# Effect of pH on H<sub>2</sub>O<sub>2</sub> Production in the Radiolysis of Water

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ABSTRACT: The yields of hydrogen peroxide have been measured in the radiolysis of aqueous solutions of acrylamide, bromide, nitrate, and air in the pH range of 1-13. Hydrogen peroxide is the main stable oxidizing species formed in the radiolysis of water, and its long-term yield is found to be very sensitive to the system used in the measurements. Experiments with  $\gamma$ -irradiation combined with model calculations show that the primary yields of hydrogen peroxide are nearly independent of pH in the range of 2-12. Slightly higher primary yields are suggested at very low pH in particular when O<sub>2</sub> is present, while the yields seem to decrease at very high pH. Irradiations were performed with 5 MeV H ions, 5 MeV He ions, and 10 MeV C ions to evaluate the intratrack and homogeneous kinetic contributions to H<sub>2</sub>O<sub>2</sub> formation with different ions. Many of the trends in hydrogen peroxide yields with pH observed with  $\gamma$ -irradiations are observed with irradiation by the heavy ions. The lower yields of radicals in the homogeneous phase with the heavier ions tend to minimize the effects of radicals on the hydrogen peroxide yields at long times.



# INTRODUCTION

Hydrogen peroxide,  $H_2O_{24}$  is the major stable oxidizing species produced in the radiolysis of water<sup>1</sup> and understanding the mechanisms involved in its production is important both from a fundamental science perspective and for engineering purposes, in particular, within the nuclear power industry.<sup>2</sup> Although the effects of pH on the radiolysis of water have been studied for decades, measurements of  $H_2O_2$  yields as a function of pH are relatively scarce. At neutral pH, the H<sub>2</sub>O<sub>2</sub> radiation chemical yield at one microsecond in neat water is expected to be around 0.7 molecules/100 eV of energy absorbed, as shown both by experimental data and stochastic simulations.<sup>3</sup> Radiation chemical yields, G-values, are traditionally given in units of molecules/100 eV of energy absorbed, 1 molecule/100 eV = 0.1  $\mu$ mol/J and generally refer to the primary yields at one microsecond following passage of the ionizing radiation. The primary yield of H<sub>2</sub>O<sub>2</sub> is expected to be constant at least in the range from pH 3 to 12.<sup>4,5</sup> Several reports of a higher value ( $\sim$ 0.8 molecules/100 eV) at pH < 3 can be found in the literature.<sup>4</sup> Increasing  $H_2O_2$  yields at lower pH have been found in aerated solutions using Br or formic acid as radical scavengers.<sup>6-9</sup> However, there are contradictory reports of decreasing yields at low pH in deaerated Br solutions. There are also large contradictions in the reported data at pH >12 where the published H2O2 yields range from 0.53 to 0.84 with predominance on the lower end.<sup>4</sup> Clearly, there is no major consensus on the effects of pH on H2O2 yields especially at the extremes of pH.

Much of the formation of  $H_2O_2$  occurs within the microsecond time scale,<sup>10</sup> a regime that is normally examined using pulse radiolysis techniques. However, due to its very low UV/vis absorption

 $(\sim 60 \text{ M}^{-1} \text{ cm}^{-1} \text{ at } 230 \text{ nm})$ ,<sup>11</sup> there is no satisfactory technique for measuring the time-resolved formation of H<sub>2</sub>O<sub>2</sub>. Measurement of radiolytically produced H<sub>2</sub>O<sub>2</sub> is performed at very long time scales compared to its formation time, and considerable subsequent chemistry can occur. This added complexity to the determination of H<sub>2</sub>O<sub>2</sub> yields has led to considerable confusion in the literature, especially with regard to differentiating pH effects on the primary yields from effects occurring in the homogeneous phase of radiolysis.

Almost all of the earlier work on the effects of pH in the production of  $H_2O_2$  has been performed with  $\gamma$ -radiolysis and very little information is available using heavy ion radiolysis. The tracks produced by heavy ions are known to produce significantly different yields for many water radiolysis products because of the local geometry of energy deposition.<sup>12</sup> Most heavy ion radiolysis studies have been performed under acidic conditions (mostly in 0.4 M sulfuric acid), and very little data are available for neutral and alkaline conditions.<sup>13</sup> Most studies focus on the yields of molecular hydrogen and radicals formed by water radiolysis. The relatively scarce reports of primary yields of  $H_2O_2$  show that the primary yields obtained at neutral pH using heavy ions are around 10–15% lower than those measured under acid conditions.<sup>13–16</sup>

In this study, the  $H_2O_2$  yield as a function of pH has been determined in the range of 0.5 to 13.5 in the  $\gamma$ -radiolysis of four different chemical systems: 25 mM NaNO<sub>3</sub> (argon saturated), 1 mM KBr (argon saturated), 1 mM acrylamide (argon saturated),

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and air saturated water (0.25 mM  $O_2$ ). The observed  $H_2O_2$  yields are correlated to the primary radiation chemical yield by comparison of the results with numerical simulations of the evolution of radiolysis products. Irradiations were also performed with 5 MeV <sup>1</sup>H, 5 MeV <sup>4</sup>He, and 10 MeV <sup>12</sup>C to compare with the results of  $\gamma$ -radiolysis. The mechanisms for the formation and reaction of  $H_2O_2$  in the radiolysis of water and aqueous solutions are discussed.

# EXPERIMENTAL SECTION

**Irradiations.** Irradiations with  $\gamma$ -rays were performed using a self-contained Shepherd 109–68 cobalt-60 source at the Radiation Laboratory of the University of Notre Dame. Sample cells were Pyrex tubes 10 mm in diameter and about 10 cm long. Samples were degassed with ultrahigh purity argon or left aerated and flame-sealed. The dose rate was 57.8 Gy/min, as determined using the Fricke dosimeter. Samples were irradiated at room temperature to a total dose of up to 1350 Gy.

Heavy ion irradiations were performed in continuously purged and vigorously stirred cells using the Tandem FN Van de Graaff facility of the Notre Dame Science Laboratory in the University of Notre Dame Physics Department. The ions used in these experiments were 5 MeV  $^{1}H^{+}$ , 5 MeV  $^{4}He^{2+}$ , and 10 MeV  $^{12}C^{6+}$ . These energies were incident to the sample with energy loss to windows determined using standard stopping power compilations.<sup>17</sup> Irradiation methods and ion characteristics have been described previously.<sup>15,18</sup> Absolute dosimetry techniques were used by combining ion energy with integrated beam currents. Ion beam currents were typically 1.5 nA charge and doses up to 300 Gy were used.

