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Hydrogen Peroxide Production in the Radiolysis of Water with High Radical Scavenger Concentrations

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The radiation chemical yields of hydrogen peroxide formed in the γ-radiolysis of water with scavengers for oxidizing and/or reducing radicals were measured to examine initial water decomposition pathways to oxidizing species. Hydrogen peroxide yields were found to decrease toward zero with increasing concentration of OH radical scavenger in all solutions, suggesting that the OH radical is the sole precursor to hydrogen peroxide. The yields of hydrogen peroxide in nitrate and selenate solutions are closely associated with the scavenging capacity of the precursor to the hydrated electron, suggesting that its reactions have a significant role in hydrogen peroxide formation. Observed hydrogen peroxide yields at high nitrate concentrations coupled with model calculations show that the molecular cation of water, H_2O^+, is the dominant precursor of the oxidizing species leading to hydrogen peroxide. Proton-transfer reactions of the water molecular cation give 79% of the oxidizing species, whereas other reactions such as dissociative recombination reactions account for the rest. There is a significant additional production of OH radicals in the radiolysis of selenate solutions due to the production of $^{\bullet}O^-$ and the scavenging of low-level excited water molecules.

Introduction

Hydrogen peroxide is the main oxidizing molecular product found in the γ-radiolysis of water and so it is important in both fundamental science and many applied engineering problems. It is formed by the combination reactions of OH radicals produced in the radiolytic decomposition of water. These reactions occur in the initial nonhomogeneous distribution of water decomposition products, commonly called a spur, produced by the deposition of energy by the primary γ-ray. Because no satisfactory technique exists for measuring the time-resolved formation of hydrogen peroxide, its temporal dependence has been probed by varying the concentration of efficient scavengers for OH radicals.[1−5] On the other hand, it is known that the OH radical reacts with other species, such as the hydrated electron, during the decay of the spur. It has been reported that scavenging of the hydrated electron has an effect on the yield of hydrogen peroxide.[3,6,7] In this work, the formation of hydrogen peroxide has been examined as a function of both electron and OH radical scavengers to explore the fast chemistry of this oxidizing species in the γ-radiolysis of water. A special effort was made to determine the effects due to scavenging of the precursor to the hydrated electron.

The OH radical is the primary oxidizing species produced in the radiolysis of water, whereas the hydrated electron is the main reducing species. Recent studies on the precursor to the hydrated electron have shown that it is responsible for much of the molecular hydrogen formation in deaerated water, probably through a dissociative recombination reaction with the molecular cation of water.[8,9] This reaction also produces an oxidizing species that may be an OH radical or something that is rapidly converted to it. Proton-transfer reactions of the water molecular cations also lead to OH radicals. Because there are two potential sources of OH radicals, the formation of hydrogen peroxide at very short times can have dissimilar responses to different scavengers for oxidizing and/or reducing species depending on the reaction mechanism. It is especially important to examine the dependence of hydrogen peroxide formation on the molecular cation of water, H_2O^+. This species is difficult to probe directly, but its chemistry can be examined indirectly by scavenging the precursor to the hydrated electron, which is known to be very reactive with the water molecular cation.[10−13] In addition to fundamental interest in the role of the oxidizing species in the radiolysis of water, hydrogen peroxide is important in many technological applications because of its potential to induce corrosion. Preventing oxidative damage is especially critical in the core and the circulation lines of pressurized and boiling water reactor plants.[14] Therefore, the yields of hydrogen peroxide and its kinetics during the initial stage of water radiolysis are extremely useful for reactor design and water chemistry management.

In this work, the formation of hydrogen peroxide has been examined in the γ-radiolysis of water in the presence of scavengers for both oxidizing and reducing radicals. Special care is taken in the selection of scavengers for the hydrated electron and its precursor. Scavenger concentrations are varied to probe the temporal dependence of the hydrogen peroxide yield, especially at high scavenger concentrations (which are equivalent to short times). A stochastic diffusion-kinetic model, employing simulated γ-ray track structures, is used to analyze the data to give detailed explanations of the short time chemistry in the γ-radiolysis of water.

Experimental Section

Sodium nitrate ($NaNO_3$, Aldrich, reagent grade), sodium selenate decahydrate (Na_2SeO_4, Aldrich, reagent grade), methanol (MeOH, Aldrich, HPLC grade), and nitrous oxide (N_2O, 99%) were used as received without further purification. The samples consisted of helium (ultrahigh purity) saturated aqueous solutions containing MeOH as the OH radical scavenger and either $NaNO_3$ or Na_2SeO_4 as the scavenger of the hydrated

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electron or its precursor. Saturated solutions of N_2O were used as the electron scavenger in some experiments. The concentration of MeOH was varied from 1.0×10^{-6} to 10.0 M; the concentration of $NaNO_3$ was varied from 2.5×10^{-6} to 3.0 M; and the concentration of Na_2SeO_4 was varied from 2.5×10^{-4} to 1.0 M. All solutions used in this study were prepared using water from a Millipore Milli-Q UV system.

