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Aqueous Solution of UCl_6^{2-} in O_2 Saturated Acidic Medium: An Efficient System To Scavenge All Primary Radicals in Spurs Produced by Irradiation

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Absorbance measurements find the yield of the oxidation of U(IV) to be $(8.75 \pm 0.05) \times 10^{-7}$ mol J^{-1} in the ^{60}Co γ radiolysis of aqueous solutions containing 4.4×10^{-3} mol L^{-1} U(IV) in the presence of O_2 saturated 2 mol L^{-1} Cl^- at pH = 0. This high value of oxidation yield suggests that all primary radicals formed by water decomposition are scavenged in these solutions. Simulations using a nonhomogeneous stochastic kinetic track model agree with the experimental results and are used to explain the mechanism for scavenging radicals and oxidation of U(IV).

Introduction

The direct ionization of aqueous solutions by highly energetic photons or accelerated particles leads to the decomposition of water molecules and the ultrafast formation of highly reactive radicals.[1] These radicals can initiate radiation damage in a wide variety of scenarios ranging from radiation therapy to nuclear power generation. Hydrated electrons, e^-_{hyd}, hydroxyl radicals, $^\bullet$OH, and hydrogen atoms, $^\bullet$H, produced by water decomposition are nonhomogeneously distributed in isolated spurs along the irradiation track.[2] Reactions of the sibling radicals are diffusion controlled and lead to decreasing yields on very short time scales, thereby varying the potential for radiation damage. The determination of the initial radiolytic yields (i.e., *G*-values) of the formation of these primary species on the picosecond time scale, and their evolution with time during the spur expansion, is the center of interest of many studies in the field of radiation chemistry.

Time-resolved measurements of radicals by pulse radiolysis and radical scavenging methods using steady-state radiolysis are two common techniques used to probe spur reactions. Moreover, these experimental methods are often coupled with model calculations employing stochastic or deterministic techniques to simulate the nonhomogeneous reactions to predict the temporal dependences of the radiolytic yields of the different radicals. Unfortunately, the measurement of radicals at very short times is problematic. Time-resolved techniques have proven to be accurate only in the determination of e^-_{hyd} yields. For other species, scavenger studies require a large and specific reactivity and high solute concentrations. In the framework of our research on the release of uranium in water under irradiation, studies found that an acidic solution of the UCl_6^{2-} complex constitutes an interesting system for determining the radiolytic yield of radicals induced by irradiation. Here, such a solution is shown to scavenge almost all the radicals formed by water radiolysis, resulting in a better understanding of spur reactions and providing a good estimate of the initial radiolytic yield, at the picosecond time scale, of the radicals formed by the radiolytic decomposition of water.

Experimental Section

Solutions containing 4.4×10^{-3} mol L^{-1} U(IV) (corresponding to scavenging at microseconds time range) in the presence of 2 mol L^{-1} Cl^- at pH = 0 (corresponding to scavenging at picoseconds time range) were prepared by a coulometric method from U(VI) solutions. The preparation of these solutions is based on previous studies and the details will be reported later.[3,4] Under these conditions (1 mol L^{-1} NaCl and 1 mol L^{-1} HCl) U(IV) exists as a complex in the form of UCl_6^{2-}. In the presence of air, the solutions are stable for a few days. However, they are eventually oxidized by O_2 very slowly. The UCl_6^{2-} solutions at pH = 0 exhibit characteristic absorption bands of U(IV) with maxima at 430, 495, 549, and 648 nm, as shown in Figure 1. Careful measurements determined the extinction coefficient of U(IV) under these conditions to be 62.3 L mol^{-1} cm^{-1} at 648 nm, which is slightly higher than the value reported in the literature for U(IV) in the absence of Cl^- (53.4 L mol^{-1} cm^{-1}).[5] Solutions saturated with O_2 (0.7×10^{-3} mol L^{-1}) were irradiated with γ-rays using a ^{60}Co source at a rate dose of 33.8 ± 0.4 Gy min^{-1} determined by Fricke dosimetry. For calculation of the oxidation yield, the dose values were corrected by the density of the irradiated UCl_6^{2-} solutions (1.04 kg L^{-1}).