**Materials.** Chemicals of the highest grade available were used as received without further purification. The main systems examined were aqueous solutions of (1) 25 mM NaNO<sub>3</sub> (Aldrich) argon saturated, (2) 1 mM KBr (Fischer Scientific) argon saturated, (3) 1 mM acrylamide (Sigma) argon saturated, or (4) aerated water without added solute. Experiments using aerated solutions with varying KBr concentration were also performed. Argon used for purging was of ultrahigh purity. The pH of the solutions was varied from 0.5 to 13.5 by addition of H<sub>2</sub>SO<sub>4</sub> (Fischer Scientific) or KOH (Fischer Scientific). The pH of each solution was determined prior to irradiation using an Orion 420A pH meter. Water was 10<sup>18</sup>  $\Omega \cdot$  cm as obtained from Radiation Laboratory in-house H2Only system, which consists of UV lamps and multiple filters.

Analysis. The hydrogen peroxide concentration was measured using the Ghormley method, <sup>19,20</sup> which is based on the oxidation of I<sup>-</sup> to I<sub>3</sub><sup>-</sup> by H<sub>2</sub>O<sub>2</sub> and the spectrophotometrical determination of I<sub>3</sub><sup>-</sup> at 350 nm. The reaction between H<sub>2</sub>O<sub>2</sub> and I<sup>-</sup> was carried out in slightly acidic solutions buffered with 100 mM phthalic acid/phthalate (Aldrich) or 1 M acetic acid/ acetate (Sigma-Aldrich), depending on the pH of the sample. A total of 2 mL of sample solution was added to 1 mL of buffer solution and 1 mL of reagent solution containing 0.4 M KI (Sigma-Aldrich) and 160  $\mu$ M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (Aldrich). The absorbance of the solution was measured using a diode array spectrophotometer (Hewlett-Packard HP8453). The extinction coefficient was 24135 M<sup>-1</sup> cm<sup>-1</sup>, which is consistent with previous studies.<sup>10,15</sup>

Irradiation of aerated, acidic solutions containing relatively high concentrations of Br<sup>-</sup> results in the formation of significant

amounts of Br<sub>2</sub>, which interfere with the determination of H<sub>2</sub>O<sub>2</sub> concentrations by the Ghormley method.<sup>21</sup> To eliminate the influence of Br<sub>2</sub>, extraction by CCl<sub>4</sub> was employed for aerated solutions at pH 1 with Br<sup>-</sup> concentrations  $\geq$  10 mM. Two to three extractions using twice the sample volume were performed prior to the H<sub>2</sub>O<sub>2</sub> analysis.

# RESULTS AND DISCUSSION

**H**<sub>2</sub>**O**<sub>2</sub> **Formation and Reaction.** Water decomposes within a few picoseconds of the energy deposition by ionizing radiation to give  $e_{aq}^-$ , H<sup>•</sup>, OH<sup>•</sup>, HO<sub>2</sub><sup>•</sup>, and H<sub>2</sub>. These species are located in spurs along the incident ion/photon path. The spatial distribution of the spurs is strongly dependent on the radiation type and energy. The term Linear Energy Transfer (LET = -dE/dx, the stopping power) is used to describe the energy absorbed by the irradiated material as a function of distance traveled by the incident particle. With increasing LET, the spurs from heavy, highly charged ions overlap to give a columnar track, whereas lighter, less charged ions with low LET give widely spread, isolated spurs. The γ-rays used in this work are in the Compton region and lead to the formation of two secondary electrons of low LET.

The initial water decomposition products are characterized by a nonhomogeneous spatial distribution about the initial point of energy deposition, which essentially defines the geometry of the spur or track.<sup>12</sup> Reaction of species within the spur or track competes with outward diffusion into the bulk liquid. All geminate reactions will occur within this early nonhomogeneous phase of the kinetics. The distribution of reactive species is nearly homogeneous within a few microseconds following the passage of  $\gamma$ rays. This point in time is usually used to define primary radiation chemical yields, which are also often called escape yields because the species have survived beyond the lifetime of the spur or track. Second order radical reactions occur to a negligible extent beyond this time and most subsequent chemistry is due to radicals reacting with stable molecular products.

The chemistry occurring within the spur or track can be described by 10 or so main radical reactions of the sibling produced by water decomposition.<sup>22</sup> Of these reactions, combination of OH radicals is the main process leading to  $H_2O_2$  formation.<sup>10</sup>

$$OH^{\bullet} + OH^{\bullet} \rightarrow H_2O_2$$
  
 $k = 5.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (1)

Rate constants throughout the manuscript are from Buxton et al.<sup>23</sup> unless otherwise stated. Previous studies have probed the temporal dependence of  $H_2O_2$  formation by measuring its yield as a function of the scavenging capacity of OH radical.<sup>10,15</sup> The limiting  $H_2O_2$  yield at low OH radical scavenging capacity corresponds to the escape yield, provided that the  $H_2O_2$  is completely protected from radical attack during the homogeneous phase of radiolysis. Reaction 1 competes in the spur or track with the scavenging of OH radicals by H atoms and  $e_{aq'}^{-}$  reactions 2 and 3.

$$e_{aq}^{-} + OH^{\bullet} \rightarrow OH^{-}$$
  $k = 3.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (2)

$$H^{\bullet} + OH^{\bullet} \rightarrow H_2 O \quad k = 7.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \quad (3)$$

Radicals that escape reactions within the track may react with  $H_2O_2$  in the homogeneous phase to effectively reduce its

Table 1. Values of  $pK_a$  for the Radiolysis Products of Water<sup>24</sup>

	pK <sub>a</sub>
$H^{\bullet} \leftrightarrows e^{-}_{aq} + H^{+}$	9.77
$H_2O_2 \hookrightarrow HO_2^- + H^+$	11.65
$OH^{\bullet} \leftrightarrows O^{-\bullet} + H^+$	11.9
$\mathrm{HO}_{2}^{\bullet} \leftrightarrows \mathrm{O}_{2}^{-\bullet} + \mathrm{H}^{+}$	4.57

apparent yield.

$$H^{\bullet} + H_2O_2 \rightarrow OH^{\bullet} + H_2O$$
  
 $k = 9.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (4)

$$e_{aq}^{-} + H_2 O_2 \rightarrow OH^{\bullet} + OH^{-}$$
  
 $k = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (5)

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$$
  

$$k = 2.7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
(6)

These latter reactions may also occur within the tracks of heavy ions leading to a reduction in the escape yield. The suppression of reactions 4-6 is the specific reason why radical scavengers must be added to the solutions in order to determine  $H_2O_2$  yields.