Irradiations were carried out using a Gammacell 220 ^{60}Co γ-ray source at the Radiation Laboratory of the University of Notre Dame. The dose rate was 10 Gy/min as determined using the Fricke dosimeter.[1,15] Samples solutions were irradiated to total a dose of 25 to 600 Gy at room temperature. Density corrections were applied in the determination of the dose at high scavenger concentrations.

The concentrations of hydrogen peroxide (H_2O_2) were determined by the Ghormley tri-iodide method with KI, in which I^- is oxidized to I_3^- by the hydrogen peroxide.[16,17] Sample solutions were placed in a 1-cm quartz cell, and the absorbance was measured at 350 nm (the wavelength of maximum absorption for I_3^-), using a diode array spectrophotometer (Hewlett-Packard HP8453). Reference samples containing the solutes at the concentrations under study and the reagent were prepared and measured simultaneously with irradiated samples. The molar extinction coefficient of I_3^- at 350 nm was taken as 25 500 M^{-1} cm^{-1}.[5] Error limits for H_2O_2 yields are estimated to be about ±2%, except in the case of large scavenger concentrations and low yields, where it was ±4%.

Diffusion Kinetic Modeling

Diffusion-kinetic modeling of the experimental systems was performed using the stochastic independent reaction times (IRT) approach, employing simulated track structures. This technique has been described extensively in the literature.[18] A track structure was obtained by modeling the collision-to-collision attenuation of a 1 MeV electron, and its daughters, using cross-sections appropriate for liquid water.[19] The nonhomogeneous chemistry was then modeled from the spatial configuration of the radiation-induced reactants. An ensemble of random reaction times was generated using the inter-reactant separations employing the independent pairs approximation. The kinetics of the track was obtained by repeatedly taking the minimum reaction time of the ensemble, with a new reaction time being generated for "reactive products" as they are formed.

The diffusion and reaction parameters for the diffusion-kinetic simulations were derived from the compilations of Buxton et al.[20] Typically, 10^2 to 10^3 different track structures were averaged to give a prediction for the kinetics of an irradiated solution.

Results and Discussion

Radiation chemistry experiments are usually performed at doses as low as possible, to avoid the buildup of products that may interfere with the chemistry of interest. This interference can be readily determined by examining the formation of products as a function of dose. Figure 1 shows that the absorbance, which is proportional to the hydrogen peroxide concentration, of irradiated 10^{-4} M MeOH and 25 mM NO_3^- solutions is a linear function of the irradiation dose for a wide range of doses. Similar results were observed over the entire range of MeOH and nitrate concentrations used here. However, the figure also shows that 10^{-4} M MeOH and 25 mM SeO_4^{2-} solutions are nearly independent of dose above about 150 Gy. Products from the reactions of electrons with selenate are scavenging the OH radicals and preventing the formation of hydrogen peroxide. Conventionally, radiation chemical yields, *G* values, are given in units of molecules per 100 eV of energy absorbed in the total solution. *G* values are proportional to the initial slopes of the data as presented in Figure 1. Extremely low doses must be used in the selenate solutions to obtain initial yields. Accordingly, the *G* values of hydrogen peroxide formation, $G(H_2O_2)$, in the γ-radiolysis of NO_3^- and SeO_4^{2-} systems were calculated from doses below 150 and 25 Gy, respectively.

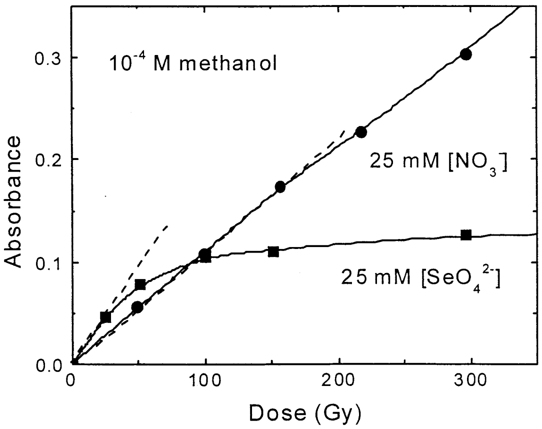

Figure 1. Dependence of the absorbance on the irradiation dose with 10^{-4} M methanol and (●) 25 mM sodium nitrate or (■) 25 mM sodium selenate. The dashed lines are the initial rates used for the calculation of the yield of hydrogen peroxide.

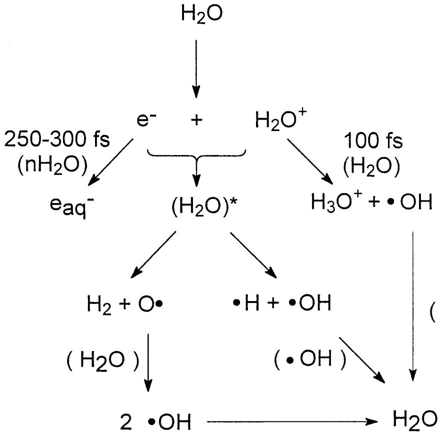

Figure 2. Schematic for the decomposition of water leading to the formation of hydrogen peroxide.

