

mechanism, it was important to examine the thus formed C_2 $Cr(CO)_4(^{13}CO)(pip)$ for possible CO scrambling processes.²⁹⁻³¹ C_2 $Cr(CO)_4(^{13}CO)(pip)$ was sublimed at 52 °C under vacuum to yield a yellow crystalline material. Subjection of this sublimed sample to IR and ^{13}C NMR analysis (vide supra) illustrated that the species maintained the integrity of its CO ligands; i.e., no rearrangement of CO ligands was observed.

Equipment. In previous papers, the equipment used to achieve cryogenic temperatures was described, together with photolysis sources and spectrometers.¹⁵⁻¹⁷ The samples were evaporated by using an oven and the slow spray-on method. The evaporation time varied

between 45 and 90 min. The oven temperatures for the Cr, Mo, and W complexes were 0-5 °C, room temperature, and 40-50 °C, respectively. The $Mo(CO)_5(pip)$ complex was very sensitive to collisions with the glass wall, and decomposition into $Mo(CO)_6$ was detected to be a function of the glass surface. During decomposition the temperature of the NaCl window never exceeded 10 K and the vacuum was better than 10^{-6} torr. Argon with a purity of 99.9997% was employed and sprayed on through a needle valve.

Registry No. $Cr(CO)_5(pip)$, 15710-39-1; $Mo(CO)_5(pip)$, 19456-57-6; $W(CO)_5(pip)$, 31082-68-5; C_2 $Cr(CO)_4(pip)$, 74764-03-7; C_2 $Mo(CO)_4(pip)$, 74764-04-8; C_2 $W(CO)_4(pip)$, 74764-05-9; C_2 $Cr(CO)_4(^{13}CO)(pip)$, 65255-66-5; C_2 $W(CO)_4(^{13}CO)(pip)$, 65255-68-7; C_1 *fac*- $Cr(CO)_3(^{13}CO)(pip)$, 74764-06-0; C_1 *mer*- $Cr(CO)_3(^{13}CO)(pip)$, 74806-96-5; C_1 *fac*- $W(CO)_3(^{13}CO)(pip)$, 74764-07-1; C_1 *mer*- $W(CO)_3(^{13}CO)(pip)$, 74806-97-6; C_{20} $Cr(CO)_4(pip)_2$, 65255-70-1; C_{40} $Cr(CO)_4(^{13}CO)(pip)$, 65620-49-7; $Cr(CO)_5$, 26319-33-5; $Mo(CO)_5$, 32312-17-7; $W(CO)_5$, 30395-19-8.

- (29) D. J. Darensbourg, *Inorg. Chem.*, **18**, 14 (1979).
 (30) D. J. Darensbourg and B. J. Baldwin, *J. Am. Chem. Soc.*, **101**, 6447 (1979).
 (31) D. J. Darensbourg, B. J. Baldwin, and J. A. Froelich, *J. Am. Chem. Soc.*, **102**, 4688 (1980).

Contribution from Olson Laboratories of Rutgers—State University, Newark, New Jersey 07102, and Allied Chemical Corporation, Morristown, New Jersey 07960

Photoinduced Electron Transfer from the Cerous Ion Excited State to Cupric Ion

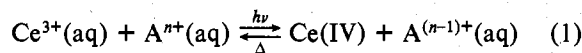
R. P. ASBURY, G. S. HAMMOND,^{1a} P. H. P. LEE,^{1b} and A. T. POULOS*^{1b}

Received March 26, 1980

Photoinduced electron transfer between $Ce^{3+}(aq)$ and $Cu^{2+}(aq)$ in sulfate solution has been studied by microsecond-flash excitation techniques. The photoproducts are cerium(IV) sulfate complexes and Cu^+ , which rapidly undergo reverse electron transfer which can be monitored by kinetic spectrophotometry. The rate constant of this thermal reaction ($k = 1.25 \times 10^6 M^{-1} s^{-1}$ at 25 °C in 1.0 M acetonitrile) can be slowed by greater than 2 orders of magnitude by varying the solvent from water to 3 M aqueous acetonitrile. There is evidence that the primary photochemical act is bimolecular collision of the lowest energy $4d \rightarrow 5f$ excited state of cerous ion with cupric ion. Both fluorescence quantum yields and lifetimes can be correlated with cupric ion concentration and fit Stern-Volmer kinetics. Rate constants for dynamic quenching of Ce^{3+} emission by $Cu^{2+}(aq)$, $Fe^{3+}(aq)$, $Cr^{3+}(aq)$, $Tl^{3+}(aq)$, and $Eu^{3+}(aq)$ are also reported.

Introduction

Ultraviolet excitation of $4f \rightarrow 5d$ electronic transitions² of $Ce^{3+}(aq)$ in aqueous solution initiates photopolymerization of vinyl compounds and nitriles³ and causes electron transfer to the hydronium ion⁴ and the persulfate anion.⁵ The products result from a primary photochemical event followed by thermal reactions; consequently, it is difficult to determine primary-process quantum yields and to study changes in reaction medium on the primary process. To extend understanding of $Ce^{3+}(aq)$ excited-state behavior, yet avoid complications by secondary reactions, we undertook a search for reversible, photoinduced, one-electron-transfer reactions of the type



Incidentally, such reactions *in principle* can generate photogalvanic current.⁶ The acceptors, A^{n+} , were chosen by the following criteria: (1) lack of thermal reactivity with $Ce^{3+}(aq)$ or $Ce(IV)$, (2) existence of a stable lower oxidation state, (3) lack of strong ultraviolet absorption in the region of some of the cerous $4f \rightarrow 5d$ bands, and (4) low probability of forming ground-state complexes with $Ce^{3+}(aq)$.