Results and Discussion

The decay of the UCl_6^{2-} concentration (deduced from the absorbance measurement at 648 nm) is shown in Figure 2 as a function of the irradiation dose. For O_2 saturated solutions, the slope of the dependence of the concentration of the UCl_6^{2-} complex on the irradiation dose gives a radiolytic yield for the oxidation of U(IV) as $(8.75 \pm 0.05) \times 10^{-7}$ mol J^{-1} for O_2 saturated solutions. A concurrent increase in the formation rate

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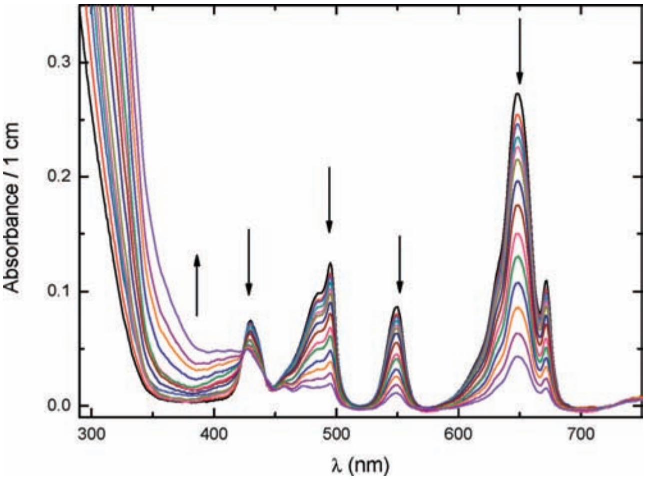

Figure 1. Absorption spectra in the ^{60}Co γ-irradiation of O_2 saturated solutions showing the radiolytic oxidation of U^{IV} into U^{VI}. The initial concentration of U^{IV} is 4.4×10^{-3} mol L^{-1}, optical path = 1 cm. Arrows indicate increasing dose.

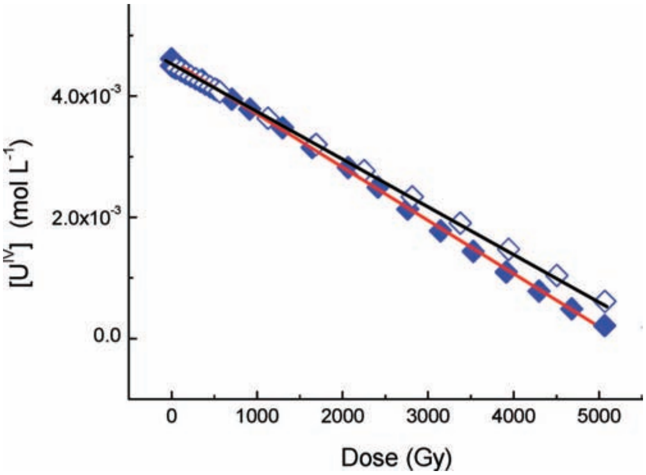

Figure 2. Concentration of U(IV) as a function of irradiation dose obtained from the experimental data of Figure 1 (close symbols) and from model simulation using FACSIMILE method (open symbols).

TABLE 1: Reactions and Rate Coefficients Used in the Submicrosecond Simulations[a]