The absorption of energy by a water molecule leads to its decomposition in a scheme shown in Figure 2, which gives the main reactions leading to the formation of hydrogen peroxide based on previous studies of molecular hydrogen production.[21] Ionization to produce an electron and a molecular cation of water is quickly followed by hydration of the electron and proton transfer by the cation, or by their dissociative recombination. This scheme proposes two very different processes leading to the OH radical, the precursor to hydrogen peroxide. Scavenging of the precursor to the hydrated electron should increase the yield of OH radicals formed by the water molecular cations, because the combination reaction is prevented. On the other hand, scavenging the electron precursor decreases the amount of dissociative recombination reactions giving reactive oxygen species. The relationship between hydrogen peroxide production and the scavenging of the precursor to the hydrated electron will give information about the relative importance of the pathways of water decomposition when analyzed with the aid of model calculations.

TABLE 1: Yields of Hydrogen Peroxide [$G(H_2O_2)$ (molecules/100 eV)] in the γ-Radiolysis of Aqueous Solutions Containing Methanol and Nitrate

MeOH	$NaNO_3$ concentration										
(M)	2.5 μM	10 μM	25 μM	100 μM	250 μM	2.5 mM	25 mM	250 mM	1 M	2.5 M	3 M
10^{-6}		0.17	0.30	0.49	0.57	0.68	0.75	0.79	0.78	0.65	0.57
10^{-5}	0.03	0.13	0.27	0.50	0.58	0.69	0.73	0.78	0.76	0.63	0.56
10^{-4}	0.02	0.06	0.25	0.50	0.57	0.68	0.75	0.79	0.80	0.68	0.59
10^{-3}	0.02	0.07	0.21	0.49	0.58	0.66	0.75	0.81	0.80	0.67	0.58
10^{-2}	0.02	0.06	0.20	0.47	0.56	0.63	0.73	0.80	0.80	0.67	0.58
10^{-1}	0.01	0.03	0.14	0.40	0.49	0.58	0.64	0.72	0.75	0.64	0.56
10^{0}	0.02	0.03	0.08	0.25	0.35	0.37	0.43	0.47	0.56	0.52	0.49
10^{1}	0.01	0.01	0.01	0.05	0.03	0.08	0.09	0.11	0.12	0.20	0.17

The dominant reactions of OH radicals immediately following their formation are with sibling radicals formed in the spur:

$$^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \qquad 2k_1 = 1.1 \times 10^{10}\ M^{-1}\ s^{-1} \tag{1}$$

$$^{\bullet}OH + e_{aq}^{-} \rightarrow OH^{-} \qquad k_2 = 3.0 \times 10^{10}\ M^{-1}\ s^{-1} \tag{2}$$

All rate coefficients are from the compilation of Buxton et al.[20] Hydrogen peroxide is mainly formed by the combination reaction of OH radicals, reaction 1. Reactions of OH radicals with H atoms are considered to be negligible because of the low H atom yield in neutral water. The hydroperoxyl radical, HO_2, can lead to hydrogen peroxide formation, but this species is not important in the γ-radiolysis of deaerated solutions.

Hydrogen peroxide will react with radicals to re-form water, unless it is protected by suitable scavengers.

$$H_2O_2 + e_{aq}^{-} \rightarrow {}^{\bullet}OH + OH^{-} \qquad k_3 = 1.1 \times 10^{10}\ M^{-1}\ s^{-1} \tag{3}$$

$$H_2O_2 + {}^{\bullet}H \rightarrow {}^{\bullet}OH + H_2O \qquad k_4 = 9.0 \times 10^{7}\ M^{-1}\ s^{-1} \tag{4}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}HO_2 + H_2O \qquad k_5 = 2.7 \times 10^{7}\ M^{-1}\ s^{-1} \tag{5}$$

In this work, sodium nitrate or sodium selenate was added to the system to minimize the attack of hydrogen peroxide by the e_{aq}^{-} and H atom.

Methanol was used as an OH radical scavenger to protect the hydrogen peroxide, but more importantly to compete with the production of hydrogen peroxide in reaction 1.

$$CH_3OH + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2OH + H_2O \qquad k_6 = 9.7 \times 10^{8}\ M^{-1}\ s^{-1} \tag{6}$$

With increasing MeOH concentration reaction 6 will compete more favorably with reaction 1, resulting in a decrease in hydrogen peroxide formation. The lifetime of the OH radical, and therefore hydrogen peroxide production, with respect to reaction 6 is related to the inverse of the scavenging capacity, *s* (equal to the product of the scavenger concentration and the rate coefficient for the scavenging reaction, in units of s^{-1}). Previous studies have focused on increasing OH radical scavenger concentrations using sufficient concentrations of scavengers for the reducing species to protect the hydrogen peroxide formed.[4,5] The present work will examine the outcome of increasing the concentrations of scavengers for both the reducing and oxidizing species with the goal of studying the oxidizing precursors to hydrogen peroxide.

