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Scavenging of the Precursor to the Hydrated Electron by the Selenate Ion

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Electron pulse radiolysis experiments have been used to investigate the scavenging of the precursor to the hydrated electron in aqueous solutions of selenate, a relatively good scavenger of the prehydrated electron. The yields of the total electrons scavenged are compared to those obtained with cadmium, a hydrated electron only scavenger. At scavenging capacities greater than about 10^6 s^{-1} (1 mM selenate), the yield of total electrons is greater with selenate than with cadmium. The results are thought to be due to the scavenging of the prehydrated and hydrated electrons by the selenate anion, whereas the cadmium scavenges only the hydrated electron. Scavenging of the prehydrated electron occurs at relatively low concentrations of selenate, and other similarly reactive solutes may have noticeable effects on the outcome of water radiolysis.

Introduction

The hydrated or aqueous electron, e_{aq}^-, produced in the radiolysis of water has been studied extensively, and its chemistry is well defined.[1] However, much less is known about the chemical consequences of its precursor, e_{pre}^-, the prehydrated electron. Several early experimental investigations suggested that the precursor to the hydrated electron could be involved in radiation chemical processes other than the production of the hydrated electron.[2−5] Recent measurements give it a lifetime of about 240 fs.[6] There is some discrepancy in the estimates of this lifetime,[7] but its value is on this order of magnitude so the precursor to the hydrated electron will react with most solutes only when they are at extremely high concentrations. However, such conditions are commonly found in natural or industrial conditions. Furthermore, some solutes have extremely high rate coefficients for reaction with the prehydrated electron and not with the hydrated electron. Either of these conditions may lead to noticeable effects on the subsequent radiation chemistry. Detailed track model calculations suggest that molecular hydrogen formation and the yield of the hydrated electron can be effected by even low concentrations of selected scavengers.[8] Therefore, it is extremely important to experimentally verify if scavengers for the prehydrated electron can influence the yields of other species found in water radiolysis.

The yield of e_{aq}^- in scavenger solutions has been measured by Hunt and co-workers[9,10] and by Jonah et al.[5,11] at the picosecond time scale. A scavenger-dependent parameter, C_{37}, is used to describe the fraction of the surviving hydrated electrons, f, at a particular time as a function of the scavenger concentration [S] using the empirical equation $f = \exp(-[S]/C_{37})$. The absolute magnitude of the C_{37} value is not as important as the relative rate coefficient for scavenging the prehydrated electron to that for the hydrated electron. In the presence of the selenate ion, it was found that the fraction of surviving electrons is lower than that predicted by a simple time-dependent rate coefficient mechanism.[5] The rate coefficient of the reaction between the selenate ion and the hydrated electron (1) has been measured,[12] whereas that for the reaction with the prehydrated electron (2) has been calculated using the C_{37} value.[8]

$$SeO_4^{2-} + e_{aq}^- \rightarrow SeO_3^- \qquad k_1 = 1.1 \times 10^9\ M^{-1}\ s^{-1} \qquad (1)$$

$$SeO_4^{2-} + e_{pre}^- \rightarrow SeO_3^- \qquad k_2 = 1 \times 10^{13}\ M^{-1}\ s^{-1} \qquad (2)$$

At sufficiently high concentrations, one would expect that the selenate ion could scavenge prehydrated electrons before they decay. Furthermore, Monte Carlo track modeling simulations predict that the scavenging of the prehydrated electron should be evident even in dilute solutions. The high reactivity of selenate toward the prehydrated electron makes it possible to perform suitable experiments while avoiding complicating factors such as direct radiation effects that occur at high solute concentrations.

In this work, the concentration of the selenate ion is varied over a wide range and the yield of the SeO_3^- product is determined. The results obtained with the selenate ion are compared to those obtained with the cadmium ion, which is used at low concentration as a hydrated electron-only scavenger, and to model calculation predictions.