The hypothesis most often used to explain the increase in  $H_2O_2$  yield at low pH is that  $e^-_{aq}$  is completely converted to H atoms by reaction 7 within the spur.<sup>4</sup>

$$H^+ + e_{aq}^- \rightarrow H^{\bullet} \quad k = 2.8 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
 (7)

Because the rate constant for scavenging of OH radicals by H atoms is lower than the corresponding rate constant for  $e_{aq}^{-}$  (reactions 2 and 3), the conversion of  $e_{aq}^{-}$  to H atom leads to protection of OH radical, which in turn could lead to increased H<sub>2</sub>O<sub>2</sub> production in the spurs by reaction 1. However, the rate constant for the decomposition of H<sub>2</sub>O<sub>2</sub> is also lower for the H atom than for  $e_{aq}^{-}$  (reactions 4 and 5). Hence, the conversion of  $e_{aq}^{-}$  to H atoms also leads to the protection of H<sub>2</sub>O<sub>2</sub> in the homogeneous phase of radiolysis. The first process would lead to an increase H<sub>2</sub>O<sub>2</sub> escape yield, whereas the second process would only affect the measured yields at long time scales.

Radiation chemistry at high pH is dominated by reactions of the basic forms of the common radiolytic products. In Table 1, the  $pK_as$  for radiolysis products of neat water are listed. At pH above about 12, the  $H_2O_2$  is converted to  $HO_2^-$  and the OH radical is converted to  $O^{-\bullet}$ . Transformation of the OH radical into  $O^{-\bullet}$  in the spurs would imply that  $H_2O_2$  would mainly be produced according to reaction 8 and, to some extent, reaction 9.

$$O^{-\bullet} + O^{-\bullet} + H_2 O \rightarrow HO_2^- + OH^-$$
  
 $k = 1.0 \times 10^9 / [H_2 O] \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  (8)<sup>24</sup>

$$OH^{\bullet} + O^{-\bullet} \rightarrow HO_2^{-}$$
  
 $k = 2.5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (9)<sup>24</sup>

The lower rate for reaction 8 compared to reaction 1 would lead to a decrease in  $H_2O_2$  production and a decreased escape yield at increasing pH. In the homogeneous phase, the deprotonation of OH radicals and  $H_2O_2$  will lead to increased rates of  $\mathrm{H_2O_2}$  decomposition, reactions 10, 11,  $^{24}$  and 12 compared to reaction 6.

$$OH^{\bullet} + HO_2^{-} \rightarrow HO_2^{\bullet} + OH^{-}$$
$$k = 7.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
(10)

$$O^{-\bullet} + H_2 O_2 \rightarrow O_2^{-\bullet} + H_2 O$$
  

$$k = 5.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
(11)

$$O^{-\bullet} + HO_2^{-} \rightarrow O_2^{-\bullet} + OH^{-}$$
  

$$k = 4.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
(12)

The differences in these rate constants will cause the yield of  $H_2O_2$  at long time scales to decrease with increasing pH.

**Modeling.** The homogeneous chemistry of the  $H_2O_2$  can be best examined by comparison of the experimental data with a kinetic model. A simple deterministic model is sufficient since the local geometry of the track has dissipated on these time scales and the subsequent chemistry involves homogeneously distributed species. Whereas the track chemistry can be sufficiently described by about ten fast reactions, the inclusion of considerably more reactions is required to mimic the homogeneous chemistry. The scavenging reaction schemes and rate coefficients for the systems used in this work are given in Table 2.<sup>23,25–39</sup> As can be seen in Table 2, the reaction scheme for the interactions between radiolysis products and scavengers becomes very complex and the evolution of the system is difficult to follow without the aid of a kinetic model.

The deterministic homogeneous model used to simulate the homogeneous phase of radiolysis in this work is essentially a series of differential equations describing the various reactions. The differential equations were solved in time using the FACSI-MILE model, which is based on the Gear algorithm.<sup>40</sup> The extensive chemistry presented by Elliot and McCracken has been used<sup>24</sup> and this is the same chemistry used on previous work on  $H_2O_2$  radiation chemistry.<sup>18</sup> The escape yields used as input to the homogeneous model are the *G* values presented in Pastina and LaVerne,<sup>18</sup> which are valid for neat water. A further effort to use diffusion kinetic models to simulate short time intratrack processes and elucidate the mechanism leading to the formation and short time reaction of  $H_2O_2$  at various pH is forthcoming but will require considerable development, especially for heavy ions.

Experimental values of the dose response, not shown, give a linear increase in  $H_2O_2$  concentration as a function of dose throughout the studied dose range for most systems. In cases where nonlinearity was observed, the reported yields correspond to the initial value. Yields obtained by the homogeneous model showed nonlinearity in some cases, here the reported yields correspond to the doses used for the experimental data.

 $\gamma$ -Radiolysis of Acrylamide Solutions. Acrylamide is a very good scavenger of all the major water decomposition radicals:  $e_{aq\nu}^-$  H atoms, and OH radicals, as given by reactions A1–A4. Very little is known about the products of these reactions and it has been assumed here that they do not influence the H<sub>2</sub>O<sub>2</sub> chemistry. The scavenging capacities for both reducing radicals and the OH radical in this system are low enough to not significantly affect the spur reactions. Hence, the H<sub>2</sub>O<sub>2</sub> escape yield in this system is expected to be identical to the escape yield in neat water at about 0.7 molecule/100 eV.

Figure 1 shows the results for  $H_2O_2$  yields in 1 mM acrylamide solutions over the entire pH ranges examined here. This figure also gives the results of Draganic, and the agreement is very good,