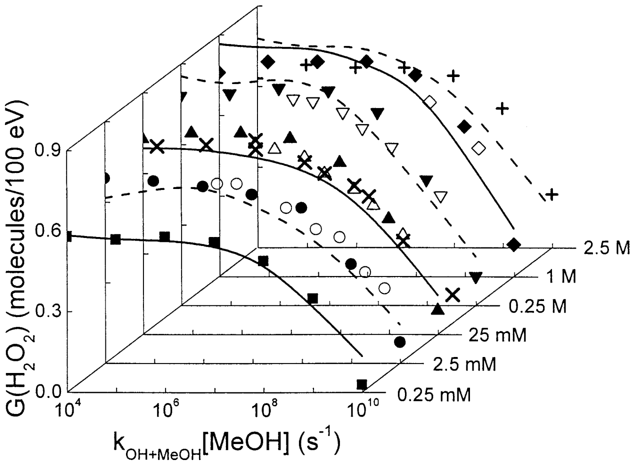

Figure 3. Hydrogen peroxide yields in the γ-radiolysis of water as a function of the scavenging capacity for OH radical with different concentrations of NO_3^-: (■) 0.25 mM, (●) 2.5 mM, (▲) 25.0 mM, (▼) 0.25 M, (◆) 1.0 M, and (+) 2.5 M, this work; (○), 2.5 mM, (△) 25.0 mM, (▽) 0.25 M, and (◇) 1.0 M, ref 3; (×) 25.0 mM, ref 4. The lines are from the model calculations.

Nitrate Scavenger. The nitrate anion reacts very rapidly with the hydrated electron. Its reaction with the H atom is much slower, but sufficient to compete with hydrogen peroxide at reasonable concentrations of solute.

$$NO_3^{-} + e_{aq}^{-} \rightarrow {}^{\bullet}NO_3^{2-} \qquad k_7 = 9.7 \times 10^{9}\ M^{-1}\ s^{-1} \tag{7}$$

$$NO_3^{-} + {}^{\bullet}H \rightarrow {}^{\bullet}HNO_3^{-} \qquad k_8 = 1.4 \times 10^{6}\ M^{-1}\ s^{-1} \tag{8}$$

Experimentally measured yields of hydrogen peroxide in the γ-radiolysis of solutions containing nitrate and MeOH are presented in Table 1. Nitrate concentrations above a few millimolar are sufficient to shield hydrogen peroxide from reactions with the reducing radicals produced in radiolysis. At higher concentrations, the nitrate begins to scavenge the precursor to the hydrated electron, thereby influencing hydrogen peroxide formation.

Figure 3 shows $G(H_2O_2)$ values for some of the higher concentrations of nitrate as a function of the scavenging capacity for the OH radical. With increasing scavenging capacity for the OH radical, $G(H_2O_2)$ decreases toward zero in all solutions. These results suggest that the OH radical is the only precursor to hydrogen peroxide. The present data are in good agreement with the previous results of Draganic and Draganic.[2,3] However, the present work covers a much wider range of both electron and OH radical scavenging capacities. At low scavenging capacity for the OH radical, $G(H_2O_2)$ reaches a constant value at between 0.6 and 0.7 molecules/100 eV. These yields are only slightly dependent on the nitrate concentration and represent the limiting or escape yield after the spatial relaxation of the spur. The escape yield of hydrogen peroxide in the γ-radiolysis of 25 mM nitrate solutions is 0.75 in this work, which agrees well with previous results.[4,5]

TABLE 2: Yields of Hydrogen Peroxide [$G(H_2O_2)$ (molecules/100 eV)] in the γ-Radiolysis of Aqueous Solutions Containing Methanol and Selenate

MeOH	Na_2SeO_4					
(M)	25 μM	250 μM	2.5 mM	25 mM	250 mM	1 M
10^{-5}	0.27	0.57	0.76	0.86	1.03	1.12
10^{-4}	0.27	0.59	0.82	0.92	1.19	1.47
10^{-3}	0.28	0.62	0.81	0.93	1.19	1.49
10^{-2}	0.30	0.57	0.74	0.87	1.09	1.29
10^{-1}	0.23	0.50	0.63	0.64	0.74	0.99
1	0.13	0.30	0.44	0.42	0.43	0.60
10	0.07	0.09	0.14	0.11	0.18	

At high scavenging capacities for the OH radical, the $G(H_2O_2)$ values increase with increasing concentration of nitrate. For instance, the hydrogen peroxide yield doubles from 2.5 mM to 3 M nitrate in 10 M MeOH solutions. One explanation for this increase in hydrogen peroxide yields at such early times is that the precursor to the hydrated electron is being scavenged. The water molecular cation is then less likely to neutralize and more probable to undergo a proton-transfer reaction to give OH radicals, which will ultimately give hydrogen peroxide. However, it has also been reported that the nitrate can scavenge the molecular cation of water by an electron-transfer reaction:[22]

$$NO_3^- + H_2O^+ \rightarrow {}^{\bullet}NO_3 + H_2O \qquad k_9 = \sim 1 \times 10^{12}\ M^{-1}\ s^{-1} \quad (9)$$

This reaction will lead to a decrease in OH radical production at high nitrate concentrations, as discussed later.