We report that electron transfer from excited $Ce^{3+}(aq)$ can be observed spectroscopically with $Cu^{2+}(aq)$ but not with $Fe^{3+}(aq)$, $Cr^{3+}(aq)$, or $Eu^{3+}(aq)$, even though the latter ions efficiently quench Ce^{3+} emission. Studies on the mechanism of the reaction with Cu^{2+} are reported here.

Experimental Section

Reagents. All materials were reagent grade and used without further purification, except for $Ce_2(SO_4)_3$ (Alfa Products), which was recrystallized from water by adding concentrated sulfuric acid to a saturated solution of the salt and allowing the mixture to stand overnight. The concentration of Ce(III) aqueous solutions used for flash excitation or emission quenching was determined by weight or was determined spectrophotometrically from the $4f \rightarrow 5d$ band extinction coefficients.⁷ $Eu(ClO_4)_3$ (Alfa) and $Cu(SO_4)_2 \cdot 5H_2O$ (Mallinckrodt) concentrations were determined by weight of dry samples. Cr(III) concentrations of $Cr(ClO_4)_3$ (Alfa) solutions were determined by spectrophotometric analysis of the ethylenediaminetetraacetate complex.⁸ Fe(III) in solutions of ferric sulfate was determined by weight and from the extinction coefficient ($2.175 \times 10^3 M^{-1} cm^{-1}$ at 305 nm) in 0.8 N H_2SO_4 .⁹ Tl(III) concentrations were determined by weight of the dry perchlorate salt.

Flash Photolysis. The conventional flash photolysis apparatus was constructed at the University of California—Santa Cruz. The flash tube (Xenon Corp. N-108C) and a 15×1 cm² sample cell (Pyrex or quartz) were held at the focal points of an elliptical aluminum cavity by ebonite brackets. Up to 100 J of excitation energy (20- μs duration) could be supplied by a Xenon Corp. Model 457A Micropulser. The

- (1) (a) Allied Chemical Corp. (b) Rutgers University.
 (2) C. K. Jørgensen and J. S. Brinen, *Mol. Phys.*, **6**, 629 (1963).
 (3) (a) F. H. C. Edgecombe and R. G. W. Norrish, *Nature (London)*, **197**, 282 (1963). (b) F. Hussain and R. G. W. Norrish, *Proc. R. Soc. London, Ser. A*, **275**, 161 (1963).
 (4) L. J. Heidt and A. F. McMillan, *J. Am. Chem. Soc.*, **76**, 2135 (1954).
 (5) R. W. Matthews and T. J. Sworski, *J. Phys. Chem.*, **79**, 681 (1975).
 (6) M. S. Wrighton, *Chem. Eng. News*, **57**, 29 (1979).

- (7) H. L. Greenhans, A. M. Feibush, and Louis Gordon, *Anal. Chem.*, **29**, 1531 (1957).
 (8) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 5670 (1953).
 (9) J. Jortner and G. Stein, *J. Phys. Chem.*, **66**, 1258 (1962).

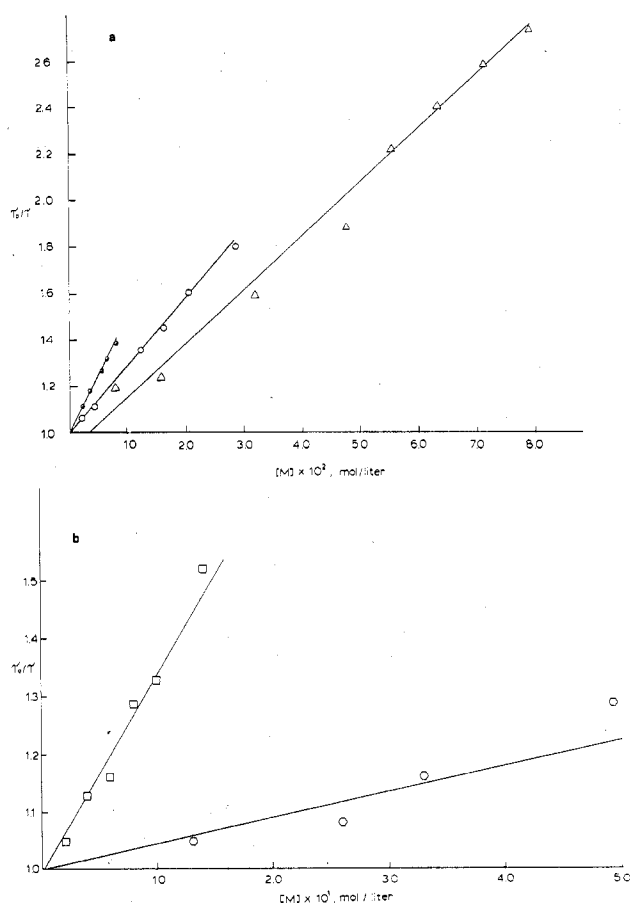


Figure 1. Stern-Volmer plot of $\text{Ce}^{3+}(\text{aq})$ emission lifetime shortening (a) by Fe^{3+} (half-filled circles), Tl^{3+} (open circles), and Cu^{2+} (open triangles) and (b) by Cr^{3+} (squares) and Eu^{3+} (hexagons).

cavity design caused excitation radiation to pass through the 1-cm width of the sample cell. Changes in the transmittance of the solution at a single wavelength as a function of time were monitored by passing light from a quartz-iodine dc lamp through the 15-cm cell length into a 0.25-m monochromator (Oriel Model 7240, slit width = 5 nm) and then a 1 P28 photomultiplier. Oscilloscope scans of the photomultiplier output voltage were recorded on Type 47 Polaroid film. Unless specified otherwise, sample solutions were saturated with nitrogen.