				k (L mol^{-1} s^{-1})	ref
1	$e^-_{hyd} + e^-_{hyd} + 2H_2O$	→	$H_2 + 2OH^-$	5.5×10^9	9
2	$e^-_{hyd} + H_3O^+$	→	$H^\bullet + H_2O$	1.3×10^{10}	14
3	$e^-_{hyd} + H^\bullet + H_2O$	→	$H_2 + 2OH^-$	2.5×10^{10}	9
4	$e^-_{hyd} + {}^\bullet OH$	→	OH^-	3.0×10^{10}	9
5	$e^-_{hyd} + H_2O_2$	→	${}^\bullet OH + OH^-$	1.1×10^{10}	9
6	$H_3O^+ + OH^-$	→	$2H_2O$	1.4×10^{11}	9
7	$H^\bullet + H^\bullet$	→	H_2	7.8×10^9	9
8	$H^\bullet + {}^\bullet OH$	→	H_2O	7.0×10^9	9
9	$H^\bullet + H_2O_2$	→	${}^\bullet OH + H_2O$	9.0×10^7	9
10	${}^\bullet OH + {}^\bullet OH$	→	H_2O_2	5.5×10^9	9
11	$e^-_{hyd} + O_2$	→	$O_2^{\bullet -}$	1.9×10^{10}	9
12	$H^\bullet + O_2$	→	$HO_2^\bullet$	2.1×10^{10}	9
13	$H_3O^+ + O_2^{\bullet -}$	→	$HO_2^\bullet + H_2O$	3.8×10^{10}	9
14	${}^\bullet OH + Cl^-$	→	$ClOH^{\bullet -}$	4.3×10^9	12
15	$ClOH^{\bullet -}$	→	${}^\bullet OH + Cl^-$	6.1×10^9	12
16	$ClOH^{\bullet -} + H_3O^+$	→	$Cl^\bullet + 2H_2O$	2.1×10^{10}	13
17	$Cl^\bullet + Cl^-$	→	$Cl_2^{\bullet -}$	8.5×10^9	8
18	$Cl_2^{\bullet -} + Cl_2^{\bullet -}$	→	$Cl_3^- + Cl^-$	2.0×10^9	10
19	$H^\bullet + Cl_2^{\bullet -} + H_2O$	→	$H_3O^+ + 2Cl^-$	8.0×10^9	11
20	$U(IV) + HO_2^\bullet + H^+$	→	$U(V)O_2 + H_2$	1.0×10^7	9
21	$U(IV) + Cl_2^{\bullet -}$	→	$U(V) + 2Cl^-$	8×10^3	3
22	$U(IV) + Cl_3^-$	→	$U(V) + Cl_2^{\bullet -} + Cl^-$	8×10^3	
23	$U(IV) + H_2O_2$	→	$U(VI) + 2OH^-$	1×10^1	30

[a] The last three reactions with U(IV) occurs at longer time range.

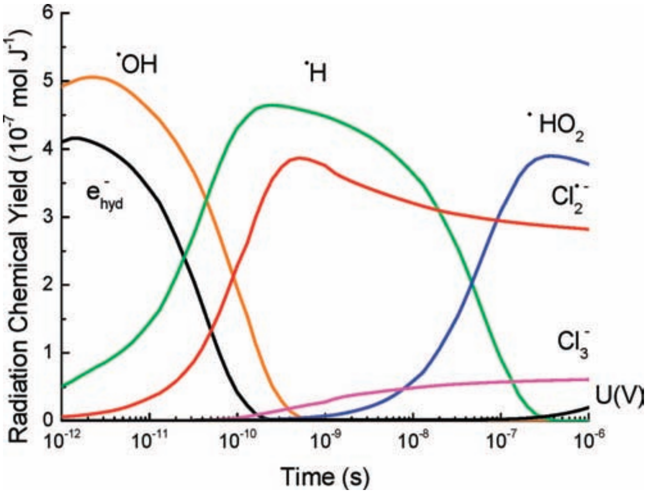

Figure 3. Simulation performed with a nonhomogeneous stochastic kinetic track model of the time dependences in the radiolysis of O_2 saturated solutions at pH = 0 and 2 mol L^{-1} Cl^-.

of U(VI) indicates that the U(IV) is stochiometry oxidized to U(VI). In fact, U(V) is known to be unstable in solution.[6] Under the present conditions, the U(VI) is mainly in the form of UO_2Cl_2. The high yield for the oxidation of UCl_6^{2-} complex is the result of the scavenging of all the radicals produced under irradiation. Such a high value finding has never been reported in radiation chemistry. In the case of the deaerated Fricke dosimeter for which there is no amplification step and ${}^\bullet H$, ${}^\bullet OH$, and H_2O_2 all oxidize react with Fe^{2+}, the oxidizing yield is reported to be $(8.5 \pm 0.12) \times 10^{-7}$ mol J^{-1}.[7]

The most important reactions to occur on the submicrosecond time scale under the conditions used in this work are listed in Table 1. Rate coefficients for these reactions are well-known and were obtained from a variety of sources.[8−14] Hydrated electrons are rapidly converted to ${}^\bullet H$ atoms in highly acidic medium by reaction 2. All of the other e^-_{hyd} reactions are negligible, especially the important spur reaction (4) between ${}^\bullet OH$ and e^-_{hyd}, which is the main radical termination step. In oxygenated solutions, ${}^\bullet H$ atoms are scavenged by molecular oxygen to form ${}^\bullet HO_2$ by reaction 12. ${}^\bullet OH$ radicals are efficiently scavenged by Cl^- and converted to $Cl_2^{\bullet -}$ into Cl_3^- by reactions 14−17. A small amount of disproportionation reaction of $Cl_2^{\bullet -}$ occurs within the microsecond time scale. The net result of these scavenging reactions is the production of the three species $Cl_2^{\bullet -}$, Cl_3^-, and ${}^\bullet HO_2$ that all readily oxidize U(IV).

