less the number of force constants to be fitted, and the sum is carried out over all observations.

In order to carry out this process, one must calculate the Jacobian. The elements of the Jacobian are found by calculating that part of the potential matrix which corresponds to the group of force constants, $K_j$, but in which the elements are not multiplied by $K_j$. This matrix is then transformed by the transformation which diagonalizes the full potential matrix (i.e., the eigenvector matrix). The derivative of frequency $\nu_i$ with respect to force constant $K_j$ is then proportional to the *ii* element of this latter matrix. This is equivalent to using the Hellman–Feyman theorem to find the derivatives. This method is much faster than a finite difference method. Computational details of the program NORCRD may be found in ref 16.

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# Photochemical Electron Transfer from Cerous Ions to the Lowest Excited State of Uranyl Ions in Aqueous Media, Studied by Laser Photolysis

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*(Received: August 3, 1981; In Final Form: May 24, 1982)*

A high-intensity beam of a Nd laser at 353.3 nm was used to produce the first excited state of the uranyl ion. Cerous ions, in acidic aqueous solutions, were found to react with it. The products of this reaction are ceric ions and uranium(V) ions. The absorption of the Ce(IV) ions was followed and the yields and decay kinetics of the ions were studied. The quantum yield of Ce(IV) formation is 0.85 ± 0.15, 1.00 ± 0.2, and 0.95 ± 0.25 in 0.1–0.5 M $H_2SO_4$, 0.57–2 M $HNO_3$, and 2 M $HClO_4$, respectively. The photochemical electron transfer is followed by a reaction of the products to produce the ground states of the initial reactants by a second-order reaction. The rate constant of this reaction is $5 \times 10^6$ $M^{-1}$ $s^{-1}$ in 0.1–0.5 M $H_2SO_4$, $\sim 2 \times 10^7$ $M^{-1}$ $s^{-1}$ in 2 M $HNO_3$, and $\sim 3 \times 10^7$ $M^{-1}$ $s^{-1}$ in 2 M $HClO_4$. The interpretation of the photochemical results is supported by pulse radiolysis experiments.

The interest in photochemical electron transfer has steadily increased in the last decade, particularly since it became evident that such reactions are of potential value in photochemical conversion and storage of solar light.[1,2] Most of the previous work on electron-transfer reactions involving excited states was carried out by using photosensitizers which are either organic molecules or coordination compounds with organic ligands.[1-3] Such systems may undergo irreversible side reactions.[4] It is therefore tempting to investigate purely inorganic systems which are completely reversible. As a model system we have chosen the uranyl ion (as the photosensitizer) together with the cerous ion (the electron donor). Uranyl ions have an optical absorption in the shorter wavelength of the visible spectrum and produce a relatively long-lived excited state,[5] $*UO_2^{2+}$. This excited state shows fluorescence and absorbance peaking at 510–520 and 590 nm, respectively.[5-7] The lifetime of this excited state depends on the medium, the nature of the acid present,[6] and the uranyl ion concentration.[7] The nature of $*UO_2^{2+}$ has been previously discussed.[8,9] Although the extinction coefficient of the ground state of the uranyl ion is relatively small, the combined properties of the ground state and the excited uranyl ions make it convenient to investigate this system.

The reactions of $*UO_2^{2+}$ with several inorganic ions have been previously studied. Matsushima et al.[10] have studied the quenching effect of both metal and inorganic ions on the luminescence of $*UO_2^{2+}$. They suggested redox quenching based on the relation between the quenching rate constant, $k_q$, and the redox potentials of the quenchers. Yokoyama et al.[11] have also proposed an electron-transfer mechanism in quenching of uranyl luminescence by halide ions, based on fluorescence measurements only. Burrows et al.[12,13] have reported a flash

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photolytic study of the photooxidation of some inorganic ions by the uranyl ion. They observed the formation of optical absorption which was attributed to the oxidized species ($I_2^-$, $Br_2^-$, $(SCN)_2^-$, $CO_3^-$, and $Mn^{3+}$). These results were produced by oxidation of $I^-$, $Br^-$, $CNS^-$, and $CO_3^{2-}$, and $Mn^{2+}$, respectively, upon the reaction with $*UO_2^{2+}$. This demonstrates for the first time a direct reversible photochemical electron transfer in the uranyl systems. The quantum yields were not reported;[12,13] however, measurements carried out recently in our laboratory[14] showed (except for $Mn^{2+}$) that they are of the order of a few percent and the major fraction of the quenching processes did not involve net electron transfer. In the case of $Mn^{2+}$ the quantum yield of electron transfer was found to be close to unity.[15]

The only other uranyl system where net photochemical reversible electron transfer has been found so far to be the major quenching reaction is the $UO_2^{2+}$–tris(bipyridine)ruthenium(2+) ($Ru(bpy)_3^{2+}$) in 2 M $H_3PO_4$.[16] We intend to expand this research to other uranyl systems, particularly inorganic ones. In the present manuscript we report results obtained in the uranyl–Ce(III) system. Again, previous work carried out in this system involved luminescence measurements only. Evidently, neither quantum yields for the possible reactions nor kinetics of the reactions between photochemical products was reported. Although electron transfer from Ce(III) to $*UO_2^{2+}$ was postulated,[10,13,17,18] it was not directly measured.