Emission Lifetime Studies. The emission intensities from aqueous cerous perchlorate as a function of time in the presence and absence of quenchers were measured by using an Ortec Single-Photon Counting System (Model 9200). The housing of the excitation pulse lamp, sample cell, and photomultiplier tube was constructed to enable a 254-nm interference filter (10-nm fwhm) to be inserted between the lamp and sample cell and a cutoff filter (zero percent transmittance at $\lambda < 300$ nm) to be inserted between the sample cell and photomultiplier tube. Lifetimes were measured at constant pH (1 N HClO_4) and constant ionic strength (1.1 M NaClO_4) in air-saturated solutions of 2.3×10^{-2} M $\text{Ce}(\text{ClO}_4)_3$. An emission lifetime of 44 ns was measured for $\text{Ce}^{3+}(\text{aq})$ in the absence of added quenchers under these conditions. The same lifetime was measured under an atmosphere of nitrogen.

Results

Quenching of $\text{Ce}^{3+}(\text{aq})$ Emission by $\text{Fe}^{3+}(\text{aq})$, $\text{Tl}^{3+}(\text{aq})$, $\text{Cu}^{2+}(\text{aq})$, and $\text{Eu}^{3+}(\text{aq})$. The emission lifetime of aqueous $\text{Ce}(\text{ClO}_4)_3$ was decreased by salts of each of the above cations. The decay profiles in the presence and absence of metal ions fitted a single exponential function. Plots of τ_0/τ against quencher concentration (τ_0 = unquenched emission lifetime = 44 ns; τ = emission lifetime with quencher) were linear functions of quencher concentration to a reasonable degree of precision (Figure 1).

Second-order quenching constants, k_q , are shown in Table I, along with the reduction potentials for one-electron transfer

Table I. Correlation between Constants for the Dynamic Quenching of $\text{Ce}^{3+}(\text{aq})$ Emission and Metal Ion Reduction Potentials^a

metal ion	$k_q, \text{M}^{-1} \text{s}^{-1}$	$E_{1/2}, \text{V}$	metal ion	$k_q, \text{M}^{-1} \text{s}^{-1}$	$E_{1/2}, \text{V}$
Fe^{3+}	1.1×10^9	+0.77	Cr^{3+}	7.7×10^7	-0.41
Tl^{3+}	6.7×10^8	+1.25 ^b	Eu^{3+}	1.1×10^7	-0.43
Cu^{2+}	5.2×10^8	+0.15			

^a One-electron potentials relative to the hydrogen electrode unless otherwise specified. ^b Two-electron potential.

Table II. $\Delta G_{\text{ET}}^\circ$ Values for One-Electron Oxidation of $(\text{Ce}^{3+}(\text{aq}))^*$ by Quenchers Calculated from $\Delta G_{\text{ET}}^\circ = \Delta G_{1/2}^\circ \text{Ox} + \Delta G_{1/2}^\circ \text{Red} - \Delta E_{0,0}^\circ$

quencher	$\Delta G_{1/2}^\circ \text{Red}, \text{kcal/mol}$	$\Delta G_{\text{ET}}^\circ, \text{kcal/mol}$
Fe^{3+}	-17.8	-73.4
Tl^{3+}	-28.9	-84.5
Cu^{2+}	-3.6	-59.2
Cr^{3+}	+9.48	-46.1
Eu^{3+}	+9.95	-45.6

^a $\Delta E_{0,0}^\circ$ = the energy gap between $\text{Ce}^{3+}(\text{aq})$ emitting and ground states = 88.8 kcal, $\Delta G_{1/2}^\circ \text{Ox}$ = thermal oxidation potential of $\text{Ce}^{3+}(\text{aq})$ = 33.2 kcal.

(hydrogen electrode reference),¹⁰ except for that of Tl^{3+} , for which only the two-electron reduction potential is available. There is an approximate correlation between k_q and $E_{1/2}$, in that the most easily reduced cations are also the best quenchers. This is consistent with a charge-transfer quenching mechanism.

Approximate ΔG° values for hypothetical one-electron oxidation of the emitting state of Ce^{3+} by the quenchers can be calculated by the equation of Weller¹¹ (see Table II). The highly negative values indicate that reaction 1 is thermodynamically possible with all the quenchers. These results prompted our search for spectroscopic evidence of photoinduced one-electron transfer.

Flash Excitation of $\text{Ce}^{3+}(\text{aq})$ in the Presence of $\text{Fe}^{3+}(\text{aq})$, $\text{Cr}^{3+}(\text{aq})$, and $\text{Eu}^{3+}(\text{aq})$. Concentrations of Fe^{3+} or Eu^{3+} sufficient to effect greater than 30% quenching of the Ce^{3+} emitting state did not cause the appearance of detectable new transients in flash excitation of Ce^{3+} in aqueous sulfuric acid. (In all cases, the spectrum after pulsing was monitored throughout the region 680–385 nm; production of cerium(IV) sulfate complexes should be observable as an increase in absorbance at $\lambda \leq 410$ nm.) Cr^{3+} caused transient absorbance changes in the region of 400–385 nm which were too small for kinetic studies.