The chemistry in the isolated spur was examined using a nonhomogeneous stochastic model previously developed.[15] Figure 3 shows that the short-time kinetics of the spur is essentially complete within one microsecond with the formation of the $Cl_2^{\bullet -}$, Cl_3^-, and ${}^\bullet HO_2$ and H_2O_2 oxidizing species. Oxidation of U(IV) to U(V) is just beginning on this time scale. The total oxidizing equivalent predicted by the simulations at 1 μs is 8.46×10^{-7} mol J^{-1}, which is slightly lower than the experimental value of 8.75×10^{-7} mol J^{-1}. Although this discrepancy is about 4%, it is significant enough to reevaluate the accepted values for the picosecond yields of radicals in the radiolysis of water.

Studies incorporating both experimental scavenging results with model predictions suggest that the picosecond yield for H_2 is about 0.16×10^{-7} mol J^{-1}, for H_2O_2 is essentially zero, and for the ${}^\bullet H$ atom is about 0.62×10^{-7} mol J^{-1}.[16−18] Time correlated spectroscopy studies of the picosecond radiolysis of water have directly observed the relative decay of the e^-_{hyd} from

10−20 ps to a few hundred nanoseconds. Careful calibration to absolute yields puts the picosecond yield of e^{-}_{hyd} at about 4.35×10^{-7} mol J^{-1}.[19−21] A recent reevaluation of the e^{-}_{hyd} extinction coefficient does not affect the short time extrapolated yield because it is based on a relative scaling of the observed time dependent absorbance change.[22] A direct spectroscopic observation study of the $^{\bullet}$OH radical proposed a yield of about 6.1×10^{-7} mol J^{-1} at 200 ps.[23] However, there was a large error in that work on the assignment of the $^{\bullet}$OH radical extinction coefficient and on the yield of e^{-}_{hyd} used for dosimetry. Later scavenger studies suggest an $^{\bullet}$OH radical yield closer to 5.4×10^{-7} mol J^{-1} would be more appropriate.[24] More recent picosecond pulse radiolysis studies have found the values of 4.4×10^{-7} and 5.0×10^{-7} mol J^{-1} for the yield of $^{\bullet}$OH at 100 ps based on the extinction coefficients for e^{-}_{hyd} of 19 000 and 22 700 L mol^{-1} cm^{-1}, respectively.[14] The value of 9.69×10^{-7} mol J^{-1} is predicted at 1 ps by the model simulations, which agrees well with the experimental measurement of this work of 8.75×10^{-7} mol J^{-1}. Uncertainty in the short-time measurement of the $^{\bullet}$OH radical yield seems to be a limiting factor in the determination of the radiolytic decomposition of water at 1 ps. Additional oxidation of the U(IV) due to the direct absorption of energy by Cl^{-} is assumed to be negligible at the concentration of Cl^{-} used in this work as suggested by previous studies.[25]

The long-time yield for the oxidation of U(IV) is calculated using a homogeneous deterministic model in which the coupled differential equations for the various reactions were stepped in time by using FACSIMILE.[26−28] Water radiolysis reactions were as proposed by Elliot and McCracken.[29] This model incorporates about 80 equations for water radiolysis and includes the chloride chemistry of Table 1 and oxidation of the U(IV) by $Cl_2^{\bullet -}$, Cl_3^{-}, and $^{\bullet}HO_2$. Input yields for each of the reactive species were obtained from the microsecond yields of the nonhomogeneous model, as shown in Figure 3. The calculated dose-dependence for the oxidation of U(IV) is shown in Figure 2 and agrees well with the experimental results, suggesting that there are no major additional reactions of U(IV). The small variation between experiment and model at the high dose seems to be due to secondary reaction that slightly decreases the oxidizing equivalents for U(IV). Significant uncertainties exist for several rate coefficients and also in the mechanisms for the slow oxidation reactions converting U(IV) to U(VI). Slight modifications in the solute concentrations coupled with model calculations may be able to minimize secondary reactions. The results presented here strongly suggest that the oxidation of U(IV) could be a very useful system for measuring the total radical yields produced in the radiolysis of water.

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