We have investigated this system under experimental conditions which enable us to follow the electron-transfer product Ce(IV). The relatively low and overlapping absorbances of $UO_2^{2+}$, $*UO_2^{2+}$, and Ce(IV) limit the range of conditions that could be used for the measurements. Nevertheless, concentration of the laser beam and fine tuning of the analytic system enable us to follow the absorbance of Ce(IV) in the range 370–390 nm and to measure its quantum yield and back-reaction with $UO_2^{2+}$ under various conditions.

## Experimental Section

*Materials.* Uranyl nitrate and uranyl sulfate were BDH (reagent grade) products and were usually used without further purification (since double recrystallization had no effect on $*UO_2^{2+}$ luminescent lifetime or on the results obtained in the pulse radiolysis experiments). Uranyl perchlorate was produced by dissolving uranyl carbonate (which was prepared by precipitating as a carbonate) in the appropriate amount of perchloric acid.

Cerous nitrate (Fluka, puriss), cerous sulfate (BDH reagent grade), and cerous perchlorate (Chemical City Co., purified) were used as received. The concentration of Ce(III) sulfate was determined spectrophotometrically by measuring the absorbance at 254 nm using a molar extinction coefficient of 685 in 0.4 M $H_2SO_4$.[19] Ceric sulfate and ceric ammonium nitrate were Merck's and Baker's (analytical grade) and were used as received. Ceric solutions were prepared from stock solutions which were kept up to 1 week in concentrated acid.[20] The concentrations of Ce(IV) in $Ce(SO_4)_2$ and $(NH_4)_2Ce(NO_3)_6$ stock solutions were determined by dilution of the stock solution to 0.4 M $H_2SO_4$ and measuring the absorbance at 320 nm ($\epsilon$ = 5600 $M^{-1}$ $cm^{-1}$ (ref 20)). The acids were $HNO_3$ (Palacid, Israel, A.R.), $HClO_4$ (70% Merck, A.R.), and $H_2SO_4$ (BDH, 98%, A.R.).

TABLE I: $UO_2^{2+}$-Ce(III) System in Aqueous $H_2SO_4$ Solution

| $[H_2SO_4]$, M | $10^{-5}k_2$, $s^{-1}$ | $10^{-7}k_3$, $M^{-1}$ $s^{-1}$ | $10^{-3}\epsilon^{380}$,[a] $M^{-1}$ $cm^{-1}$ | $\phi_{*UO_2^{2+}}\phi_{et}$ |
|---|---|---|---|---|
| 0.4-0.5 | 2.3 ± 0.2 | 5.0 ± 0.5 | 1.9 | 0.85 ± 0.15 |
| 0.09 | 4.2 ± 0.4 | 11 ± 1 | 1.8 | 0.80 ± 0.15 |

[a] Extinction coefficient at 380 nm.

*Apparatus.* Laser photolysis at 353.3 nm was performed by using a neodymium glass frequency tripled laser (Laser-Associated Model 505), which has been previously described.[21] In order to achieve high intensities of the laser beam required due to the relatively low absorbances of Ce(IV) (the light path was 1 cm), we concentrated the laser beam to a diameter of about 0.5 mm. This small diameter required that the analytical light be carefully aligned in order to achieve a good overlap with the laser exciting beam. The overlap was checked with aqueous solutions of tetrakis(sulfonatophenyl)porphyrin in which the laser pulse produced optical absorption of >96% at 460 nm. This shows that at least 96% of the analyzing light overlapped with the laser beam. Intensities of the Nd laser beam were varied by using neutral glass filters. The number of photons per pulse was measured with $Ru(bpy)_3^{2+}$, $Fe(ClO_4)_3$ in 1 M $HClO_4$ solution. The bleaching in optical density at 452 nm is due to the formation of the long-lived $Ru(bpy)_3^{3+}$ in the $HClO_4$–Fe system[22,23] and was used to calculate the laser intensity. The ion $Ru(bpy)_3^{3+}$ absorbs slightly at 452 nm in the $HClO_4$ system. The absorption was neglected.[24] For the measurement we used $\epsilon(\lambda = 452 \text{ nm}) = 14200$ $M^{-1}$ $cm^{-1}$ for $Ru(bpy)_3^{2+}$ and a quantum yield of unity.[22,23] Note that the actinometry could not be carried out under full laser intensity conditions due to the nonlinear effects in the actinometer.[23] Appropriate glass filters were usually used to protect the solution from excessive exposure to the analytical light. The laser intensity under our experimental conditions was up to 4 × $10^{-4}$ einstein $L^{-1}$ $pulse.^{-1}$ Most of the laser photolysis experiments were carried out by using the Nd laser set up, under the conditions described above. However, in several experiments the laser photolyses were performed at 337.1 nm by using a 10-ns, 0.5-mJ pulse of an $N_2$ Avco-Everett laser which has been previously described.[25]

