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Low LET radiolysis escape yields for reducing radicals and H_2 in pressurized high temperature water

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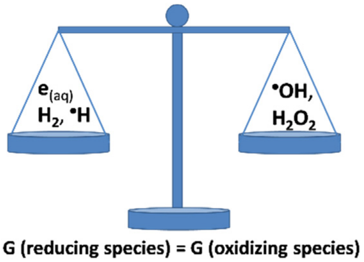
HIGHLIGHTS

- Water radiolysis escape yields for (G (e-$_{aq}$)+G(H)), and G(H_2) are measured to 350 °C.
- Resulting high temperature escape yields are on a much better quantitative foundation.
- Reconsideration of available high-temperature G(OH) shows that analysis is flawed.
- New interpolation formulas are recommended for all of the radiolytic escape yields.

GRAPHICAL ABSTRACT



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ABSTRACT

Low Linear Energy Transfer (LET) radiolysis escape yields (*G* values) are reported for the sum (G($^{\bullet}$H)+G (e-)$_{aq}$) and for G(H_2) in subcritical water up to 350 °C. The scavenger system 1–10 mM acetate/0.001 M hydroxide/0.00048 M N_2O was used with simultaneous mass spectroscopic detection of H_2 and N_2 product. Temperature-dependent measurements were carried out with 2.5 MeV electrons from a van de Graaff accelerator, while room temperature calibration measurements were done with a ^{60}Co gamma source. The concentrations and dose range were carefully chosen so that initial spur chemistry is not perturbed and the N_2 product yield corresponds to those reducing radicals that escape recombination in pure water. In comparison with a recent review recommendation of Elliot and Bartels (AECL report 153-127160-450-001, 2009), the measured reducing radical yield is seven percent smaller at room temperature but in fairly good agreement above 150 °C. The H_2 escape yield is in good agreement throughout the temperature range with several previous studies that used much larger radical scavenging rates. Previous analysis of earlier high temperature measurements of G_{esc}($^{\bullet}$OH) is shown to be flawed, although the actual G values may be nearly correct. The methodology used in the present report greatly reduces the range of possible error and puts the high temperature escape yields for low-LET radiation on a much firmer quantitative foundation than was previously available.

1. Introduction

Kinetic models of chemistry induced by water radiolysis are widely used in the nuclear power industry to understand the effects of the radiation field on cooling water of nuclear power

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plants (Sims et al., 2010; Elliot and Stuart, 2008; Elliot, 1990; Takiguchi et al., 2004; Christensen, 1995). Understanding the chemistry is extremely important for mitigation of the effects of radiation-enhanced corrosion, particularly stress-corrosion cracking of components (Was et al., 2011), and also to minimize the transport of radioactive species through the cooling loop, which strongly impacts the radiation dose to workers (Lin, 2009). The most important basic mechanisms of water radiolysis have been established for over half a century (Spinks and Woods, 1990; Buxton, 1987; Draganic and Draganic, 1971; Hart and Anbar, 1970), but measurements of transients have been made at the ca. 250–350 °C operating temperatures of pressurized water reactors only within the last two decades (Marin et al., 2002; Takahashi et al., 2002; Marin et al., 2002; Marin et al., 2003; Takahashi et al., 2004; Marin et al., 2005; Janik et al., 2007; Marin et al., 2007; Stanisky et al., 2010; Wu et al., 2000; Katsumura et al., 2001; Wu et al., 2001; Lin et al., 2004; Lin et al., 2005; Miyazaki et al., 2006; Miyazaki et al., 2006; Lin et al., 2008). The most important starting input for kinetics simulation is the yield or G value, characterizing the number of radical or molecular products formed per unit of radiation energy (Spinks and Woods, 1990) in the overall radiolysis process:

$$H_2O \rightarrow (e\text{-})_{aq} + (H^+)_{aq} + {}^{\bullet}OH + {}^{\bullet}H + H_2 + H_2O_2 \qquad (1)$$

The G values depend on Linear Energy Transfer (LET) of the radiation as this determines the initial density of free radicals created in tracks and the probability for recombination. Water in a nuclear reactor core is subjected to a mixed field of low-LET gamma and high-LET neutron irradiation (Elliot and Bartels, 2009). In the present manuscript we consider only G values for low-LET gamma and electron radiolysis.