Selenate Scavenger. Other scavengers for electrons were desired to verify the results with nitrate and to give a different relative scavenging of the hydrated electron and its precursor. Unfortunately, most of the other common scavengers for the electron interfered with the detection method used for hydrogen peroxide. Selenate was found to be compatible with the hydrogen peroxide analysis up to very high concentrations, and it is a poor scavenger of the hydrated electron compared to nitrate. The major scavenging reactions of selenate for the hydrated electron and H atom were thought to be very similar to the reactions of nitrate.

$$SeO_4^{2-} + e_{aq}^- \rightarrow {}^{\bullet}SeO_4^{3-} \rightarrow {}^{\bullet}SeO_3^- + 2OH^- \qquad k_{10} = 1.1 \times 10^9\ M^{-1}\ s^{-1} \quad (10a)$$

$$SeO_4^{2-} + {}^{\bullet}H \rightarrow {}^{\bullet}HSeO_4^{2-} \qquad k_{11} = 1.1 \times 10^6\ M^{-1}\ s^{-1} \quad (11)$$

The yields of hydrogen peroxide measured with all the selenate concentrations used here are given in Table 2. As observed with nitrate, concentrations of selenate above a few millimolar are necessary to minimize the reactions of the hydrogen peroxide with radicals produced in the radiolysis. The escape yield of hydrogen peroxide is 0.76 molecules/100 eV for 2.5 mM selenate, which is in excellent agreement with the nitrate studies. At the highest selenate concentration, the yield of hydrogen peroxide passes through a maximum with decreasing MeOH concentration. This decrease in hydrogen peroxide yield is probably due to depletion of the MeOH at the doses used here, because higher doses result in a shift of the maximum to appropriately higher MeOH scavenging capacity. The results presented here are for the lowest possible dose, 25 Gy, using the present techniques. Higher order reactions such as OH radical reaction with hydrogen peroxide occur upon depletion of the MeOH.

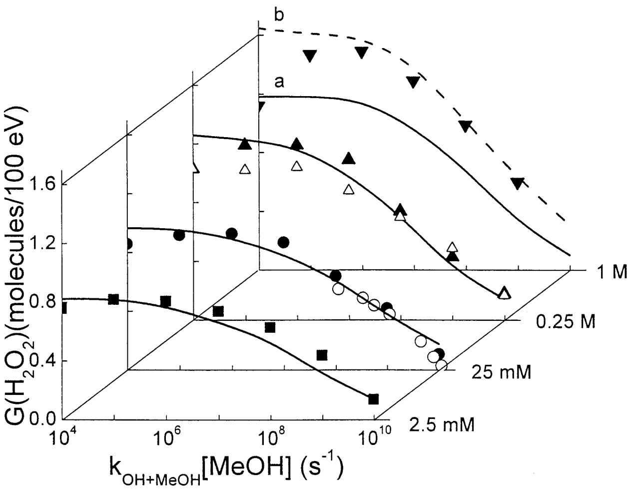

Figure 4. Yields of hydrogen peroxide in the γ-radiolysis of water as a function of the scavenging capacity for OH radical with different concentrations of SeO_4^{2-}: (■) 2.5 mM, (●) 25.0 mM, (▲) 0.25 M, and (▼) 1.0 M, this work; (○) 25.0 mM, ref 4; (△) saturated N_2O, this work. The lines are from the model calculations. Lines for 1 M SeO_4^{2-} are (a, solid line) normal scavenging reactions and (b, dashed line) scavenging of the lowest excited states of water by SeO_4^{2-} to give additional oxidizing species (see text).

Figure 4 shows the $G(H_2O_2)$ values measured as a function of the scavenging capacity for OH radical with the higher concentrations of selenate. The $G(H_2O_2)$ in all the selenate systems decreases toward zero with increasing scavenging capacity for the OH radical. This result confirms that the OH radical is the precursor to hydrogen peroxide. At very high OH radical scavenging capacities, the yields of hydrogen peroxide in selenate solutions are comparable to those found in solutions with an equivalent concentration of nitrate. Both solutes have about the same reactivity toward the precursor to the hydrated electron, whereas selenate is a relatively poor scavenger of the hydrated electron.

The $G(H_2O_2)$ values of about 1.2 measured at high selenate concentrations and low MeOH concentration are larger than those of the nitrate system, which has a maximum G value of 0.8 molecules/100 eV. Selenate solutions should give a slightly larger yield of OH radicals (and therefore H_2O_2) than the corresponding concentrations of nitrate solutions. Selenate is a poor scavenger of hydrated electrons compared to nitrate, but both solutes are similar in their scavenging of the precursor to the hydrated electron. At a given scavenging capacity for hydrated electrons, selenate leaves fewer hydrated electrons to react with OH radicals because it scavenges more of the precursors to hydrated electron than does nitrate. However, diffusion kinetic calculations show that this increase in the yield of OH radical is not sufficient to give the relatively large yields of hydrogen peroxide measured with selenate. In fact, the magnitude of the increased H_2O_2 yield suggests that there is an increased production of OH radicals in the radiolysis of selenate solutions.