Pulse radiolysis experiments were carried out by using a Varian Model V77158 linear accelerator. The basic feature of the system has been described before.[26] Unless otherwise stated, a 4-cm cell was used. The analyzing light

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was a 150-W Xe lamp. Most measurements were carried out at 380 nm. The accelerator was operated at 5 MeV and 200 mA. The pulse duration varied from 0.4 to 1.5 μs.

Absorption spectra were measured on Cary-14 or Beckman-DP-G spectrometers, before and after laser photolysis experiments. No permanent absorbance changes were detected.

The deoxygenation was carried out by bubbling ultrapure argon (Matheson) through the optical cells for 10 min prior to irradiation.

## Results

*Aqueous $H_2SO_4$ Solutions.* Aqueous solutions of $UO_2^{2+}$ were normally used at a concentration of 0.1–0.22 M in 9 × $10^{-2}$–0.5 M $H_2SO_4$. A pulse of the Nd laser at 353.3 nm induces fluorescence attributed to $*UO_2^{2+}$ according to reaction 1, with a peak at about 520 nm. This luminescence, in the absence of Ce(III), decays by a first-order rate law usually followed up to 90% reaction in accordance with reaction 2. The reaction rate constant, $k_2$ does not depend

$$UO_2^{2+} \xrightarrow{h\nu} *UO_2^{2+} \qquad (1)$$

$$*UO_2^{2+} \rightarrow UO_2^{2+} + h\nu' \qquad (2a)$$

$$*UO_2^{2+} \rightarrow UO_2^{2+} \qquad (2b)$$

on ($O_2$) (0–1 atm). It depends however on the acid concentration (Table I) and on the uranyl ion concentration, i.e., $k_2$ values of 1.2 × $10^5$, 2.5 × $10^5$, and 3 × $10^5$ $s^{-1}$ were measured in 0.8 N $H_2SO_4$ for 0.018, 0.1, and 0.18 M uranyl, respectively. At lower uranyl concentrations, $k_2$ decreases, similarly to the results reported by Benson, Cox, and Kemp[7] for perchloric acid. In view of the claim that a double fluorescence decay has been observed in several uranyl systems,[27] we carried out measurements using 0.15 and 0.008 M uranyl in 0.8 N $H_2SO_4$ where the kinetics of the fluorescence decay was followed up to 97% reaction, showing the same first-order law with no indication for a double decay. (These experiments were performed by using the 337-nm laser excitation.)

When $UO_2^{2+}$ is submitted to the laser pulse in the presence of Ce(III), quenching of the $*UO_2^{2+}$ takes place, and an enhanced decay of $*UO_2^{2+}$ emission is observed, accompanied by an optical absorbance at 370–390 nm. Optical absorbance measurements were carried out at these wavelengths due to the high absorption of the ground state of the uranyl ion outside this wavelength range, both in the presence and in the absence of Ce(III). The time resolution for the absorbance measurements was about 2 μs. This relatively long time resolution in the $N_2$ laser system resulted from relatively low absorbance changes which were distorted in the first mircosecond by noise (from pickup of scattered light). Under normal working conditions the effect of such noise is not observed beyond the first 20 ns. In our experiments, on the other hand, due to the small absorbance changes we were forced to collect and average up to 128 pulses, so that the initial pickup noise also became visible.

When $UO_2^{2+}$ is irradiated with the $N_2$ laser, an absorption signal builds up in the 370–390-nm region both in the absence and in the presence of Ce(III). In the absence of Ce(III) the signal builds up within the time resolution of the system to a value of $D$ = 1.7 × $10^{-3}$ per pulse and then decays in a few microseconds, with a lifetime similar to that of the decay of the $*UO_2^{2+}$ emission. This absorption is therefore attributed to that of the $*UO_2^{2+}$. However, when Ce(III) is also present, an additional absorption is also observed in the 370–390-nm range due to the production of Ce(IV). This absorption signal which is about 4 times greater than that in the absence of Ce(III) builds up predominantly in the first microseconds after absorption of the laser light with a half-lifetime approximately equal to that of the decay of the $*UO_2^{2+}$ emission under the same conditions. (Due to a combination of small absorbance changes, fast reactions, and relatively long time resolution, only semiquantitative kinetic calculations were done.) We attribute this process to reaction 3. This is supported by

