s}^{-1}$
0.000	0.978
0.333	1.62
0.833	2.86
1.17	3.72
1.67	4.16
2.00	5.36
2.50	6.40

^a In 0.5 mM HCl

Table A6. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ by $\text{Fe}(\text{C}_5\text{Me}_5)_2^{\text{a}}$

$[\text{Fe}(\text{C}_5\text{Me}_5)_2]/10^{-3} \text{ M}$	$k_{\text{obs}}/10^4 \text{ s}^{-1}$
0.000	0.715
0.300	1.19
0.500	1.56
1.00	2.22
1.50	3.66
2.00	4.34
2.50	5.10
3.00	6.30

^a In neutral solution

Table A7. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ by TMPD^a

[TMPD]/10 ⁻³ M	k _{obs} /10 ³ s ⁻¹
0.000	0.376
0.333	0.809
0.833	0.856
1.20	1.60
1.67	1.00
2.50	2.00
3.30	3.20
4.20	4.33
5.00	4.90

^a In neutral solution

Table A8. Quenching of $^{\ast}\text{Eu}_{\text{aq}}^{3+}$ by DPPD^a

[DPPD]/10 ⁻³ M	k _{obs} /10 ³ s ⁻¹
0.000	1.38
0.333	1.46
0.833	1.60
1.67	1.86
2.50	2.04

^a In neutral solution

Table A9. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ by $\text{Fe}(\text{C}_5\text{H}_5)_2^{\text{a}}$

$[\text{Fe}(\text{C}_5\text{H}_5)_2]/10^{-3} \text{ M}$	$k_{\text{obs}}/10^4 \text{ s}^{-1}$
0.000	0.684
0.667	1.08
1.33	1.60
2.00	2.07
2.67	2.56
3.33	2.87
4.00	3.26

^a In neutral solution

Table A10. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ by $\text{Fe}_{\text{aq}}^{2+}$ ^a

$[\text{Fe}_{\text{aq}}^{2+}]/10^{-2} \text{ M}$	$k_{\text{obs}}/10^2 \text{ s}^{-1}$
0.00	4.08
1.74	4.62
3.48	5.44
5.25	6.32
6.97	7.10
8.71	8.14
10.5	9.52

^a In neutral solution**Table A11.** Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ by $\text{Fe}_{\text{aq}}^{2+}$ at different acid Concentrations^a

$[\text{H}^+]/10^{-2} \text{ M}$	$k_{\text{obs}}/10^3 \text{ s}^{-1}$
1.00	0.952
2.50	1.00
6.50	1.06

^a $[\text{Fe}_{\text{aq}}^{2+}] = 0.1 \text{ M}$

Table A12. Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ by $\text{Co}(\text{NH}_3)_6^{3+}$ ^a

$[\text{Co}(\text{NH}_3)_6^{3+}]/10^{-3} \text{ M}$	$k_{\text{obs}}/10^3 \text{ s}^{-1}$
0.000	8.73
0.417	9.18
0.833	9.32
1.25	9.60
2.50	9.01

^a In neutral solution**Table A13.** Quenching of $^*\text{Eu}_{\text{aq}}^{3+}$ by $\text{Mn}_{\text{aq}}^{2+}$ ^a

$[\text{Mn}_{\text{aq}}^{2+}]/10 \text{ M}$	$k_{\text{obs}}/10^2 \text{ s}^{-1}$
0	3.48
0.50	4.06
1.0	4.42

^a In neutral solution

Table A14. Quenching of *BA by $\text{Eu}_{\text{aq}}^{3+}$ ^a

$[\text{Eu}_{\text{aq}}^{3+}]/10^{-2} \text{ M}$	$k_{\text{obs}}/10^4 \text{ s}^{-1}$
0.000	1.78
0.383	2.22
1.55	4.95
2.72	7.06
3.88	10.6
5.83	13.3

^a In neutral solution

Table A15. Quenching of $^*Eu_{aq}^{3+}$, formed by energy transfer from biacetyl, by $[Ru(NH_3)_6^{2+}]^a$

$[Ru(NH_3)_6^{2+}]/10^{-4} \text{ M}$	$k_{obs}/10^4 \text{ s}^{-1}$
0.000	0.917
0.833	0.950
1.67	0.960
4.17	1.29
5.83	1.35
8.33	1.77
10.0	2.12

^a In 0.5 mM HCl

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Last First Middle

Print corrections on the appropriate lines when information is inaccurate or incomplete

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Parent/Guardian/Spouse Name _____ (25)
Last First Middle

Parent/Guardian/Spouse _____ (1) P - Parent, G - Guardian, D - Deceased
S - Spouse, O - Other

Mr./Mrs. _____ (1) Use 3 for Mr. & Mrs., Use 1 for Mr., Use 2 for Mrs., and Use 4 for Ms.

Street _____ (26)

City/State _____ (26)

Zip Code _____ (5)

Student Signature _____ Date _____

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