The dependence of hydrogen peroxide yields as a function of the OH radical scavenging capacity is shown in Figure 5 at the same scavenging capacity for the precursor to the hydrated electron. If reaction 10a was dominant in the reaction mechanism, a selenate solution should give a slightly smaller yield of OH radicals (and thereby H_2O_2) than the corresponding nitrate solution. The selenate and nitrate solutions allow the same percentage conversion of the hydrated electron precursor to the hydrated electron, but the nitrate solution then scavenges more of the resulting hydrated electrons. This effect should leave

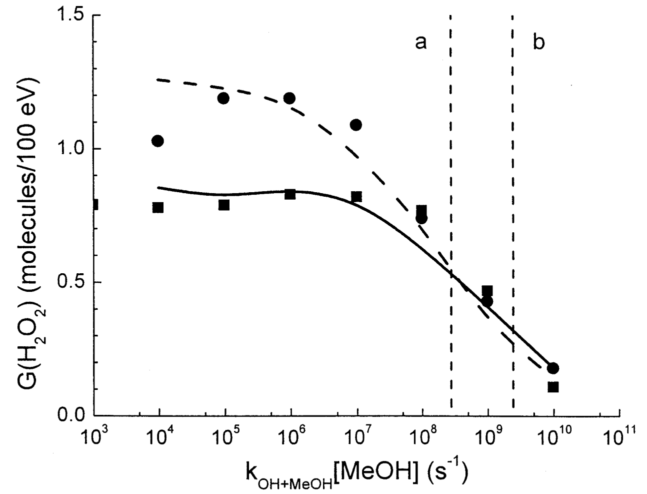

Figure 5. Yields of hydrogen peroxide in the γ-radiolysis of water as a function of the scavenging capacity for OH radicals at the same scavenging capacity for the precursor to the hydrated electron: (●) 250 mM SeO_4^{2-} and (■) 250 mM NO_3^-, this work. The solid and dashed lines are from the model calculation, and the dotted lines are where the scavenging capacity for the OH radical is equal to that for the hydrated electron using (a) SeO_4^{2-} and (b) NO_3^-.

fewer hydrated electrons to react with OH radicals and so give a higher yield of H_2O_2 compared to selenate. Exactly the opposite effect is observed to be true.

The radiation chemistry of Se(IV)/Se(V)/Se(VI) systems has received only limited attention.[23–26] Reaction 10a has been suggested as the dominant reducing reaction of the hydrated electron on SeO_4^{2-}; however, the following equilibria involving the $HSeO_4^{2-}$ radical anion are documented:[25]

$$^{\bullet}HSeO_4^{2-} \leftrightarrows SeO_3^{2-} + {}^{\bullet}OH \qquad k_{12a} = 7.3 \times 10^5\ s^{-1} \qquad k_{-12a} = 3.5 \times 10^9\ M^{-1}\ s^{-1} \qquad (12a)$$

$$^{\bullet}HSeO_4^{2-} \leftrightarrows {}^{\bullet}SeO_3^{-} + OH^- \qquad k_{12b} = 6.4 \times 10^8\ s^{-1} \qquad k_{-12b} = 5 \times 10^8\ M^{-1}\ s^{-1} \qquad (12b)$$

$$^{\bullet}HSeO_4^{2-} + OH^- \leftrightarrows SeO_3^{2-} + {}^{\bullet}O^- + H_2O \qquad k_{13} = 3.9 \times 10^5\ M^{-1}\ s^{-1} \qquad k_{-13} = 1.1 \times 10^7\ M^{-1}\ s^{-1} \qquad (13)$$

Figure 6 shows $G(H_2O_2)$ for equivalent nitrate and selenate scavenging capacities for the hydrated electron as a function of the scavenging capacity of the OH radical. The clear implication of the experimental data is that some of the scavenging reactions of the hydrated electron, and its precursor, by SeO_4^{2-} result in the production of $^{\bullet}O^-$ or $^{\bullet}OH$ by reaction 10b.

$$SeO_4^{2-} + e_{aq}^- \ (\text{or } e_{pre}^-) \rightarrow {}^{\bullet}SeO_4^{3-} \rightarrow SeO_3^{2-} + {}^{\bullet}O^- \qquad (10b)$$

In the absence of MeOH as an OH radical scavenger, this reaction would still ultimately result in the production of the $^{\bullet}SeO_3^-$ radical by the equilibria (12).

The production of $^{\bullet}O^-$ (or $^{\bullet}OH$) in the scavenging of hydrated electrons by selenate according to reaction 10b is equivalent to the scavenging of hydrated electrons by nitrous oxide.

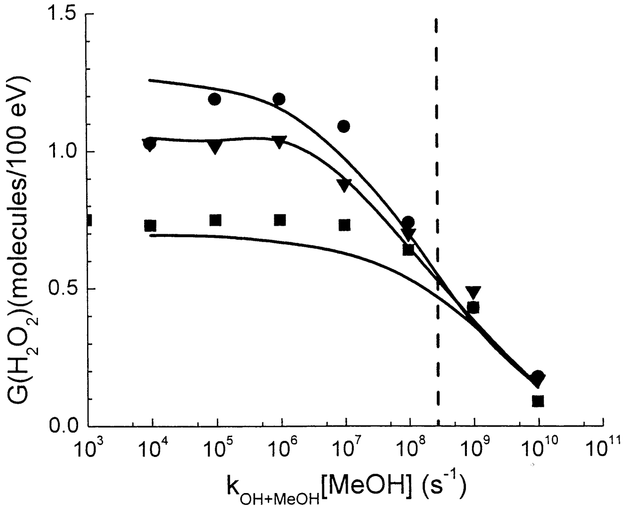

Figure 6. Yields of hydrogen peroxide in the γ-radiolysis of water as a function of the scavenging capacity for OH radicals at the same scavenging capacity for hydrated electrons: (●) 250 mM SeO_4^{2-}, (■) 25 mM NO_3^-, and (▼) 25 mM N_2O, this work. The solid lines are from the model calculation, and the dashed line is where the scavenging capacity for the OH radical is equal to that for the hydrated electron.