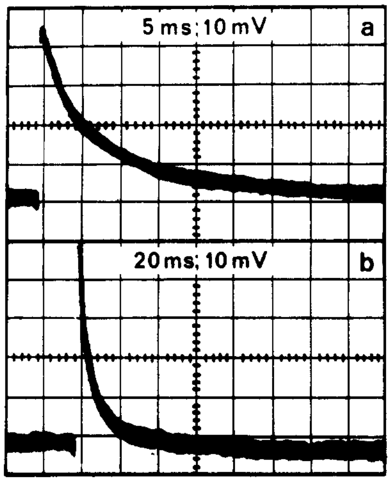

**Figure 1.** Typical laser-induced transient absorption of Ce(IV) (λ = 380 nm). [$UO_2^{2+}$] = 0.13 M, [Ce(III)] = 8.7 × $10^{-3}$ M (as sulfate) in 0.8 N $H_2SO_4$, Ar-saturated solutions. Light signal before the laser pulse was 160 mV.

$$*UO_2^{2+} + \mathrm{Ce(III)} \rightarrow UO_2^{+} + \mathrm{Ce(IV)} \qquad (3)$$

the second-order rate law by which the absorbance at 370–390 nm decays in the presence of Ce(III) in the time range of milliseconds, as compared to the first-order decay which takes place in the microsecond range when Ce(III) is absent. This will also be described in a later section. The quantum yield of electron transfer, $\phi_{et}$, can be calculated from eq 4, where $N$ is the number of photons per

$$D_\lambda = NF_u\phi_{yc}\phi_{*UO_2^{2+}}\phi_{et}\epsilon_\lambda \qquad (4)$$

pulse per liter, $F_u$ is the fraction of light absorbed by $UO_2^{2+}$, $\phi_{yc} = k_3[\mathrm{Ce(III)}]/(k_3[\mathrm{Ce(III)}] + k_2)$, $\phi_{*UO_2^{2+}}$ is the quantum yield of $*UO_2^{2+}$, and $\epsilon_\lambda$ is the extinction coefficient. For a system consisting of 0.13 M $UO_2^{2+}$ and 7.8 × $10^{-3}$ M Ce(III) we found that $\phi_{*UO_2^{2+}}\phi_{et}$ = 0.85 ± 0.15 ([$H_2SO_4$] was either 0.8 or 1 N). In these calculations, the steady-state extinction coefficients $\epsilon$ = 2.5 × $10^3$ and 1.9 × $10^3$ $M^{-1}$ $cm^{-1}$ were employed for λ = 370 and 380 nm, respectively. Oxygen had no effect on either $k_2$ or $k_3$ nor on the magnitude of the absorbance produced by the laser pulse. When working with high-intensity Nd laser pulse, considerably above the range reported, we observed nonlinear effects in the $UO_2^{2+}$ solution in the presence as well as in the absence of Ce(III). Such effects, the exact nature of which is not clear, resulted in a long-lived (time range of seconds) optical absorbance at 380 nm.

The absorption produced in the $UO_2^{2+}$–Ce(III) solutions decays within several milliseconds, obeying a second-order rate law, as might be expected if reaction 5 takes place (see Figures 1 and 2). The kinetics were measured in both 9 × $10^{-2}$ and 0.4 M $H_2SO_4$, yielding $k_5/\epsilon l$ = (2.45 ± 0.5) × $10^3$ and (3.3 ± 0.6) × $10^3$ $s^{-1}$, respectively, at λ = 380 nm.

$$UO_2^{+} + \mathrm{Ce(IV)} \xrightarrow{k_5} UO_2^{2+} + \mathrm{Ce(III)} \qquad (5)$$

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TABLE II: Photoproduction of Ce(IV) in $HNO_3$ Systems[a]

| $[HNO_3]$, M | $F_u$ | $10^{-5}k_2$, $s^{-1}$ | $10^{-7}k_3$, $M^{-1}$ $s^{-1}$ | $D_0^{380}$ | $\phi_{yc}$ | $\epsilon_{380}$,[b] $M^{-1}$ $cm^{-1}$ | $\phi_{*UO_2^{2+}}\phi_{et}$[c] |
|---|---|---|---|---|---|---|---|
| 0 | 0.9 | 6.9 | 200 | 0.00 | 1 | | |
| 0.2 | 0.84 | 5.2 | 1.9 | >0.01 | 0.7 | 320 | |
| 0.57 | 0.73 | 4.4 | 0.64 | 0.02 | 0.4 | 420 | 1.04 |
| 1 | 0.77 | 5.2 | 1.42 | 0.028 | 0.56 | 480 | 0.96 |
| 1.5 | 0.75 | 4.6 | 0.72 | 0.031 | 0.42 | 620 | 0.88 |
| 2 | 0.75 | 5.4 | 1.42 | 0.056 | 0.52 | 840 | 1.10 |

[a] The concentrations of $UO_2^{2+}$ and Ce(III) (added as nitrates) were 0.1-0.3 and $0.8 \times 10^{-2}$-$4 \times 10^{-2}$ M, respectively. The results were independent of $UO_2^{2+}$, Ce(III), and $O_2$ (0-1 atm) concentrations. [b] The extinction coefficient of Ce(IV) at 380 nm. [c] The results represent averages of a total of 20 experiments. The standard deviation was 20%.