Flash Excitation of $\text{Ce}^{3+}(\text{aq})$ in the Presence of $\text{Cu}^{2+}(\text{aq})$. Flash excitation of 7.7×10^{-2} M cerous perchlorate in 0.05 N sodium sulfate, pH 2, with excitation wavelengths greater than 280 nm, results in a transient absorbance change of 0.018 at 360 nm. This decays completely within 10 s to the solution absorbance prior to flashing (Figure 2a).

Flash excitation of 7.7×10^{-2} M cerous perchlorate, 2.0×10^{-2} M cupric perchlorate, and 0.05 M sodium sulfate at pH 2 produces large transient absorbance ($A = 0.140$ at 360 nm) which decays biphasically (Figure 2b). Higher transient absorbance changes are produced when the solvent is 1 M aqueous acetonitrile. The absorbance vs. wavelength spectrum of the transients present 100 μs after the flash (Figure 3a) has the same shape in water as it does in 1 M aqueous acetonitrile and is identical with that of authentic $\text{Ce}(\text{IV})$ at the same pH and sulfate concentration (Figure 3b). We assign the predominantly absorbing transient species in both solvents as

(10) "Handbook of Chemistry and Physics", 57th ed., CRC Press, Boca Raton, FL, pp D-141, D-142.

(11) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).

Table III. Second-Order Rate Constants for Transient Decay at Various CH₃CN Concentrations

$10^{-6} k$, $M^{-1} s^{-1}$	[CH ₃ CN], M	$10^{-6} k$, $M^{-1} s^{-1}$	[CH ₃ CN], M
7.78	0.1	1.84	0.7
4.20	0.2	1.25	1.0
2.88	0.3	0.272	3.0
2.35	0.5		

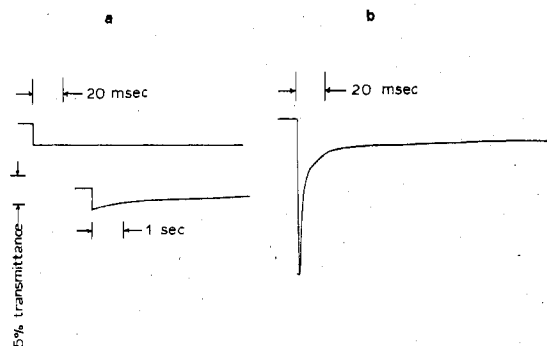


Figure 2. Transmittance vs. time oscillogram of the flash excitation of 7.7×10^{-2} M $Ce(ClO_4)_3$ in 0.05 M Na_2SO_4 in the absence (a) and presence (b) of 2.0×10^{-2} M $Cu(ClO_4)_2$. Monitoring wavelength = 360 nm.

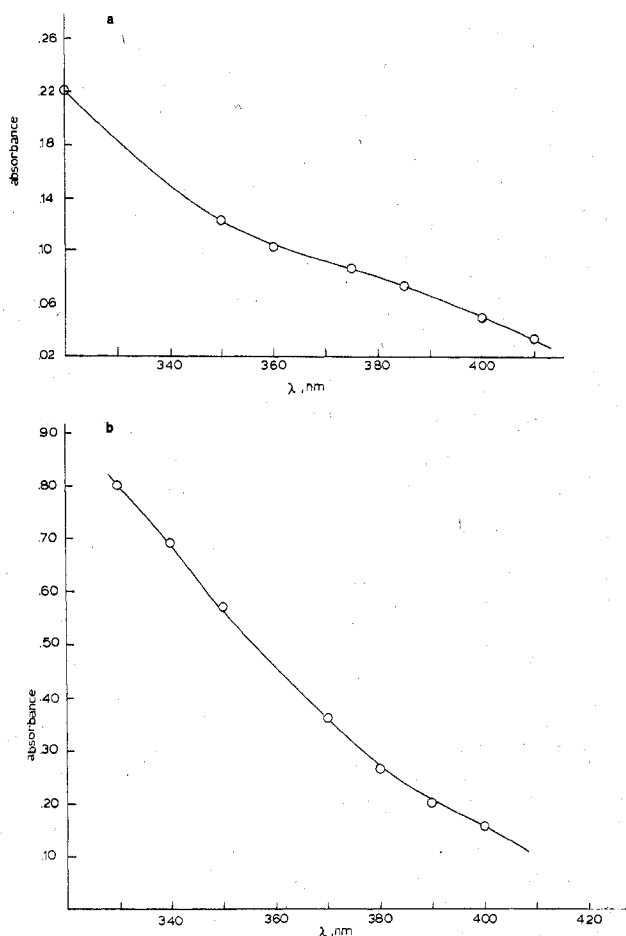


Figure 3. (a) Transient spectrum 100 μs after flash excitation of Ce^{3+} and Cu^{2+} in 0.05 M Na_2SO_4 (pH 2). (b) Absorption spectrum of authentic $Ce(IV)$ in 0.05 M Na_2SO_4 (pH 2).

$Ce(IV)$ produced by reaction 2. The decay of the transient absorbance is assigned to the reverse electron transfer, reaction 3.