$$N_2O + e_{aq}^- \rightarrow {}^{\bullet}N_2O^- \rightarrow N_2 + {}^{\bullet}O^- \qquad k_{14} = 9.1 \times 10^9\ M^{-1}\ s^{-1} \qquad (14)$$

The results of a series of experiments with solutions saturated with nitrous oxide are included in Figure 6. The dashed line shows where the scavenging capacity for OH radicals is equivalent in value to the scavenging capacity for the hydrated electron. At high MeOH concentrations (to the right of the dashed line in Figure 6) where the scavenging of OH radical occurs before the hydrated electron, $G(H_2O_2)$ from saturated N_2O solution is the same as that measured from selenate and from nitrate solutions with the same scavenging capacity for hydrated electrons. This agreement shows that the precursor to H_2O_2, i.e., OH radical, and its yield are the same in the three systems. At low MeOH concentrations, the yields measured in the solutions of the three electron scavengers differ. The selenate solution gives the highest $G(H_2O_2)$ and the nitrate solution the lowest. Nitrate is a good scavenger of the hydrated electron and of its precursor, selenate is a relatively poor scavenger of the hydrated electron and a very efficient scavenger of the precursor to the hydrated electron, and nitrous oxide is a good scavenger of the hydrated electron and a relatively poor scavenger of the precursor to the hydrated electron.

$$NO_3^- + e_{pre}^- \rightarrow {}^{\bullet}NO_3^{2-} \qquad k_{15} = 1 \times 10^{13}\ M^{-1}\ s^{-1} \qquad (15)$$

$$SeO_4^{2-} + e_{pre}^- \rightarrow {}^{\bullet}SeO_4^{3-} \qquad k_{16} = 1 \times 10^{13}\ M^{-1}\ s^{-1} \qquad (16)$$

$$N_2O + e_{pre}^- \rightarrow {}^{\bullet}N_2O^- \qquad k_{17} < 10^{12}\ M^{-1}\ s^{-1} \qquad (17)$$

The rate coefficients for the reactions of the precursor to the hydrated electron have been derived from experimental C_{37} data.[11,27,28]

Precursors to OH Radicals. The production of OH radicals, the precursor to hydrogen peroxide, is clearly dependent on the scavenging of the electrons produced in radiolysis. A series of diffusion-kinetic calculations were used to investigate the reaction mechanism at high nitrate concentrations. The results of calculations including both reactions 8 and 9 are shown in

Figure 3. The agreement with the experimental data is excellent; however, when reaction 9 is ignored, there is an overestimate of the yield of H_2O_2 at nitrate concentrations greater than 0.25 M. Clearly, the reaction of nitrate with the water molecular cation, reaction 9, at high nitrate concentrations is of importance. For instance, the simulations suggest that about 31% of the molecular cations of water are scavenged in 2.5 M nitrate solution compared to only 12% in 1.0 M solution and 3% in 0.25 M solution.

Diffusion-kinetic calculations of the radiation chemistry of aqueous solutions of selenate and MeOH were made using either reaction 10a or reaction 10b in the mechanism. When reaction 10a is used in the calculations, the predictions significantly underestimate the experimental yields of H_2O_2. Figures 4−6 show excellent agreement for selenate concentrations up to 0.25 M between experimental yields and the predictions of calculations, in which the hydrated electron and its precursor were both scavenged by selenate according to reaction 10b. The fact that electron scavenging by selenate occurs via reaction 10b is not surprising. It is well-known that the irradiation of K_2SO_4 crystals produces $^{\bullet}O^-$ and not $^{\bullet}SO_3^-$.[29] In addition, perbromate reacts with the hydrated electron,

$$BrO_4^- + e_{aq}^- \rightarrow BrO_3^- + {}^{\bullet}O^- \qquad k_{18} = 2.4 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (18)$$

to give reactive oxygen species.[30]

The yield of hydrogen peroxide is underestimated in selenate solutions of concentration greater than 0.25 M, implying that either the molecular cation of water is not scavenged by selenate, or that scavenging of excited states may also result in the production of an OH radical or its precursor.