# Table 2. Scavenging Reactions

				rate constant $(dm^3 mol^{-1} s^{-1})$	ref.
Acrelamida					
Al	H C = C U C O N H + H	→		$2.1 \times 10^{10}$	27
A1 A2	$H_2C = CHCONH_2 + H$	$\rightarrow$	CH CHCONH -	$3.1 \times 10^{10}$	37
A2	$H_2C = CHCONH_2 + e_{aq}$	$\rightarrow$		$2.2 \times 10^{9}$	23
A4	$H_2C = CHCONH_2 + OH$	$\rightarrow$		$5.9 \times 10^8$	23
117				0.5 ~ 10	57
Br <sup>-</sup>				10	
B1	$Br^- + OH$	$\rightarrow$	BrOH <sup>-</sup>	$1.1 \times 10^{10}$	25
B2	BrOH <sup>-</sup>	$\rightarrow$	$Br^- + OH$	$3.3 \times 10^{7a}$	25
B3	$Br + OH^{-}$	$\rightarrow$	BrOH <sup>-</sup>	$1.3 \times 10^{10}$	26
B4	BrOH <sup>-</sup>	$\rightarrow$	$Br + OH^{-}$	$4.2 \times 10^{\circ a}$	25
B5	$BrOH^- + Br^-$	$\rightarrow$	$Br_2^- + OH^-$	$1.9  imes 10^8$	25
B6	$Br_2^- + OH^-$	$\rightarrow$	$BrOH^- + Br^-$	$5.1 \times 10^{7}$	26
B7	$Br + Br^{-}$	$\rightarrow$	Br <sub>2</sub> <sup>-</sup>	$1.5 \times 10^{10}$	27
B8	Br <sub>2</sub> <sup>-</sup>	$\rightarrow$	$Br + Br^{-}$	$6.8 \times 10^{4a}$	26
B9	$Br_2^- + Br_2^-$	$\rightarrow$	$Br_3^- + Br^-$	$2.4 \times 10^{9}$	28
B10	$BrOH^- + H^+$	$\rightarrow$	$Br + H_2O$	$4.4 \times 10^{10}$	25
B11	$Br + H_2O$	$\rightarrow$	$BrOH^- + H^+$	1.4	29
B12	$H + Br^{-}$	$\rightarrow$	HBr <sup>-</sup>	$1.7 \times 10^{6}$	30
B13	$Br + HO_2$	$\rightarrow$	$\mathrm{H^{+}} + \mathrm{O_{2}} + \mathrm{Br^{-}}$	$1.6 \times 10^{8}$	31
B14	$Br_2^- + H$	$\rightarrow$	$\mathrm{H^{+}+2Br^{-}}$	$1.4 imes10^{10}$	32
B15	$Br_2^- + H_2O_2$	$\rightarrow$	$\mathrm{HO}_{2} + \mathrm{H}^{+} + 2\mathrm{Br}^{-}$	$1.0 \times 10^{3}$	33
B16	$Br_2^- + HO_2$	$\rightarrow$	$\mathrm{O_2} + \mathrm{H^+} + 2\mathrm{Br^-}$	$1.0 \times 10^{8}$	31
B17	$Br_2^- + O_2^-$	$\rightarrow$	$2Br^- + O_2$	$1.7 \times 10^8$	31
B18	$Br_2^- + e_{aq}^-$	$\rightarrow$	2Br <sup>-</sup>	$1.1  imes 10^{10}$	32
B19	$Br_3^- + H$	$\rightarrow$	$\mathrm{H}^{+} + \mathrm{Br_2}^{-} + \mathrm{Br}^{-}$	$1.2 \times 10^{10}$	32
B20	$Br_3^- + HO_2$	$\rightarrow$	$\mathrm{H^{+}} + \mathrm{Br_{2}^{-}} + \mathrm{O_{2}} + \mathrm{Br^{-}}$	$1.0  imes 10^7$	34
B21	$Br_{3}^{-} + O_{2}^{-}$	$\rightarrow$	$O_2 + Br_2^- + Br^-$	$1.5 \times 10^{9}$	35
B22	$Br_3^- + e_{aq}^-$	$\rightarrow$	Br <sub>2</sub>	$2.7 \times 10^{10}$	36
$NO_3^{-}$					
N1	HNO <sub>3</sub> <sup>-</sup>	$\rightarrow$	$NO_3^{2-} + H^+$	$1.6 imes10^{3a}$	38
N2	$NO_{3}^{2-} + H^{+}$	$\rightarrow$	HNO <sub>3</sub>	$5.0 imes10^{10}$	38
N3	HNO <sub>2</sub>	$\rightarrow$	$NO_2^- + H^+$	$3.0 imes10^{7a}$	38
N4	$NO_2^- + H^+$	$\rightarrow$	HNO <sub>2</sub>	$5.0 \times 10^{10}$	38
N5	$NO_3^- + e_{aq}^-$	$\rightarrow$	NO <sub>3</sub> <sup>2-</sup>	$9.7 \times 10^{9}$	38
N6	$NO_3^- + H$	$\rightarrow$	HNO <sub>3</sub> <sup>-</sup>	$1.0  imes 10^7$	38
N7	$NO_3^{2-} + H_2O$	$\rightarrow$	$NO_2 + 2OH^-$	$1.0  imes 10^3$	38
N8	HNO <sub>3</sub> <sup>-</sup>	$\rightarrow$	$NO_2 + OH^-$	$2.0  imes 10^{5a}$	38
N9	$NO_{3}^{2-} + OH$	$\rightarrow$	$NO_3^- + OH^-$	$3.0  imes 10^9$	38
N10	$NO_2 + NO_2$	$\rightarrow$	$NO_3^{-} + NO_2^{-}$	$4.7  imes 10^7$	39
N11	$NO_2 + OH$	$\rightarrow$	ONOOH	$4.5 \times 10^{9}$	38
N12	$NO_2 + H$	$\rightarrow$	HNO <sub>2</sub>	$1.0  imes 10^{10}$	38
N13	$NO_2 + O_2^{-}$	$\rightarrow$	$O_2 NOO^-$	$5.0 \times 10^{9}$	38
N14	O <sub>2</sub> NOO <sup>-</sup>	$\rightarrow$	$NO_{2}^{-} + O_{2}$	$1.0^{a}$	38
N15	$NO_2^- + OH$	$\rightarrow$	$NO_2 + OH^-$	$6.0  imes 10^9$	38
N16	$NO_2^- + H$	$\rightarrow$	HNO <sub>2</sub> <sup>-</sup>	$7.1 \times 10^8$	38
N17	$NO_2^- + e_{aq}^-$	$\rightarrow$	$NO_2^{2-}$	$4.1 \times 10^{9}$	38
N18	$HNO_2 + H_2O_2$	$\rightarrow$	$\mathrm{H^{+} + NO_{3}^{-} + H_{2}O}$	$4.6 imes10^3 imes[\mathrm{H^+}]$	38
N19	$NO_2^- + O^-$	$\rightarrow$	$NO_2 + OH^-$	$3.1 \times 10^8$	38
<sup><i>a</i></sup> Units of $s^{-1}$ .					

except at the very highest pH values.<sup>9</sup> As can be seen in Figure 1, the calculated  $H_2O_2$  yield is virtually identical to the escape yield at low pH. This result is expected due to the complete scavenging

of the radicals formed by water decomposition. A slight decrease in  $H_2O_2$  yield occurs at pH above about 4. The inflection point is determined by the competition between the  $e^-_{aq}$  scavenging