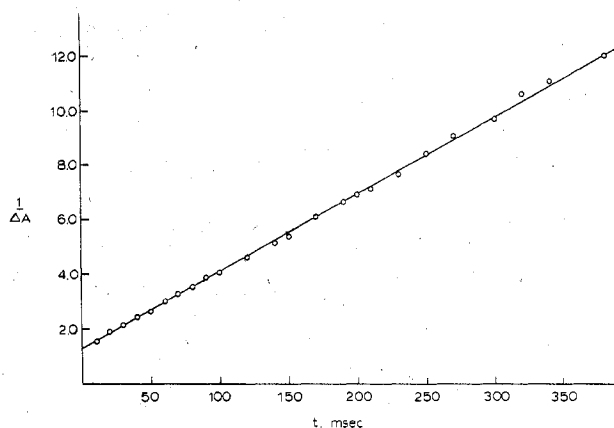
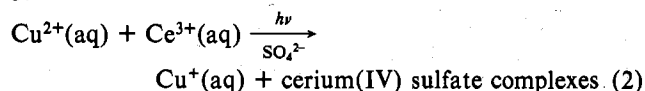
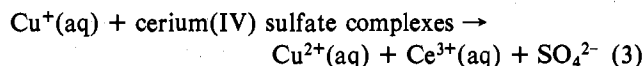


Figure 4. Kinetic plot (second order, equal reactant concentrations) for decay of transient produced by flash excitation of Ce^{3+} (7.7×10^{-2} M) and Cu^{2+} (4.4×10^{-2} M) in 0.05 M Na_2SO_4 (pH 2, 1.0 M CH_3CN). ΔA = transient absorbance at time t after the pulse - absorbance at $t = 10$ s after pulse. Monitoring wavelength = 360 nm.



Five observations support these assignments. (1) Parts a and b of Figure 3 show agreement. (2) In 1 M aqueous acetonitrile, the transient decay fits a second-order kinetics plot for systems in which both reactants are in equal concentrations. (Figure 4). (3) In 1 M aqueous acetonitrile, authentic Cu^+ (added to the solution as $Cu(CH_3CN)_4BF_4$) and $Ce(IV)$ (added to the solution as ceric ammonium sulfate¹²) increase the transient decay rate. For $[Ce(IV)] > 5 \times 10^{-6}$ M, an average second-order rate constant of $1.1 \times 10^6 M^{-1} s^{-1}$ is calculated from pseudo-first-order data ($Ce(IV)$ in large excess over $Cu(I)$); this value is in good agreement with the second-order rate constant, $1.25 \times 10^6 M^{-1} s^{-1}$, calculated from the slope of Figure 4 and $\epsilon_{Ce(IV)} = 3.06 \times 10^3 M^{-1} cm^{-1}$.¹³ (4) The transient decay time is strongly increased by high concentrations of acetonitrile (Table III). This is consistent with the expected lower reactivity of acetonitrile complexes of $Cu(I)$ in comparison with that of $Cu(H_2O)_4^{2+}$ toward oxidation processes.¹⁴ (5) The magnitude of transient absorbance is enhanced by sulfate anion, consistent with the higher extinction coefficients of ceric sulfate complexes (predominantly $Ce(SO_4)_3^{2-}$).¹⁵ Plots of (transient absorbance)/(path length) or (authentic $Ce(IV)$ absorbance)/(path length) vs. sodium sulfate concentration are linear and have the same slopes, within experimental error (Figure 5).

The effect of acetonitrile on the rate of reaction 3 and the yield of reaction 2 deserve comment. While there is no effect of CH_3CN concentration on the $Ce(IV)$ transient yield in the region between 0.1 and 3 M (insolubility of cerium salts above 3 M prevented a wider range of investigation), the yield 100 μs after the pulse in aqueous solutions containing no CH_3CN was lower by roughly 50%. Control experiments show that aqueous acetonitrile does not induce a new transient absorption when flashed with Ce^{3+} . One possible origin of the yield reduction is reaction of residual O_2 with Cu^+ , followed by rapid reaction of $Ce(IV)$ with HO_2 radical prior to the fastest ob-

- (12) Stock solutions of $Ce(IV)$ were prepared in 0.4 N H_2SO_4 and diluted to pH 2. This was done to avoid formation of inert polymeric hydroxy complexes.
- (13) The cell path length was 15 cm. The extinction coefficient of $Ce(IV)$ in 5.0×10^{-2} M SO_4^{2-} at pH 2 was determined from a Beer's law plot to be $3.04 \times 10^3 M^{-1} cm^{-1}$ at 360 nm. In 4 M H_2SO_4 we determined the extinction coefficient to be $3.51 \times 10^3 M^{-1} cm^{-1}$ at 360 nm. This latter value is close to that obtained by L. A. Blatz, *Anal. Chem.*, **33**, 249 (1961), $\epsilon = 3.52 \times 10^3 M^{-1} cm^{-1}$, in 1.25 N H_2SO_4 .
- (14) R. D. Gray, *J. Am. Chem. Soc.*, **91**, 56 (1969).
- (15) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