$$SeO_4^{2-} + H_2O^+ \rightarrow {}^{\bullet}SeO_4^- + H_2O \qquad (19)$$

$$SeO_4^{2-} + H_2O^* \rightarrow {}^{\bullet}SeO_4^{3-} + H_2O^+ \qquad (20)$$

When diffusion kinetic calculations are performed ignoring the possibility of the electron transfer from SeO_4^{2-} to H_2O^+, the significant increase in H_2O_2 yield observed experimentally is not reproduced. In fact, there is good reason to expect the electron-transfer reaction does occur. Kim and Hamill have shown that SO_4^{2-} is a good donor to H_2O^+, even though it does not react effectively with the OH radical.[31] If an excited-state charge-transfer reaction is included in the calculations, then the experimental yields are reproduced, see curve b in Figure 4. This mechanism is clearly feasible. The transfer of energy from excited states of water to anionic solutes has been studied in depth.[32] Furthermore, Bartels and Crowell have suggested that low-energy photoionization of water takes place via a dissociative proton-coupled electron transfer to a preexisting trap[33] and the scavenging ability of the selenate anion for the precursor to the hydrated electron implies that it would be a suitable trap.

The effect of nitrate concentration on the radiation-induced yield of hydrogen peroxide from 1 mM MeOH solution is shown in Figure 7. As the nitrate concentration increases, the yield of hydrogen peroxide first increases and then decreases at high nitrate concentrations. The plateau region of the hydrogen peroxide occurs between about 0.3 and 1.3 M nitrate. The initial increase in the yield of hydrogen peroxide with increasing nitrate concentration is due to the scavenging of hydrated electrons by nitrate. Removal of the hydrated electrons reduces the amount of (e_{aq}^- + OH) reaction and leaves more OH radicals within the spur and available to produce hydrogen peroxide. Nitrate is an effective scavenger of the precursor to the hydrated electron. At ~0.3 M, the scavenging capacity of the solution for the precursor to the hydrated electron is the same as the pseudo-first-order rate coefficient for its solvation. The scavenging of the precursor to the hydrated electron results in a decrease in the number of dissociative recombination reactions, which yield H_2 and two OH radicals. It does, however, allow the sibling molecular cation to undergo proton transfer to give an OH radical. The net result is a small reduction in the number of OH radical equivalents, which causes the yield of hydrogen peroxide to plateau. At a nitrate concentration of about 1.3 M, the pseudo-first-order rate coefficient for the molecular cation reaction with nitrate is about the same as the pseudo-first-order rate coefficient for proton transfer to the solvent.[22] In this regime, the H_2O^+ is efficiently scavenged by the nitrate. This scavenging decimates the production of OH radicals and consequently significantly reduces the production of hydrogen peroxide. Model calculations predict that 79% of the precursors to hydrogen peroxide, i.e., OH radicals, are produced by the proton-transfer reactions of the molecular cation of water, whereas other reactions such as the dissociative recombination reaction account for the rest.

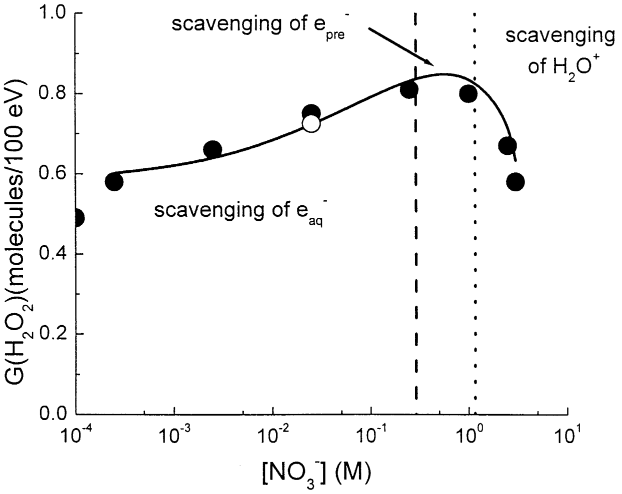

Figure 7. Yields of hydrogen peroxide in the γ-radiolysis of water as a function of the scavenging capacity for hydrated electrons in 1 mM methanol solutions: (●) NO_3^-, this work; (○) NO_3^-, ref 4. The solid line is from the model calculation. The dashed line is where the scavenging capacity for the precursor to the hydrated electron is equivalent to its solvation lifetime, and the dotted line is where the scavenging capacity of the water molecular cation is equivalent to the inverse lifetime of the protonation reaction.

Conclusions

The radiation chemical yields of hydrogen peroxide formed in the γ-radiolysis of water with scavengers for oxidizing and/or reducing radicals were determined. Hydrogen peroxide yields were found to decrease toward zero with increasing concentration of OH radical scavenger in all solutions, suggesting that the OH radical is the sole precursor to hydrogen peroxide. The scavenging of the precursor to the hydrated electron can have a significant role in hydrogen peroxide formation, probably because one of its main reactions is with the molecular cation of water, H_2O^+. Hydrogen peroxide yields at high nitrate concentrations coupled with model calculations show that the molecular cation of water is the dominant precursor of the oxidizing species leading to hydrogen peroxide. Proton-transfer reactions of the water molecular cation give 79% of the oxidizing species, and other reactions such as dissociative recombination reactions account for the rest. There is a significant additional production of OH radicals in the radiolysis of selenate solutions due to the production of $^{\bullet}O^{-}$ and the scavenging of low-level excited water molecules.

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