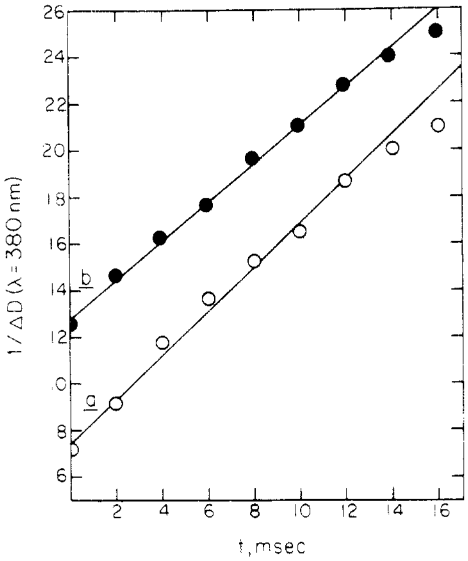

**Figure 2.** Second-order decay (reaction 5) of Ce(IV): (a) $N = 1.7 \times 10^{-4}$, (b) $N = 9.8 \times 10^{-5}$ einstein $L^{-1}$ $pulse^{-1}$. $[UO_2^{2+}] = 0.152$ M, $[Ce(III)] = 9.5 \times 10^{-3}$ M (as sulfate in 1 N $H_2SO_4$.

From this, $k_5$ was calculated to be $k_5 = (4.4 \pm 0.9) \times 10^6$ and $(6.3 \pm 1.1) \times 10^6$ $M^{-1}$ $s^{-1}$ at the low and high acid concentrations, respectively. The identification of reaction 5 as a second-order reaction is supported by the effect of the laser pulse intensity (Figure 2).

It should be noted that the formation of U(IV) from disproportionation of $UO_2^+$ is a relatively slow process.[28] Indeed, we found no evidence for U(IV) in our system. Had U(IV) formed, a slower stage of the U(IV) decay would have been observed due to the slowness of the reaction between Ce(IV) and U(IV) in $H_2SO_4$ systems.[29] The absorption of $UO_2^{2+}$ ions in the ground state limited the measurements to 370–390 nm. The product of reaction 3 had optical absorption which was identical with the steady-state spectrum of $Ce(SO_4)_2$ solution in the same media measured with the same detection system (of the laser setup). We conclude that the most reasonable way to account for these results is to suggest that the product of reaction 3 is indeed Ce(IV), formed with a quantum yield of about unity, being identical with the species existing in Ce(IV) solution in $H_2SO_4$. This means that Ce(IV) produced photochemically quickly reacted to form the same equilibrium mixture of Ce(IV) complexes with $H_2SO_4$ as exist under steady conditions. The identification of the product of reaction 3 is further supported by pulse radiolysis experiments, as will be seen later.

*Aqueous $HNO_3$ Solutions.* The $UO_2^{2+}$–Ce(III) system in aqueous $HNO_3$ media behaves similarly to the system in $H_2SO_4$ and the observation can be discussed in terms of reactions 1–5. Substitution of $H_2SO_4$ by $HNO_3$ resulted, however, with lower absorption signals, apparently due to lower quenching efficiencies and lower extinction coefficients of the Ce(IV). Therefore, the results, based on the measurements summarized in Table II are less accurate. In solutions containing Ce(III) and $UO_2^{2+}$ nitrates, without added $HNO_3$ we could not observe any Ce(IV) formation even when $\phi_{yc} = 1$.

TABLE III: Rate Constant $k_5$ in $HNO_3$ Systems

| $[HNO_3]$, M | $\epsilon_{380}$,[a] $M^{-1}$ $cm^{-1}$ | $10^{-4}k_5/\epsilon l$,[b] $s^{-1}$ | $10^{-7}k_5$,[b] $M^{-1}$ |
|---|---|---|---|
| 0.57 | 590 | 4.6 | 2.7 |
| 1 | 640 | 2.3 | 1.5 |
| 1.5 | 800 | 3.3 | 2.6 |
| 2 | 1080 | 2.1 | 2.8 |

[a] See footnote b in Table II. [b] The maximum deviation was 30%.