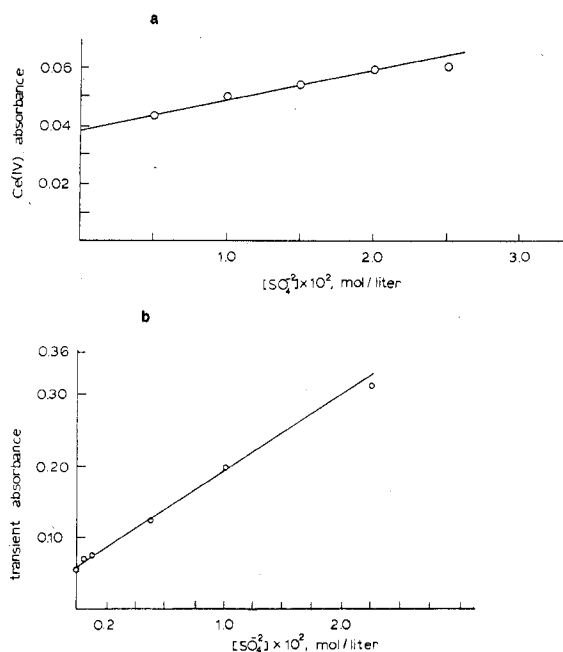


Figure 5. (a) Absorbance of authentic Ce(IV) as a function of $[\text{SO}_4^{2-}]$ (pH 2, path length = 1.0 cm): $\Delta[\text{Ce(IV)}]/\Delta[\text{SO}_4^{2-}] = (\Delta A/(\epsilon \times 1.0 \text{ cm}))/\Delta[\text{SO}_4^{2-}] = 1.05/\epsilon$. (b) Absorbance of transient as a function of $[\text{SO}_4^{2-}]$ (pH 2, path length = 15.0 cm): $\Delta[\text{Ce(IV)}]/\Delta[\text{SO}_4^{2-}] = (\Delta A/(\epsilon \times 15.0 \text{ cm}))/\Delta[\text{SO}_4^{2-}] = 0.89/\epsilon$.

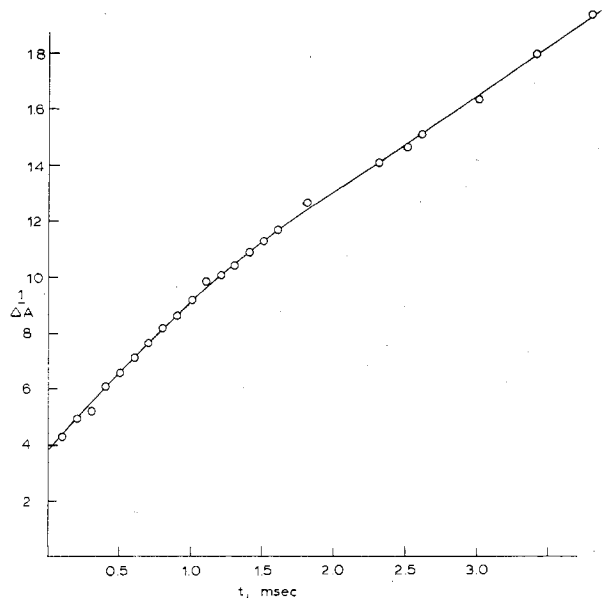


Figure 6. Kinetic plot (second order, assuming equal reactant concentrations) for decay of transient produced by flash excitation of Ce^{3+} ($6.91 \times 10^{-2} \text{ M}$) and Cu^{2+} ($1.0 \times 10^{-1} \text{ M}$) in $0.05 \text{ M Na}_2\text{SO}_4$ (pH 2, no acetonitrile).

ervation time of the spectrophotometer. Consistent with this is the downward curvature of the $1/(\text{transient absorbance})$ vs. time plot when no acetonitrile is present (Figure 6). The fast process still observable in the first 2 ms after the pulse may represent reaction of Ce(IV) with both Cu^+ and HO_2 .

Another unusual feature of the acetonitrile effect is that the second-order rate constant for reaction 3 varies linearly with $1/[\text{CH}_3\text{CN}]$ (Figure 7), implicating $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ as the reactive species, with $\text{Cu}(\text{CH}_3\text{CN})(\text{H}_2\text{O})_3^+$ unreactive under the experimental conditions. On the contrary, the rate of reaction of Cu(I) with molecular oxygen was found by Gray to be proportional to $1/[\text{CH}_3\text{CN}]^2$.^{14,16}

(16) For a summary of rate data for autoxidation of Cu(I) complexes see A. L. Crumbliss and A. T. Poulos, *Inorg. Chem.*, **14**, 1529 (1975).

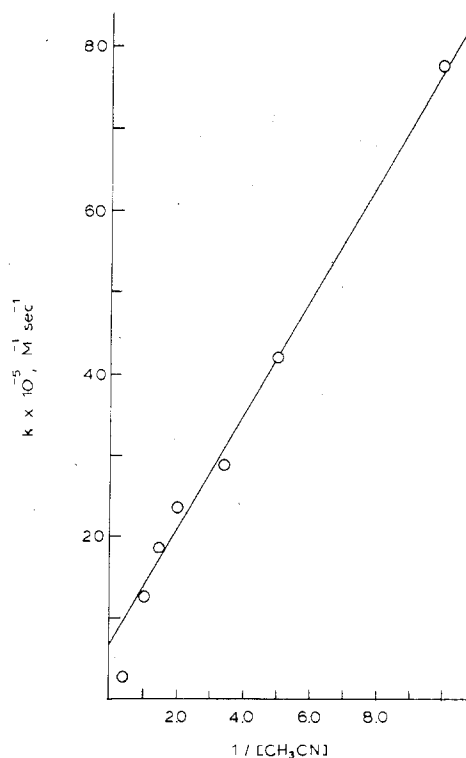
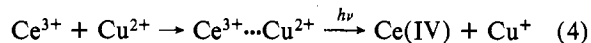
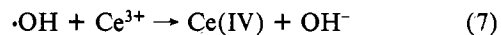
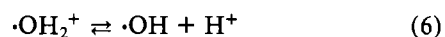
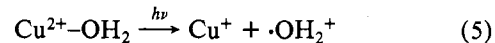


Figure 7. Second-order rate constants for transient decay as a function of $1/[\text{CH}_3\text{CN}]$.