Experimental Section

Pulse radiolysis experiments were performed using a linear electron accelerator, LINAC (TB-8/16−1S), with single pulse length of about 5 ns. The dose was varied from 2.8 to 18 Gy per pulse as measured with the thiocyanate dosimeter using $\epsilon_{472} = 7580$ dm^3 mol^{-1} cm^{-1} and $G = 6.14$ molecules/100 eV. A quartz sample cell of 1 cm path length was used, and the irradiations were performed at room temperature. The analyzing light was provided by a 1000 W high-pressure Xenon lamp (Oriel 6140) and directed on a Spex 270M monochromator with an attached photomultiplier (Stanford Research System, model PS310). The signal was sampled and stored using a LeCroy 7200A fast digital storage oscilloscope. The software processing of the signal has been described elsewhere.[13] The kinetics were followed at time scales between 200 ns and 200 μs (full scale) after the LINAC pulse.

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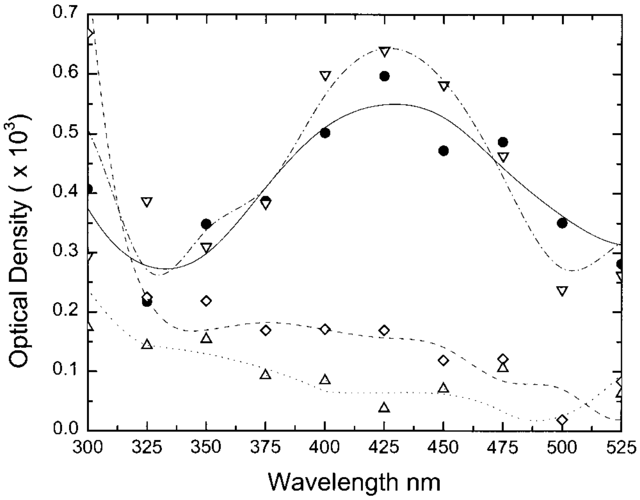

Figure 1. Absorption spectra at about 1.5 μs of 0.1 mM selenate solutions with different scavengers: (●) N_2-saturated solution; (◇) air-saturated solution; (△) N_2O-saturated solution; (▽) N_2-saturated solution in the presence of 0.1 M *t*-ButOH. Dose ≈ 18 Gy.

Sodium selenate decahydrate (Na_2SeO_4, Aldrich, 99.99%) and cadmium perchlorate ($Cd(ClO_4)_2$, Aldrich, 99.99%) were used as received. The solutions are prepared using water from a Milli-Q UV system. The pH adjustments were made by the addition of NaOH or $HClO_4$ or using a borate buffer ($Na_2B_4O_7$ Aldrich, 99%) and measured with an Orion Research pH meter. The concentration of selenate was varied from 0.1 mM to 1 M; that of cadmium perchlorate varied from 0.01 to 20 mM. For selenate concentrations higher than 0.1 M, the dose has been corrected for the change in the electron density of the solution.

Results and Discussion

Selenate Radiolysis. The characteristics of the SeO_3^- radical anion have been studied by different authors with some discrepancies between the results.[13−16] Transient spectra of selenate solutions were measured between 300 and 800 nm under different chemical conditions. Figure 1 shows the spectrum of deaerated 0.1 mM sodium selenate aqueous solution at 1.5 μs following the LINAC pulse. The small absorbances in this system make it difficult to obtain clean spectra, but an absorption peak with a maximum at 425 nm can be observed. The spectra of aerated and N_2O-saturated 0.1 mM selenate solutions are shown for comparison. It can be seen that the peak at 425 nm disappears in N_2O- and air-saturated solutions due to the scavenging of the hydrated electrons. Figure 1 also shows the spectrum of an N_2-saturated solution of 0.1 mM selenate with 0.1 M of *t*-butanol, *t*-ButOH. The absorption peak at 425 nm is observed in the presence of an OH radical scavenger like *t*-ButOH. Therefore, the absorption peak at 425 nm has been attributed to the product of the reaction between the hydrated electron and the selenate ion, the SeO_3^- radical anion, in agreement with the data in the literature.[14−17] The spectrum obtained with N_2O-saturated solutions does not show any additional bands in the range of wavelengths studied. There has been a report of absorption at 525 nm due to the reaction of the selenate ion with the OH radical.[17] A number of different systems were examined in order to confirm this observation, but due to the very small absorbances, it was impossible to unambiguously attribute this peak to the OH radical reaction.

At high concentrations, the selenate ion scavenges the hydrated electron and its precursor,[5] but the spectrum of 1 M deaerated sodium selenate, Figure 2, does not show any supplementary band compared to the very diluted solutions where no prehydrated electron scavenging occurs. Moreover, the absorption at 425 nm increases steadily with increasing selenate concentration. Therefore, it is assumed that the product formed by the reaction of the selenate ion with the precursor to the hydrated electron is either the SeO_3^- radical anion or it is transformed very quickly to this species.