Figure 1.  $H_2O_2$  yields as a function of pH in 1 mM acrylamide solutions: experimental data ( $\blacksquare$ ) this work and ( $\Box$ ) Draganic;<sup>48</sup> escape yields at neutral pH (dashed line) and long time yields obtained by FACSIMILIE simulations (solid line).

by  $H^+$  and by acrylamide (and  $H_2O_2$ ). At higher pH, there is a small fraction of scavenging of  $e_{aq}$  by  $H_2O_2$  leading to a slight reduction in the latter. H atoms are less prone to attack  $H_2O_2$  and acrylamide is also slightly more reactive toward H atoms compared to  $e_{aq}^{-}$  which leads to the protection of  $H_2O_2$  at low pH values. At pH above 12, the experimental data show a strong decrease in H<sub>2</sub>O<sub>2</sub> yield that is not reproduced by the simulation. This decrease could be due to reactions of H<sub>2</sub>O<sub>2</sub> with products of the acrylamide scavenging reactions or conversion of the acrylamide to its basic form with potentially a low scavenging capacity for reactions with the water decomposition radicals. Another possible reason for the observed discrepancy between the model and the experiment at high pH is that the short time chemistry in the track leads to a significant reduction in  $H_2O_2$ yields from that expected for neutral water. The yields for the short time chemistry are used to seed the homogeneous model and the simplistic approach used in this work assumes that the escape yield is independent of pH. Yields that are too high as given by the track model will cause the homogeneous model to overestimate H2O2 yields. Further track modeling studies will be required to resolve this issue.

 $\gamma$ -Radiolysis of KBr Solutions. The primary reactions in the KBr system are scavenging of OH radicals and H atoms according to reactions B1 and B12. Br is a very efficient scavenger of OH radicals and can lower H<sub>2</sub>O<sub>2</sub> formation in the spur if present at high concentrations. At the present scavenging capacity for OH radicals  $(1.1 \times 10^7 \text{ s}^{-1})$ , the H<sub>2</sub>O<sub>2</sub> escape yield is expected to be 0.59 molecule/100 eV.<sup>15</sup> This value is slightly lower than the value of about 0.7 molecule/100 eV in neat water due to the scavenging of OH radicals in the spurs,<sup>15</sup> and has been used in the homogeneous model throughout the pH range. Br<sup>-</sup> was used in this work to prevent interference of the OH radical on the homogeneous chemistry in the system, reaction 6. Hence, the homogeneous chemistry is expected to be controlled by reactions of H atom and  $e_{aq}$ , reactions 4 and 5. The reaction of Br<sup>-</sup> with H atoms is relatively slow with a rate constant about 4 orders of magnitude lower than for the reaction with OH radicals. Br does not react with  $e_{aq}^{-}$ ; however, this species is to some extent scavenged by secondary products such as  $Br_2^-$  and  $Br_3^-$ .

The production of  $H_2O_2$  as a function of pH obtained for 1 mM Br<sup>-</sup> solutions is shown in Figure 2 along with the data of



**Figure 2.**  $H_2O_2$  yields as a function of pH in 1 mM Br<sup>-</sup> solutions: experimental data ( $\blacksquare$ ) this work and ( $\square$ ) Hochanadel;<sup>20</sup> escape yields at neutral pH (dashed line) and long time yields obtained by FACSIMILIE simulations (solid line).

Hochanadel.<sup>20</sup> The agreement between the different sets of data is very good and the present results extend to much lower pH values. At pH > 5, both the measured and calculated  $H_2O_2$  yields are very low. The  $H_2O_2$  yield increases with decreasing pH and is nearly constant at pH below  $\sim$ 3.

Solutions of Br<sup>-</sup> essentially offer no protection of  $H_2O_2$  for reactions by  $e_{aq}^-$ . The very low yield of  $H_2O_2$  at near neutral pH and above is due to  $e_{aq}^-$  scavenging of  $H_2O_2$  at long times in reaction 5. With increasing concentration of  $H^+$ , reaction 7 leading to the conversion of  $e_{aq}^-$  to H atoms begins to compete with the reaction of  $e_{aq}^-$  with  $H_2O_2$ . H atoms are scavenged to a greater extent than  $e_{aq}^-$  by Br<sup>-</sup> and to some extent also by reaction with  $H_2O$  and radiolytically formed  $O_2$ . The increased protection against the reducing radicals leads to an increase in  $H_2O_2$  yields at low pH. The yield reaches its maximum value of 0.48 molecules/100 eV between pH 0 and 3.

The difference between the measured yield at pH 0-3 and the predicted escape yield at pH below about 3 is attributed to the incomplete scavenging of H atoms leading to partial consumption of  $H_2O_2$  in reaction 4. Overall, the agreement between the model calculations and experiment are very good and confirm the mechanistic interpretation of this system.

 $\gamma$ -Radiolysis of Nitrate Solutions. The radiation chemistry of aqueous nitrate solutions has been studied extensively.<sup>41</sup> The primary reactions occurring in this system are the scavenging of  $e_{aq}^{-}$  and H atoms by NO<sub>3</sub><sup>-</sup> (reactions N5 and N6), followed by a series of reactions of which the most important are presented in Table 2. As can be seen in the table,  $NO_3^-$  is a good scavenger for e<sup>\_</sup>ag but it reacts slower with H atoms and not at all with OH radicals. The OH radical is scavenged to some extent by products further down in the reaction chain. At 25 mM nitrate concentration, the H<sub>2</sub>O<sub>2</sub> escape yield is expected to be 0.75 molecules/ 100 eV at neutral pH.<sup>10</sup> This value is slightly higher than that obtained for pure water (0.7 molecule/100 eV) due to a small amount of  $e_{aq}$  scavenging in the spurs and has been used in the homogeneous model throughout the pH range. This loss of  $e_{aq}^{-}$ increases the OH radical yields through a cooperative effect in the spur and thereby increases H<sub>2</sub>O<sub>2</sub> escape yields.<sup>10</sup>

The *G* values are plotted as a function of initial pH of the solutions in Figure 3. As can be seen in the figure, the *G* values obtained at neutral pH agree well with previous data.<sup>10,15,42,43</sup> According to the homogeneous simulation, the measured (long time) yield at



**Figure 3.**  $H_2O_2$  yields as a function of pH in 25 mM NO<sub>3</sub><sup>-</sup> solutions: experimental data (**■**) this work and ( $\diamond$ ) Daniels and Wigg,<sup>42</sup> ( $\bigcirc$ ) Pastina and LaVerne,<sup>15</sup> ( $\diamond$ ) Hiroki et al.,<sup>10</sup> and ( $\square$ ) Faraggi et al.;<sup>43</sup> escape yields at neutral pH (dashed line) and long time yields obtained by FACSIMILIE simulations (solid line).

neutral pH is expected to be slightly lower than the escape yield. This effect is due to the lack of OH radical scavenger in the system, which leads to consumption of  $H_2O_2$  in the homogeneous phase (reaction 6).