The decay of the Ce(IV) absorbance (measured at λ = 370 and 380 nm) obeyed a second-order rate law and the values of $k_5/\epsilon l$ were unaffected by the presence of $O_2$ or by the laser intensity (Table III).

In a previous communication[30] we reported that $O_2$ was produced by photolysis of $UO_2^{2+}$–Ce(III) in the presence of 2 M $HNO_3$, when a $RuO_2$ colloid was present. Additional steady-state experiments confirmed these earlier results; however, it was found that the oxygen originated from a small fraction of light that was absorbed by the Ce(III) due to a red shift in the Ce(III) spectrum in the presence of $HNO_3$. In other systems ($H_2SO_4$, $HClO_4$), where only $UO_2^{2+}$ absorbed the light, no $O_2$ was obtained. No $O_2$ was obtained in the $HNO_3$ system when a filter was used transmitting only the light that is absorbed by $UO_2^{2+}$. Pulse Nd laser studies on the $H_2SO_4$ system indicate that the mixture of $TiO_2$ and $RuO_2$ colloid system catalyzed the reaction between the products of reaction 5, while it had no effect on the lifetime of $*UO_2^{2+}$. Recently doubts have been raised as to whether $RuO_2 \cdot xH_2O$ colloid functions as a redox catalyst or not.[31] We believe that under our experimental conditions $RuO_2$ does not behave as a catalyst for $O_2$ production and thus reaction 5 describes the major pathway (in the presence or absence of the catalyst) for the decay of the electron-transfer products.

*Aqueous $HClO_4$ Solutions.* The perchlorate ion, $ClO_4^-$, is considered as a noncomplexing agent. We therefore studied the reaction between $*UO_2^{2+}$ and Ce(III) in $HClO_4$ aqueous solutions. The laser photolysis experiments were performed on systems consisting of $UO_2^{2+}$, Ce(III), $ClO_4^-$, and $H^+$. The phenomena observed were similar to those

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TABLE IV: Effect of $HClO_4$ on $k_2$ and on $k_3$

| $[HClO_4]$, M | $[UO_2^{2+}]$,[a] M | [Ce(III)],[a] M | $10^{-5}k_2$, $s^{-1}$ | $10^{-6}k_3$, $M^{-1}$ $s^{-1}$ | $D(\lambda = 370$ nm) |
|---|---|---|---|---|---|
| 0.5 | 0.13 | 0.405 | 2.9 | 1.3 | 0.01 |
| 1 | 0.165 | 0.45 | 1.8 | 2.6 | 0.014 |
| 2 | 0.195 | 0.45 | 1.5 | 3.4 | 0.011 |

[a] Added as a perchlorate salt. [b] Separate experiments in 0.5, 1 and 2 M $HClO_4$ showed that neither $k_2$ nor $k_3$ is affected by $[UO_2^{2+}]$ in the range 0.08–0.2 M nor by the presence of $O_2$.

described for the $H_2SO_4$ and $HNO_3$ systems; i.e., Ce(III) quenched the lowest excited state of $UO_2^{2+}$ by a process which yielded Ce(IV). The results are summarized in Table IV. The efficiency of electron transfer, $\phi_{*UO_2^{2+}}\phi_{et}$, was calculated by using eq 4. If the value of $\epsilon(\lambda = 380$ nm) = 265 $M^{-1}$ $cm^{-1}$ (which was obtained by a steady-state spectrophotometric technique) is used in eq 4, we obtain a value of 1.6 ± 0.3 for the above product. At 370 nm ($\epsilon$ = 356 $M^{-1}$ $cm^{-1}$) this product is 1.35 ± 0.3. Pulse radiolysis experiments (to be discussed later) gave $\epsilon(\lambda = 380$ nm) = 410 $M^{-1}$ $cm^{-1}$ and $\epsilon(\lambda = 370)$ = 550 $M^{-1}$ $cm^{-1}$. Inserting these values of $\epsilon$ into eq 4 yields $\phi_{*UO_2^{2+}}\phi_{et}$ = 1.05 ± 0.25 and 0.91 ± 0.22 for 380 and 370 nm, respectively. (The above results were measured in 2 M $HClO_4$.)

As in the other media, the back-reaction 5 is again a second-order reaction. In 2 M $HClO_4$ $k_5/\epsilon l$ ($\lambda$ = 370 nm) = (7 ± 3.5) × $10^4$ $s^{-1}$ and is unaffected by the presence of $O_2$. No accurate values of $k_5/\epsilon l$ could be determined at lower $[HClO_4]$ due to low absorption signals. The rate of reaction 5, however, seems to depend little, if at all, on $[HClO_4]$.

*Pulsed Radiolysis. Rate Constant of the Reaction between Ce(IV) and $UO_2^+$.* Pulse radiolysis measurements were carried out in 0.18 and 0.8 N $H_2SO_4$.