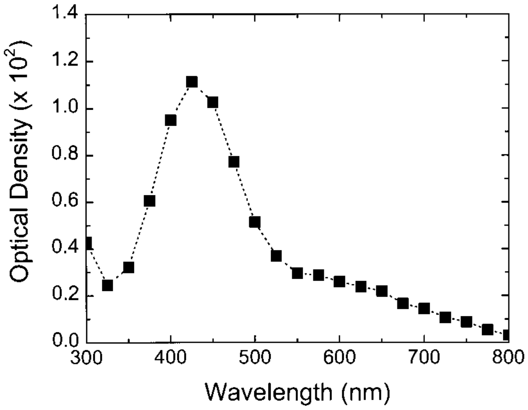

Figure 2. Absorption spectrum of a deaerated 1 M sodium selenate solution 1 μs after a single pulse: dose ≈ 18 Gy; pH 9.

The kinetics of the formation of the absorbance peak at 425 nm corresponds to the disappearance of the hydrated electron by reaction 1. The rate coefficient for this reaction was determined to be $k_1 = (1.4 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$ in agreement with the published data.[12] No ionic strength effect was observed on the pseudo-first-order decay of the hydrated electron with up to 0.2 M of sodium selenate. (Experimental determination of the rate above this concentration could not be performed with the current instrumentation.) Therefore, a constant value for the rate coefficient was used throughout the selenate concentration range. The absence of an ionic strength effect on the rate coefficient for the hydrated electron has been observed by Jonah et al. for IO_4^- and CrO_4^{2-} anions.[18] It was proposed that the electron reacts by a tunneling mechanism rather than by diffusion in the case of these large anions where the reaction radii are larger than the distance at which the Coulombic interaction equals *kT*, the product of the Boltzmann constant and temperature. According to Jonah et al.,[5] the reaction radii for SeO_4^{2-}, IO_4^-, and CrO_4^{2-}, anions are 9.8, 11.0, and 11.5 Å, respectively.

The SeO_3^- radical disappears by a second-order process with a rate coefficient of $2k_3 = (1.5 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$ in reasonable agreement with the literature value of $1.04 \pm 1 \times 10^9\ M^{-1}\ s^{-1}$.[16] This decay has been attributed to the disproportionation of Se(V).[14,16]

$$SeO_3^- + SeO_3^- \rightarrow Se(IV) + Se(VI) \qquad (3)$$

It was beyond the scope of the present work to examine this reaction further.

According to Tamba and Badiello, the SeO_3^- radical undergoes a protonation equilibrium at a pH between 6 and 10.[14]

$$HSeO_3 \rightleftarrows H^+ + SeO_3^- \qquad pK_4 = 7.4\ (\text{ref } 14) \qquad (4)$$

The two species both absorb at 425 nm, but the extinction coefficients are very different. Figure 3 shows the variation of the extinction coefficient as a function of pH as measured in deaerated solutions of 1 mM Na_2SeO_4. It is assumed that $G(SeO_3^-) = G(e_{aq}^-) = 2.65$ molecules/100 eV. There is good agreement between the present results and those by Tamba and

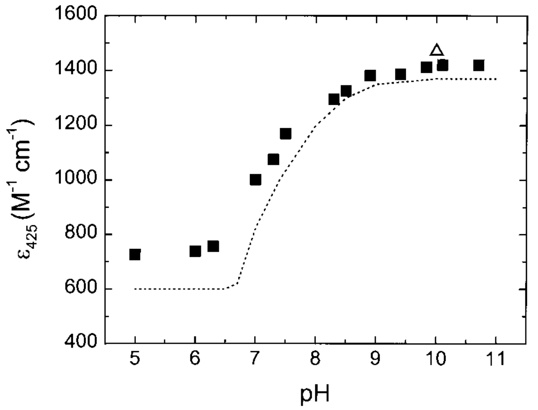

Figure 3. Change in extinction coefficient at 425 nm as a function of pH: (■) this work (1 mM Na_2SeO_4 saturated with N_2, dose ≈ 2.8 Gy, pH 6); (- - -) ref 14; (△) ref 16.