As can been seen in Figure 3, the H<sub>2</sub>O<sub>2</sub> yield is constant between about pH 5 and 9. Outside this range, the yield changes dramatically with both increasing and decreasing pH. As discussed above, the conversion of  $H_2O_2$  to  $HO_2^-$  and OH to O<sup>-•</sup> at pH above about 10 leads to noticeably increased H<sub>2</sub>O<sub>2</sub> decomposition when no OH radical scavenger is present due to the generally higher rate constants for the reactions involving the deprotonated species. This decrease is observed both in the experimental and the simulated results. However, the simulation predicts the H<sub>2</sub>O<sub>2</sub> yield to reach a constant level of 0.2 molecules/100 eV above pH 12, while the experimentally observed yields decrease to essentially zero. One possible reason for the low observed yields is the conversion of one of the species in the scavenging chain shown in Table 2 to its basic form and subsequent reaction with H<sub>2</sub>O<sub>2</sub>. Another possibility is that the track model predicts too high H<sub>2</sub>O<sub>2</sub> yields at in the high pH region. A very similar overestimation of H<sub>2</sub>O<sub>2</sub> yields is observed in the acrylamide system.

On decreasing the pH below about 5 an increase in  $H_2O_2$  yield is observed, followed by a sharp decrease below pH 4. This behavior can be explained by the nitrate chemistry. When the H<sup>+</sup> concentration is increased to a certain point the H<sup>+</sup> scavenging of  $e_{aq}^{-}$  exceeds that of other species in the system (in this case  $NO_3^{-}$ ). As the  $e_{aq}^{-}$  is converted to H atom, the production of  $NO_2$  and  $NO_2^-$  is promoted because the formation of  $NO_2$  from  $HNO_3^{-}$  is 2 orders of magnitude faster than from  $NO_3^{-2}$ . (reactions N7 and N8). There is then the combination of two  $NO_2$  to form  $NO_2^-$  through reaction N10. Both species react with OH radicals, which leads to the protection of H2O2 according to reactions N11 and N15. When pH is decreased further,  $NO_2^{-}$  protonates (p $K_a = 3.2$ ) and produces HNO<sub>2</sub>, which consumes H<sub>2</sub>O<sub>2</sub> according to reaction N18, accounting for the decrease in  $H_2O_2$  yield at low pH. The model calculation agrees well with the experimental data at pH below 11.

 $\gamma$ -Radiolysis of Aerated Solutions. Oxygen is a very good scavenger of both  $e_{aq}$  and H atoms according to reactions 13 and 14.

$$O_2 + e_{aq}^- \rightarrow O_2^{-\bullet} \quad k = 1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
 (13)

$$O_2 + H^{\bullet} \rightarrow HO_2^{\bullet} \quad k = 2.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$
 (14)

The products of these reactions  $(HO_2^{\bullet}/O_2^{-\bullet})$  either recombine to form  $H_2O_2$  according to reactions 15–17 or scavenge OH radicals according to reactions 18–21.

$$HO_{2}^{\bullet} + HO_{2}^{\bullet} \rightarrow H_{2}O_{2} + O_{2}$$
  

$$k = 7.0 \times 10^{5} \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}$$
(15)<sup>24</sup>

$$HO_{2}^{\bullet} + O_{2}^{-\bullet} \rightarrow HO_{2}^{-} + O_{2}$$
  

$$k = 8.0 \times 10^{7} \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1} \qquad (16)^{24}$$

$$O_2^{-\bullet} + O_2^{-\bullet} + 2H_2O \rightarrow H_2O_2 + O_2 + 2OH^-$$
  
$$k = 1 \times 10^2 / [H_2O]^2 \text{ dm}^9 \text{ mol}^{-1} \text{ s}^{-1} \quad (17)^{24}$$

$$HO_{2}^{\bullet} + OH^{\bullet} \rightarrow O_{2} + H_{2}O$$
  

$$k = 6.6 \times 10^{9} \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}$$
(18)

$$O_2^{-\bullet} + OH^{\bullet} \rightarrow O_2 + OH^-$$
  
 $k = 7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (19)

$$HO_{2}^{\bullet} + O^{-\bullet} \rightarrow O_{2} + OH^{-}$$
  

$$k = 6 \times 10^{9} \text{ dm}^{3} \text{ mol}^{-1} \text{ s}^{-1}$$
(20)<sup>24</sup>

$$O_2^{-\bullet} + O^{-\bullet} + H_2 O \rightarrow O_2 + 2OH^-$$
  
 $k = 6 \times 10^8 \text{ dm}^6 \text{ mol}^{-1} \text{ s}^{-1}$  (21)

The  $H_2O_2$  escape yield in this system is expected to be identical to the escape yield in neat water because the scavenging capacities for the  $e_{aq}^-$  H atom, and OH radical are not high enough to influence the spur reactions significantly. Steady state experiments have shown that the presence of  $O_2$  has an important role in the production of  $H_2O_2$  at a variety of pH values.<sup>44</sup>

The results for the yields of  $H_2O_2$  in aerated water are shown as a function of pH in Figure 4. The results of the present work are in good agreement with the literature values,  $^{6,45-47}$  and they greatly extend the data into the high pH range. As can be seen in the figure, the long time yield at pH 7 is 0.3 molecules/100 eV higher than the escape yield. This increase can be attributed to the additional formation of  $H_2O_2$  through the  $HO_2^{\bullet}/O_2^{-\bullet}$ combination reactions, mainly reaction 16.

The  $H_2O_2$  yield in a system without OH radical scavenger is expected to decrease at high pH due to the changes in reactivity upon deprotonation of  $H_2O_2$  and the OH radical. In the aerated system the rates of reaction 15-17 are enhanced at increasing pH at the expense of reactions 18–21. The  $H_2O_2$  decomposition by OH<sup>•</sup>/O<sup>-•</sup> is indeed increased, but the effect is counteracted by increased  $H_2O_2$  production by reactions 15–17. Furthermore, the recombination of the products of the attack of OH radicals on



**Figure 4.** H<sub>2</sub>O<sub>2</sub> yields as a function of pH in aerated solutions: experimental data (■) this work and (□) ref 45 ( $1.3 \times 10^{-5}$  M KBr), ( $\triangle$ ) Allen and Holroyd<sup>46</sup> ( $3 \times 10^{-5}$  M KBr), ( $\bigcirc$ ) Lemaire et al.,<sup>47</sup> ( $\times$ ) Sworski;<sup>6</sup> escape yields at neutral pH (dashed line) and long time yields obtained by FACSIMILIE simulations (solid line).