When only Ce(IV) (as sulfate) was present, bleaching of its absorbance at 380 nm was observed to take place after an electron pulse. This is demonstrated in Figure 3a. This bleaching is due to $H_2O_2$ produced as a molecular product and by OH radicals recombination in the bulk of the solution. In this system, hydrated electrons were quickly converted to H atoms by reacting with $H^+$. H atoms did not reduce Ce(IV) under our conditions—note the lack of any initial fast bleaching which can be attributed to H. (A fraction of the H atoms is expected to have reacted with OH while another fraction must have recombined to produce $H_2$.) When $UO_2^{2+}$ was also present, the relatively slow bleaching that is attributed to the reduction of Ce(IV) by $H_2O_2$ was preceded by a faster bleaching process as demonstrated in Figure 3b. Since $UO_2^{2+}$ can produce $UO_2^+$ by its reaction with the reducing radicals,[32,33] but cannot react with OH, we attribute this process to reaction 5. Although only semiquantitative measurements were carried out, we summarize the following observations: (a) The rate of the slower bleaching process, attributed to $H_2O_2$, did not depend on the presence of $UO_2^{2+}$. (b) The amount of bleaching by this process was somewhat less than that observed in the absence of $UO_2^{2+}$. It is possible that $UO_2^+$ removes some of the $H_2O_2$ by reacting with it or with its precursor, OH. Another possibility is partial decomposition of $H_2O_2$ in the presence of the uranyl ions which may form a compound with $H_2O_2$. (c) The faster bleaching process is not well separated in time from the slower process. However, its rate increases with [Ce(IV)] (up to twofold tested). From the half-lifetime, an average $k_5 \cong (4.1 \pm 0.6) \times 10^6$ and $(4.6 \times 0.7) \times 10^6$ $M^{-1}$ $s^{-1}$ could be estimated for 0.8 and 0.18 N $H_2SO_4$, respectively. This

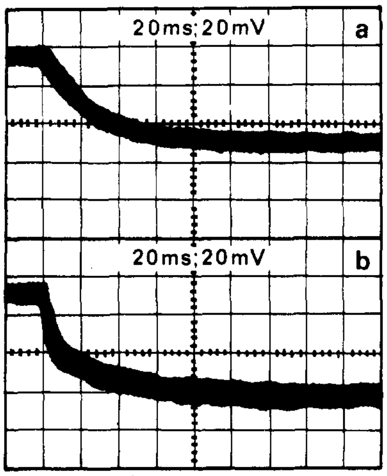

**Figure 3.** Bleaching of Ce(IV) absorption observed in pulse radiolysis of Ce(IV). [Ce(IV)] = 7.7 × $10^{-5}$ M in 0.18 N (pH = 1) $H_2SO_4$, Ar-saturated solutions, 1-μs pulse. (a) No $UO_2^{2+}$ present. Light signal before the pulse was 460 mV. (b) $[UO_2^{2+}]$ = 2.6 × $10^{-2}$ M. Light signal 530 mV.

value is in good agreement with that measured by the laser photolysis, indicating that in both systems the reaction involved the same species. This provides further support for the interpretation of the photochemical data.

*Extinction Coefficient of Ce(IV).* Pulse radiolysis was employed in order to measure the extinction coefficients of the Ce(IV) ions (the light path was 12.3 cm in the following experiments). Ce(IV) was produced by the oxidation of Ce(III) by the OH radicals which were formed by the irradiation ($G_{OH}$ = 2.7 radicals per 100 eV absorbed radiation). Dosimetry was carried out by using a 1 mM ferrocyanide solution, saturated with $N_2O$. In this system ferricyanide is produced with a $G$ value of 6, having $\epsilon$ of 1000 $M^{-1}$ $cm^{-1}$ at 420 nm. From the comparison between the absorbance of Ce(IV) and that of ferricyanide in the dosimeter, $\epsilon^{380}_{Ce(IV)}$ values of 2200 and 410 $M^{-1}$ $cm^{-1}$ were calculated for 0.8 N $H_2SO_4$ and 2 N $HClO_4$, respectively, and $\epsilon^{370}_{Ce(IV)}$ = 550 $M^{-1}$ $cm^{-1}$ for 2 N $HClO_4$. The reaction rate constant of OH with Ce(III) is not accurately known. However, we noticed that, under our experimental conditions, the formation of Ce(IV) ended within 2 μs or less. In addition, the magnitude of the absorption of the product Ce(IV) was linear with pulse intensity. This shows that, under our conditions, no radical reactions competed with the oxidation of Ce(III). Since the radical yield of OH may depend somewhat on the solutes' concentrations, the extinction coefficients of Ce(IV) ions may include a small systematic error. Nevertheless, it is evident that in the $H_2SO_4$ solutions pulse radiolysis yielded an extinction coefficient which is very close to that measured with a steady spectrophotometer. In $HClO_4$, on the other hand, there was a considerable difference. For the calculations of the quantum yield of Ce(IV) formation by photooxidation, we used the pulse radiolytic value. Had we used the steady-state extinction coefficient, a quantum yield which is considerably higher than 1 would have resulted, which is unreasonable. We believe that Ce(IV) ions produced upon oxidation may be different from the ions under

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equilibrium conditions. The pulse radiolysis technique can possibly provide information on the absorbance of the ion immediately after their formation.