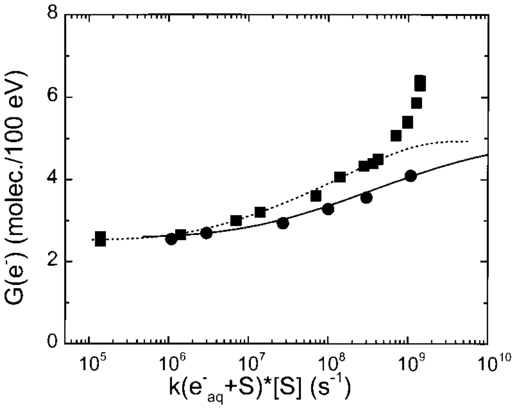

Figure 4. Total electron yield ($G(e^-) = G(e_{aq}^-) + G(e_{pre}^-)$) measured as function of the scavenging capacity of the selenate and cadmium ion: (■) SeO_4^{2-} and (●) Cd^{2+}, this work (dose ≈ 18 Gy for selenate and 2.8 Gy for cadmium); dotted line and solid line show Monte Carlo track simulations for the selenate anion and the cadmium cation, respectively (ref 8).

Badiello at high pH.[14] Their extinction coefficients at pH between 5 and 6.5 are somewhat lower than those measured in this experiment. This result of course influences the position of the pK of equilibrium 4, which is now estimated to be pK_4 = 7.

Electron Scavenging. The variation of the yield of the SeO_3^- radical anion was used as a measure of the electron yield according to reactions 1 and 2. The yield of the total electrons, prehydrated and hydrated, is set equal to $G(e^-) = G(e_{aq}^- + e_{pre}^-) = G(SeO_3^-)$. By increasing the concentration of the selenate, one is probing the radiation chemistry at earlier times in the spurs produced by the energy deposition of the incident high-energy electrons. Figure 4 shows the results for the total electron yield as a function of the scavenging capacity of the selenate for hydrated electrons. The scavenging capacity is defined as the product of the solute concentration and the rate coefficient for the scavenging reaction. It is essentially the pseudo-first-order rate coefficient, and its inverse is the lifetime of the hydrated electron with respect to the scavenging reaction. Note that with increasing selenate concentration the pH also increases. The absolute electron yields were determined from the absorbance by taking into account the change in the extinction coefficient as given in Figure 3.

The electron yields are relatively constant at low scavenging capacity because the scavenging reaction is occurring at long times where the spur structure has dissipated. At these times, the surviving hydrated electrons are essentially homogeneously dispersed throughout the medium and second-order reactions of the transients species produced in the water dissociation are too slow to notice experimentally. As the scavenging capacity increases above about 10^6 s^{-1} (1 mM selenate), the yield of electrons increases because the scavenging reaction can compete with intraspur radical combination reactions. However, it can be seen in Figure 4 that the increase in electron yield with increasing scavenging capacity is greater than that expected for the hydrated electron alone.[8,19] This difference is believed to be due to scavenging of the precursor to the hydrated electron.

It can be seen in Figure 4 that the results with selenate match well with Monte Carlo track simulations on this system that take into account the contribution of the precursor to the hydrated electron.[8] The agreement is good up to about 3×10^8 s^{-1} (0.3 M selenate). The rapid increase in SeO_3^- yield above this point is possibly due to a direct radiation effect on the selenate ion. At 1 M concentration, roughly 14% of the energy is absorbed by sodium selenate. Jonah et al.[11] estimated the initial yield of hydrated electrons and of prehydrated electrons to be 4.6 ± 0.2 and 5.4 molecule/100 eV, respectively. Our results are consistent with these values even with a contribution due to direct radiation effect on the selenate ion.

Although the results with selenate match well with the model predictions, it was thought to be desirable to eliminate any unknown systematic errors that may have unexpectedly occurred in determining absolute electron yields. Therefore, a separate set of experiments with deaerated aqueous solutions of cadmium perchlorate was performed. A comparison of the results for cadmium with those obtained with selenate will better expose any contribution to the total electron yield due to the prehydrated electron.