A recent review by Elliot and Bartels (Elliot and Bartels, 2009) (E&B) summarizes data available in 2008 for radiolysis G values and rate constants from room temperature up to 350 °C. A problem faced in compiling this information is the fact that G values for the various species are actually a function of time following energy deposition (see Supporting Information for a discussion). Picosecond and nanosecond electron radiolysis experiments have clearly shown the time-dependence of hydrated electron (Bartels et al., 2000; Muroya et al., 2012) and ${}^{\bullet}$OH (El Omar et al., 2011) radical populations as they diffuse and recombine from ca. 1 ps out to a microsecond. Scavenger experiments are designed to convert a given radical species into a stable product. Because the scavengers intercept recombination events that would otherwise occur, the scavenged product yields increase with increasing scavenger concentration (Laverne and Pimblott, 1991). Commonly this dependence is expressed as (Laverne and Pimblott, 1991)

$$G(s) = G_{esc} + (G_o - G_{esc})J(s) \qquad (2)$$

where G_o is the yield at "t=zero", G_{esc} is the pure water yield at "t=infinity", $s=k_s[S]$ is the "scavenging power", or product of rate constant and scavenger concentration for the reaction of interest, and $J(s)$ is a function which varies between unity for $s=\infty$, and zero for $s=0$. (Functional forms for $J(s)$ are discussed in the Supporting Information.) High temperature data sets compiled for the E&B review made use of different (relatively large) scavenger concentrations for the various species, and so it was not possible to rigorously define the "escape yields" G_{esc} corresponding to pure water, that are desired for reactor modeling studies.

In addition to the problem of too high scavenger concentrations, another problem in reporting escape yields is the interconversion of the hydrated electron and H· atom:

$$(e\text{-})_{aq} + (H^+)_{aq} \Leftrightarrow {}^{\bullet}H \qquad (3)$$

$$(e\text{-})_{aq} + H_2O \Leftrightarrow {}^{\bullet}H + (OH^-)_{aq} \qquad (4)$$

These reactions are quite slow in room temperature neutral water, but above 200 °C the equilibration occurs even on the microsecond timescale of spur recombination (Elliot and Bartels, 2009). It becomes difficult even to define the independent escape yields $G({}^{\bullet}H)$ and $G(e\text{-}_{aq})$, because results depend on the pH, even though their sum is largely pH-independent. The reported yield for $G(e\text{-}_{aq})$ decreases at high temperature, but $G({}^{\bullet}H)$ increases such that their sum is a nearly linear function of temperature (Elliot and Bartels, 2009). Thanks to the fast equilibration, it is actually the sum $G({}^{\bullet}H)+G(e\text{-}_{aq})$ that has most importance for the reactor modeling problem. Bartels et al. (2013) Elliot and Bartels (Elliot and Bartels, 2009) were forced to use mixed neutral and alkaline data sets in their procedure for estimating $G({}^{\bullet}H)$ above 200 °C, where no other data was available. This must introduce some degree of systematic error in the total reducing radical yield. The overall uncertainly in $G_{esc}(H^{\bullet})+G_{esc}(e\text{-}_{aq})$ could be 20% at 300 °C.

The present manuscript reports new measurements up to 350 °C for the sum $(G(e\text{-}_{aq})+G(H))$, using quite low scavenger concentrations, representing a good approximation to the pure water escape yields. This puts the reducing radical yield on a much firmer quantitative foundation than was previously available. By using a mass spectroscopy detection technique we also simultaneously measure the reduced product yield $G(H_2)$. This gives us the entire yield of reducing equivalents G(red), which by mass balance must be equal to the yield of oxidizing equivalents G(ox):

$$G(red) = G(e\text{-})_{aq} + G({}^{\bullet}H) + 2G(H_2) = G({}^{\bullet}OH) + 2G(H_2O_2) = G(ox) \qquad (5)$$

Eq. (5) represents a powerful constraint in deducing the overall yield of water dissociation due to radiation.

In the following sections we explain our experimental procedure and then describe the results. In a discussion, the Elliot and Bartels review recommendations (Elliot and Bartels, 2009) are re-examined and new interpolation functions for the G_{esc} values are suggested. In Supporting Information we provide a more detailed description of the issues involved in defining G_{esc} and in designing the particular scavenger system for this measurement.

2. Experimental details

Our determination of the yield of reducing radicals makes use of the traditional scavenger N_2O, which reacts with hydrated electrons to give stable N_2 product. Stock solutions were saturated with a mixture of 2% N_2O in argon, giving 0.00046 M concentration. All experiments included 0.001 M NaOH to quickly convert the hydrogen atoms to $(e\text{-})_{aq}$ via reaction (-4). The pH is low enough to avoid converting ${}^{\bullet}$OH radicals to the ${}^{\bullet}O^-$ radical, which would tend to change the spur recombination kinetics and the corresponding escape yields. The ${}^{\bullet}$OH radicals were scavenged with acetate anion (1–10 mM), to curtail the accumulation of H_2O_2 product which otherwise may compete with the N_2O for $(e\text{-})_{aq}$. A detailed analysis of the choice of the scavenger concentrations to isolate the radiolysis escape yields is presented in the Supporting Information part B. All reagent concentrations given in this work (molar units) refer to the room temperature solutions. For higher temperatures the concentrations should be understood as the molal concentrations because the solution density decreases.

The experimental method for temperature-dependent yield measurement has been described in detail in previous publications (Janik et al., 2007). Briefly, one or two hplc pumps are used to provide high pressure flow of aqueous scavenger solutions at 6 cc/