No pulse radiolysis measurements were carried out in $HNO_3$, because the possible reactions between $e_{aq}^-$ and H with $HNO_3$ may complicate the interpretation of the absorbance changes.

## Conclusions

Photochemical electron transfer from Ce(III) ions to the lowest excited state of the uranyl ion takes place with a quantum yield of about 1. Despite the high negative value of the free energy for the back-reaction, its rate is relatively slow, $k \simeq 10^7\ M^{-1}\ s^{-1}$ depending somewhat on the nature of the acid present and on its concentration. Under steady illumination with a 100-W visible light source, the half-lifetime of the back-reaction between $UO_2^+$ and Ce(IV) is expected to be of the order of seconds. This system is therefore a potential candidate for photochemical generation of $O_2$, provided a suitable catalyst for water oxidation by Ce(IV) is found, which will be able to compete with the back-reaction. Attempts to use $RuO_2$ for this purpose were not successful.

*Acknowledgment.* We are indebted to Mr. G. Dolan and Y. Ogdan for maintenance and operation of the laser and linear accelerator systems and to Professor G. Czapski for helpful discussions.

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# Kinetics of Diffusion-Mediated Bimolecular Reactions. A New Theoretical Framework

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We undertake here a study of the applicability of the diffusion equation (DE) to bimolecular reaction kinetics. We point out that the standard procedure, in which one solves the DE subject to the so-called radiation boundary condition (RBC), does not directly give $k_0 \equiv k(0)$, the initial value of the rate coefficient $k(t)$ of a diffusion-mediated bimolecular reaction. To delimit the domain of validity of the DE approach, we derive both the DE and the RBC within a common framework based on the Lorentz model of random flights. We go on to fabricate a modified, but equivalent, form of the RBC which leads, in the $t \rightarrow 0$ limit, to the same expression for $k_0$ as that proposed by Noyes; we demonstrate that, with this amendment, the DE approach can be made congruent with the particle-pair standpoint of Noyes.

## I. Introduction

Let $k(t)$ denote the rate coefficient of a diffusion-mediated bimolecular reaction. We wish to point out that the conclusion, reached previously by Noyes,[1] Berg,[2] and us,[3] that the formal expression for $k(t)/k(0)$ deduced by Collins and Kimball (CK)[4] may be equated to that put forward by Noyes was based on an interpretation advanced first by Collins and Kimball and accepted by many subsequent authors—an interpretation that we recant here.

## II. Brief Survey of the Works of Collins and Kimball and Noyes

By dint of a lengthy argument, Collins and Kimball (CK) showed that $k(t)$ may be defined as

$$k(t) = \Phi_M(t)/c_0 = (4\pi R^2 D/c_0)(\partial c/\partial r)_{r=R} \quad (1)$$

where $c(r,t)$ is to be found by solving the diffusion equation (DE)

$$\partial c/\partial t = D\nabla^2 c \quad (2)$$

subject to the initial condition

$$c(r,0) = c_0 \quad (3)$$

and the radiation boundary condition (RBC)

$$D(\partial c/\partial r)_{r=R} = bc(R,t) \quad (4)$$

(The notation used above is that of CK, except that their $k$ has been replaced by $b$.) The solution for $c(r,t)$ satisfying eq 2–4 has been given, for the region $r > R$, by Carslaw and Jaeger:[5]

$$\hat{c}(r,t) \equiv \frac{c(r,t)}{c_0} = 1 - \frac{1}{r}\left(R - \frac{1}{B}\right)\left\{\operatorname{erfc}\left[\frac{r-R}{2(Dt)^{1/2}}\right] - \exp\{B^2Dt + B(r-R)\}\operatorname{erfc}\left[\frac{r-R}{2(Dt)^{1/2}} + B(Dt)^{1/2}\right]\right\} \quad (5a)$$

where

$$B \equiv b/D + 1/R$$
$$\operatorname{erfc}(x) = \frac{2}{\pi^{1/2}}\int_x^\infty du\, \exp\{-u^2\} \quad (5b)$$

Using this solution, CK calculated $\Phi_M(t)$ and concluded that it "remains finite even for $t = 0$, the limiting value being in fact $4\pi R^2 bc_0$"; that is to say, they arrived at the result

$$k(t)/k_i = \hat{c}(R,t) \quad (6a)$$

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