The cadmium divalent cation, Cd^{2+}, is another good prehydrated electron scavenger,[5,11] but it also has a relatively high rate coefficient for its reaction with the hydrated electron (5).

$$Cd^{2+} + e_{aq}^- \rightarrow Cd^+ \qquad k_5 = 4.8 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (5)$$

$$Cd^{2+} + e_{pre}^- \rightarrow Cd^+ \qquad k_6 = 2.8 \times 10^{12}\ M^{-1}\ s^{-1} \qquad (6)$$

Only at very high cadmium concentrations will there be any significant contribution to the total electron yield by the prehydrated electron. The product of the hydrated electron with the Cd^{2+} cation was monitored at 300 nm. The measured extinction coefficient was found to be $\epsilon_{300} = 14\,000$ M^{-1} cm^{-1}, in agreement with the literature.[19] The measured rate coefficient for the reaction with the hydrated electron was found to be $k_5 = 4.8 \times 10^{10}$ M^{-1} s^{-1}, in excellent agreement with the published data.[20-22] Wolff et al. have shown that the rate coefficient for the reaction of the hydrated electron with $Cd(ClO_4)_2$ does not depend on the ionic strength of the solution for concentrations up to 0.2 M.[4] The maximum concentration of $Cd(ClO_4)_2$ used in this work was 0.02 M, and no correction for the ionic strength effect was necessary.

The cadmium monovalent cation, Cd^+, in concentrated solutions (0.2 M) is known to decay within the spur. However, in these experiments, the maximum concentration of $Cd(ClO_4)_2$ used was 0.02 M and the yield of Cd^+ is probably only due to scavenging of the hydrated electron. The Cd^+ absorbance signal decayed by a second-order process with a rate constant of the order of 1×10^{10} M^{-1} s^{-1}, which can be attributed to the following decay processes.

$$\mathrm{Cd^+ + Cd^+ \rightarrow Cd_2^{\,2+}} \qquad k_7 = 2.1 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ ^{20} \tag{7}$$

$$\mathrm{Cd^+ + OH \rightarrow Cd^{2+} + OH^-} \qquad k_8 = 2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}\ ^{23} \tag{8}$$

The variation in Cd^+ yield with the scavenging capacity of the solution agrees well with that expected from scavenging of the hydrated electron only (Figure 4). It is clear that even at relatively low scavenging capacities the selenate ion scavenges more electrons than the cadmium ion. The difference is attributed to the scavenging of the precursor to the hydrated electron by the selenate. The scavenging of the prehydrated electrons is observable for selenate concentrations greater than about 1 mM, whereas for the cadmium ion, this effect is not seen in the range of concentrations studied. The very low concentration needed for the selenate ion to scavenge the precursor to the hydrated electron is probably due to the difference between the rate constants of the scavenging of the prehydrated electron and the hydrated electron. The selenate ion is a much poorer hydrated electron scavenger than the cadmium ion but they are both good prehydrated electron scavengers.

Another possible reason for an apparent increase in hydrated electron yields is due to the cooperative effect with the OH radical.[24] The main reaction of the hydrated electron in the spur is with the OH radical. Scavenging the OH radical will lead to an increase in the hydrated electron yield by removing its main reaction partner. However, selenate is a poor OH radical scavenger,[14-16] and this reaction is far too slow to effect the outcome of the electron-scavenging reactions.

Conclusions

Nanosecond electron pulse radiolysis experiments have been used to investigate the scavenging of the prehydrated electron in deaerated aqueous solutions of the selenate ion. The scavenging of the prehydrated electron is observable at low concentrations of selenate because of the relatively fast rate of this reaction with respect to its reaction with the hydrated electron. The yields of the total electron scavenged are compared to those obtained with cadmium, a hydrated electron-only scavenger. At scavenging capacities greater than about $10^6\ \mathrm{s^{-1}}$ (1 mM selenate), the yield of total electrons is greater with selenate than with cadmium. The experimental results for both the selenate and cadmium solutions match very well with those predicted by Monte Carlo track simulations. At very high selenate concentrations, deviations thought to be due to direct irradiation effects appear. The selenate ion and other similar solutes with a high rate coefficient for reaction with the prehydrated electron can give total electron yields that are significantly greater than that of the hydrated electron alone. The increase in electron yield can occur at low solute concentrations. Other radiolytic products may be similarly affected. In particular, the molecular hydrogen yield could be very sensitive to the scavenging of the precursor to the hydrated electron.

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