Figure 5.  $H_2O_2$  yields as a function of OH radical scavenging capacity in aqueous Br<sup>-</sup> solutions of ( $\bullet$ ) pH 1, ( $\blacksquare$ ) 7, and ( $\blacktriangle$ ) 13.

 $H_2O_2$  ( $HO_2^{\bullet}/O_2^{-\bullet}$ ) is enhanced due to the generally high concentration of these species in the system and the radical attack to decrease  $H_2O_2$  becomes of less importance. The net result is a slight increase in  $H_2O_2$  yield with increasing pH above 7 as shown by both the experimental and calculated results in Figure 4.

An increase in  $H_2O_2$  yield is also observed as the pH is decreased below 7. Down to pH 3, this effect is due to the decreased rate of  $H_2O_2$  decomposition as  $e_{aq}^-$  is converted to H atom. Below pH 3 the increase in  $H_2O_2$  yield measured experimentally is significantly higher than predicted by the simulation. From the results shown in Figure 4, it is not clear whether the increase in  $H_2O_2$  yield below pH 3 is due to the longterm or the spur chemistry. One method that has been used previously to monitor the escape yield is to vary the OH radical scavenging capacity and thereby probe the  $H_2O_2$  production in the spurs. In Figure 5 the  $H_2O_2$  yields in aerated solutions are shown as a function of OH radical scavenging capacity using Br<sup>-</sup> as the OH radical scavenger for pH values 1, 7, and 13. As can be seen in the figure, the pH 7 and 13 solutions show a plateau at low OH radical scavenging capacity that corresponds to the escape



**Figure 6.** H<sub>2</sub>O<sub>2</sub> yields as a function of pH in 1 mM acrylamide solutions for pH values 1-13: ( $\bullet$ )  $\gamma$ -rays, ( $\blacksquare$ ) 5 MeV <sup>1</sup>H ions, ( $\blacktriangle$ ) 5 MeV <sup>4</sup>He ions, and ( $\bullet$ ) 10 MeV <sup>12</sup>C ions.

yield. The results at pH 1 appear to be shifted to higher values of  $H_2O_2$  yields over the entire scavenging capacity range and no plateau is observed. These observations suggest that the increased yield is due to a combination of homogeneous and spur chemistry. A further examination into the model parameters may resolve the discrepancy.

# HIGH LET RADIOLYSIS

Acrylamide scavenges all the water decomposition radicals resulting in little homogeneous chemistry of the H<sub>2</sub>O<sub>2</sub>. This system is the most straightforward to interpret in  $\gamma$ -radiolysis and is readily applicable to the chemistry induced by heavy ions. The measured H<sub>2</sub>O<sub>2</sub> yields in 1 mM deaerated acrylamide solutions are shown as a function of pH in figure 6. The results presented here show that the H<sub>2</sub>O<sub>2</sub> yield is constant within the pH range of 3-10, whereas under highly acidic conditions the yield is  $\sim 25\%$  higher and under highly alkaline  $\sim 25\%$  lower for all studied LETs.

The LETs for the 5 MeV H, 5 MeV He, and 10 MeV C ions are 20.7, 156, and 787 eV/nm, respectively. As the LET increases intratrack reactions between OH radicals should lead to an increase in H<sub>2</sub>O<sub>2</sub> production. Previous studies by Pastina and LaVerne<sup>15</sup> and Yamashita et al.<sup>13</sup> at neutral pH found an increase in  $H_2O_2$  yields from  $\gamma$ -rays to H ions to He ions followed by a decrease in yields at even higher LET carbon ions. Higher order intratrack reactions between OH radicals and H<sub>2</sub>O<sub>2</sub> occur at very high LET to decrease  $H_2O_2$  yields. This trend of increasing  $H_2O_2$ yields with LET followed by a decrease is observed for the entire pH range using acrylamide system. The H<sub>2</sub>O<sub>2</sub> yields presented here agree well with previous data at LET > 1000 eV/nm, whereas the present yields at lower LET are slightly higher than the previously reported values.<sup>15</sup> This difference can probably be rationalized by variations in OH radical scavenging capacities between the two different investigations. In the present work, the OH radical scavenging capacity is  $5.9 \times 10^6 \text{ s}^{-1}$  compared to the much lower value in Pastina and LaVerne<sup>15</sup> of  $9.7 \times 10^3 \text{ s}^{-1}$  and in Yamashita et al.<sup>13</sup> where no OH radical scavenger was used. At low LET a significant amount of OH radicals escape the spurs whereas this escape yield is rapidly reduced with increasing LET. Hence, at low LET a system with low or no OH radical scavenging capacity will give lower H<sub>2</sub>O<sub>2</sub> yields due to its consumption by reaction 6. However, at high LET the OH radical escape yield



**Figure 7.**  $H_2O_2$  yields as a function of pH in 1 mM Br<sup>-</sup> solutions for pH values 1–13: ( $\bullet$ )  $\gamma$ -rays, ( $\blacksquare$ ) 5 MeV <sup>1</sup>H ions, ( $\blacktriangle$ ) 5 MeV <sup>4</sup>He ions, and ( $\bullet$ ) 10 MeV <sup>12</sup>C ions.

is close to zero and the  $H_2O_2$  yield becomes independent of OH radical scavenging capacity.