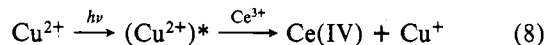
Possible excited-state origins of the photoreaction include (a) charge-transfer complexation between Ce^{3+} and Cu^{2+} (possibly through a sulfate bridge) (reaction 4), (b) photo-



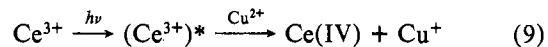
oxidation of water by coordinated Cu^{2+} (which absorbs light in the region of excitation), followed by interception of the hydroxyl radical with Ce^{3+} (reactions 5–7), (c) a long-lived



Cu^{2+} excited state as electron acceptor from Ce^{3+} (reaction 8), and (d) the Ce^{3+} excited state as electron donor and Cu^{2+}



as electron acceptor (reaction 9).



Mechanism a is disproven by the functional form of the dependence of photoreaction yield on Ce^{3+} concentration. A plot of Ce(IV) yield against concentration of added Ce^{3+} (Figure 8) in the presence of $1.0 \times 10^{-1} \text{ M Cu}^{2+}$ has a plateau at concentrations less than $2 \times 10^{-2} \text{ M}$. If mechanism a were correct, maximum yield would have been reached at Ce^{3+} concentrations greater than or equal to $1.0 \times 10^{-1} \text{ M}$. Also, the ultraviolet spectrum of a mixture of Cu^{2+} and Ce^{3+} does not show absorption different from the sum of component absorptions; charge-transfer complexes usually exhibit new spectral transitions.

For a test of mechanism b, the reactants were flashed in the presence of 1.0 M 2-propanol; 2-propanol is known to react irreversibly with $\cdot\text{OH}$ with a rate constant of $1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹⁷ No decrease of yield was observed, even at a Ce^{3+}

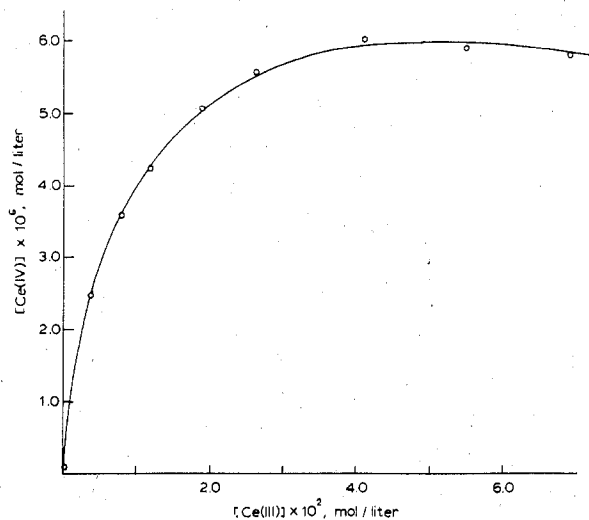


Figure 8. Yield of Ce(IV) produced by reaction 2 as a function of $[\text{Ce}^{3+}]$. For all points, $[\text{Cu}^{2+}] = 1.0 \times 10^{-1} \text{ M}$ and $[\text{SO}_4^{2-}] = 1.0 \times 10^{-1} \text{ M}$ (pH 2, $[\text{CH}_3\text{CN}] = 0$, constant-pulse intensity). $[\text{Ce(IV)}]$ was calculated from the transient absorbance at 360 nm 100 μs after the pulse by using $\epsilon_{\text{Ce(IV)}} = 3.06 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

concentration of $1.0 \times 10^{-3} \text{ M}$. In fact, a 10% increase in yield was observed, perhaps due to a medium effect on the efficiency of photoinduced electron transfer.

Mechanism c is implausible for two reasons. First, flash photolysis of Cu^{2+} in the presence of Fe^{2+} or Cl^- does not result in transient spectral changes identifiable as Fe^{3+} or Cl_2^- , despite the fact that both are more easily oxidized than Ce^{3+} . Second, the lack of emission or transient absorption changes¹⁸ upon excitation of aqueous Cu^{2+} implies an extremely short excited-state lifetime; the lifetime is presumably too short for excited Cu^{2+} to be intercepted by $7 \times 10^{-2} \text{ M}$ Ce^{3+} .

Mechanism d is reasonable. A plot of $1/(\text{Ce(IV) yield})$ against $1/[\text{Cu}^{2+}]$ is fairly linear (Figure 9), consistent with electron-transfer quenching of the cerous ion excited state by Cu^{2+} .¹⁹ The dynamic quenching of Ce^{3+} fluorescence by Cu^{2+} also supports mechanism d.