The H<sub>2</sub>O<sub>2</sub> yields measured in gamma radiolysis of bromide solutions were very sensitive to the conversion of  $e_{aq}^{-}$  to H atoms. For high LET radiation, different behavior is expected due to the decreased escape yield of radical species. The yields measured in 1 mM KBr solutions are shown in Figure 7. At the relatively low LET of H ions, the radiation response shows the same trend as for  $\gamma$ -radiolysis, that is, very low yields of H<sub>2</sub>O<sub>2</sub> at pH 5 and above and increasing yields with decreasing pH. As discussed above for  $\gamma$ -radiolysis, low yields of H<sub>2</sub>O<sub>2</sub> at high pH are due to the lack of  $e_{aq}^{-}$  scavenger in the system, which reacts with  $H_2O_2$ . At low pH, conversion of the  $e_{aq}^-$  to H atoms results in increased radical scavenging by Br<sup>-</sup> and a reduced amount of H<sub>2</sub>O<sub>2</sub> consumption in the homogeneous phase, leading to an increase in the measured H<sub>2</sub>O<sub>2</sub> yields. With increasing LET the escape yield of radical species decreases and the influence of the homogeneous chemistry is minimized. As the escape yields of radicals are very low for high LET radiolysis, no significant effect of the conversion of  $e_{aq}^{-}$  to H atoms in the homogeneous phase is expected. This result is confirmed by the experimental data shown in Figure 7. As can be seen in the figure, the pH dependence of the H<sub>2</sub>O<sub>2</sub> yields at high LET is very similar to the observations in the acrylamide systems discussed above, that is, constant  $H_2O_2$  yield at near neutral pH, slightly increased yield at very low pH, and slightly decreased yield at very high pH.

The effect of dissolved oxygen on peroxide yields in 2.5 mM nitrate solution at high LET has been studied by Yamashita et al.<sup>14,13</sup> Their studies show that at low LET, the yield of  $H_2O_2$  is  $\sim$ 0.4 molecules/100 eV higher compared to the deaerated system whereas at higher LET almost no effect of oxygen is observed. This observation is good agreement with the data from the present work presented in Figure 8. At low LET, the additional  $H_2O_2$  production can, as in the  $\gamma$ -irradiated system, be rationalized by reactions 15-17. At high LET, the decreasing effect of oxygen is simply due to the decrease in the escape yield of  $e_{aq}^{-}$ . As the  $e_{aq}^{-}$  yield decreases, the production of HO<sub>2</sub> through reaction 13 decreases and the additional H<sub>2</sub>O<sub>2</sub> production (reactions 15-17) is thereby prevented. These effects cause the increase in H<sub>2</sub>O<sub>2</sub> yield from low LET up to 100 to be less dramatic compared to deaerated solutions. The observed increase in  $\rm H_2O_2$  yield at the higher values of pH in  $\gamma\text{-radiolysis}$  is



**Figure 8.** H<sub>2</sub>O<sub>2</sub> yields as a function of pH in aerated solutions for pH values  $1-13: (\bigcirc) \gamma$ -rays, ( $\blacksquare$ ) 5 MeV <sup>1</sup>H ions, ( $\blacktriangle$ ) 5 MeV <sup>4</sup>He ions, and ( $\blacklozenge$ ) 10 MeV <sup>12</sup>C ions.

not observed at high LET due to the increased importance of the  $HO_2^{\bullet}/O_2^{-\bullet}$  chemistry.

The  $H_2O_2$  yields presented in this work under neutral conditions for LET up to 100 are slightly higher compared to the results of Yamashita 2008.<sup>13</sup> This discrepancy is probably due to the presence of nitrate in the previous work. At 2.5 mM nitrate concentration the major part of the  $e_{aq}$  will react with nitrate according to reaction 46 and only about 15% of the  $e_{aq}$  will be scavenged by  $O_2$  and participate in the  $H_2O_2$  production through reactions 15–17. In the absence of nitrate, this fraction will increase leading to higher  $H_2O_2$  yields. However, because the scavenging capacity for  $e_{aq}^-$  is about 1 order of magnitude lower than in the nitrate containing solution, the destruction of  $H_2O_2$ by reaction 5 should also increase.

# CONCLUSIONS

 $\gamma$ -Radiolysis. All systems show constant yields of  $H_2O_2$  in the pH range from 5 to 9. In general, the yields increase with decreasing pH and decrease with increasing pH outside this range. The higher yield of  $H_2O_2$  at low pH is attributed to changes in reactivity due to the conversion of  $e_{aq}^-$  to H atom. The magnitude of the observed increase was matched by the homogeneous simulations in all cases except when oxygen was present in the system. This agreement indicates that for deaerated systems the observed increase in  $H_2O_2$  is due to reactions occurring in the homogeneous phase of radiolysis, that is, the escape yield of  $H_2O_2$  is not largely affected by a decrease in pH at low values of pH. In the aerated system, the observed increase in  $H_2O_2$  yield at low pH was larger than predicted by the simulation, suggesting that the escape yield may be affected by a decrease in pH when  $O_2$  is present.

The acrylamide and nitrate systems also gave  $H_2O_2$  yields lower than predicted by the homogeneous model at pH above 12. This result could indicate that the  $H_2O_2$  escape yield decreases at high pH in favor of the OH radical yield. Indeed, the simulated  $H_2O_2$  yield decreases in these systems when the escape yield for  $H_2O_2$  is decreased and the OH radical escape yield is increased. The effect cannot be observed in the Br<sup>-</sup> system due to the lack of  $e^-_{aq}$  scavenger and the resulting low  $H_2O_2$  yields. In the aerated system, the simulated long-term  $H_2O_2$  yield is not affected by simultaneously lowering the  $H_2O_2$  escape yield and increasing the OH radical escape yield. **High LET.** In general, the  $H_2O_2$  yield is expected to increase initially with increasing LET due to the increased probability of intratrack reactions between OH radicals. At very high LET, higher order intratrack reactions of radicals with  $H_2O_2$  lead to a subsequent decrease in  $H_2O_2$  yields. All the systems studied in the present work follow this general trend. In addition to these intratrack reactions, the chemistry of the  $H_2O_2$  in the homogeneous phase can be important at low LET where the radical escape yield is reasonably high.

The pH dependence of the measured  $H_2O_2$  yields is strongly governed by the influence of  $e_{aq}^-$  and H atom chemistry in the homogeneous phase of radiolysis, which in turn is determined by the radical escape yield and the scavenging capacity. In the acrylamide system, all radicals are scavenged and the influence of the homogeneous chemistry is very low at high LET as observed in gamma radiolysis. The aerated and bromide systems show strong influence of homogeneous chemistry at LET lower than 20.7 (5 MeV H ions) and 156 eV/nm (5 MeV He ions), respectively.

At LET above 100 eV/nm all the studied systems show constant  $H_2O_2$  yields within the pH range of 3–10, whereas under highly acidic conditions the yield is ~25% higher and under highly alkaline ~25% lower compared to neutral conditions. As the escape yield of radicals at high LET is very low, the influence of the long-term chemistry on the measured  $H_2O_2$  yield is negligible and the measured  $H_2O_2$  yield should be representative for the  $H_2O_2$  escape yield. Hence, these results suggest that, for high LET radiation, the  $H_2O_2$  escape yields at extreme pH are different from the escape yield at neutral conditions.

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