Flash Photolysis of Cerium(III) Sulfate. As noted above, a small absorption transient appears upon flash excitation of $\text{Ce}^{3+}(\text{aq})$ in 0.05 M NaSO_4 at pH 2 in the absence of $\text{Cu}^{2+}(\text{aq})$. The magnitude and lifetime of this absorption change at 360 nm match that of the small, slowly disappearing absorption change seen in the presence of Cu^{2+} . Because of this, we feel justified in assuming that the transient species observed in the absence of Cu^{2+} is not the precursor to the Ce(IV) produced when Cu^{2+} is present. The two photoreactions may, however, have a common excited-state origin. We are now investigating in more detail the composition of transients produced in flash photolysis of cerium(III) sulfate in acid solution because of its possible connection to the previously observed reduction of H^+ to H_2 by irradiation of Ce(III).⁴

Discussion

Despite the thermodynamic feasibility of electron transfer from excited $\text{Ce}^{3+}(\text{aq})$ to the one-electron acceptors used in this study, this phenomenon was observed only in the case of Cu^{2+} . This cannot be attributed to failure of the acceptors to deactivate the excited state since solutions were photolyzed

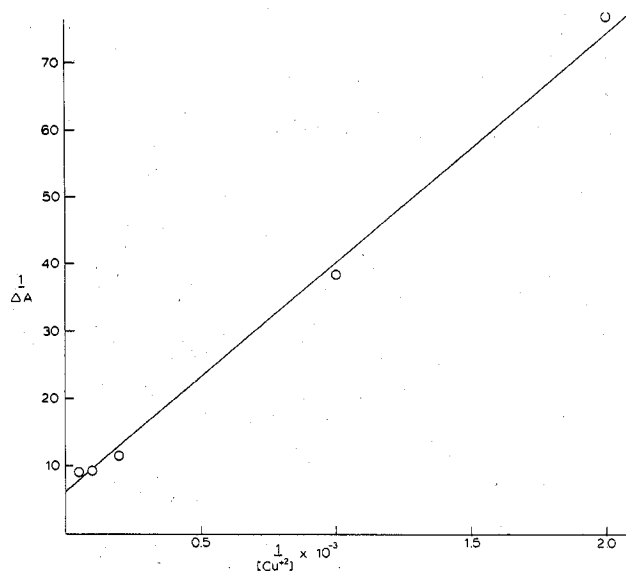


Figure 9. Reciprocal of transient absorbance for $[\text{Ce}^{3+}] = 7.7 \times 10^{-2} \text{ M}$ and $[\text{SO}_4^{2-}] = 5.0 \times 10^{-2} \text{ M}$ (pH 2, $[\text{CH}_3\text{CN}] = 0$) vs. reciprocal of $[\text{Cu}^{2+}]$.

under conditions of substantial Ce^{3+} emission quenching. Neither can absence of electron transfer be reasonably explained by a 100% efficiency of back electron transfer in the solvent cage; the geminate radicals ($\text{Ce(IV)}/\text{Fe}^{2+}$, $\text{Ce(IV)}/\text{Cr}^{2+}$, etc.) would be of the same charge (except at very high sulfate concentration), thus favoring high efficiency of cage escape in a polar solvent.²⁰

There are two reasonable explanations: (1) in the case of Fe^{3+} and Cr^{3+} , absorption of light by these species may prevent sufficient absorption by Ce^{3+} to obtain a high enough concentration of $(\text{Ce}^{3+})^*$ to give detectable photoreaction; (2) predominant deactivation of $(\text{Ce}^{3+})^*$ may occur by energy transfer. Since the ground and excited states of Ce^{3+} are of the same spin multiplicity ($S = 1/2$), the selection rule for energy transfer is simple: the acceptor must have a spin-allowed electronic transition of lower energy than the $(\text{Ce}^{3+})^* \rightarrow \text{Ce}^{3+}$ energy gap (88.7 kcal/mol).²¹ This is the case for Cu^{2+} , Fe^{3+} , Cr^{3+} , and Eu^{3+} .

The reported photoinduced electron transfer from Ce^{3+} to Cu^{2+} must arise from the first excited state of Ce^{3+} , since only the first absorption band (295 nm) is accessible to excitation through Pyrex glass.

Having established the photoreactive excited-state and primary products, it is now possible to more thoroughly examine factors which influence the quantum yield of reaction 2 such as solvent dielectric constant, solvent viscosity, added polyelectrolyte anions, magnetic field, temperature, and coordination of ligands to Cu^{2+} and Ce^{3+} .

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support to A.T.P. for research. Support from the Rutgers University Research Council (to A.T.P.) and the Department of Energy (to G.S.H.) is also gratefully acknowledged. A.T.P. wishes to thank Jane Rice and Frits van Dyck for construction of the flash cavity and the University of California—Santa Cruz for the loan of a power supply.

Registry No. Ce^{3+} , 18923-26-7; Cu^{2+} , 15158-11-9; Ce^{4+} , 16065-90-0; Cu^+ , 17493-86-6; Fe^{3+} , 20074-52-6; Cr^{3+} , 16065-83-1; Tl^{3+} , 14627-67-9; Eu^{3+} , 22541-18-0.

(17) J. H. Baxendale and A. A. Khan, *Int. J. Radiat. Phys. Chem.*, **1**, 11 (1969).

(18) Flash photolysis of cupric perchlorate does not produce significant transient absorption changes. To the authors' knowledge there is no report of cupric ion emission in fluid solution.

(19) N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings, Menlo Park, CA, 1978, p 251.

(20) R. C. Jarnagin, *Acc. Chem. Res.*, **4**, 420 (1971).

(21) This is the energy midpoint between the lowest energy absorption-band maximum and the fluorescence-band maximum in 0.4 M H_2SO_4 .