Low LET Radiolysis Escape Yields for Reducing Radicals and H₂ in Pressurized High Temperature Water

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Abstract

Low Linear Energy Transfer (LET) radiolysis escape yields (G values) are reported for the sum ($G(\text{H}) + G(\text{e}^-)_{\text{aq}}$) and for $G(\text{H}_2)$ in subcritical water up to 350°C. The scavenger system 1-10 mM acetate/0.001M hydroxide/0.00048M N₂O was used with simultaneous mass spectroscopic detection of H₂ and N₂ product. Temperature-dependent measurements were carried out with 2.5MeV electrons from a van de Graaff accelerator, while room temperature calibration measurements were done with a ⁶⁰Co gamma source. The concentrations and dose range were carefully chosen so that initial spur chemistry is not perturbed and the N₂ 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 H₂ 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 $G_{\text{esc}}(\text{OH})$ 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.

Keywords

radiolysis; hydrated electron; hydrogen atom; G values; high temperature; spur recombination

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I. 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 plants¹⁻⁵. Understanding the chemistry is extremely important for mitigation of the effects of radiation-enhanced corrosion, particularly stress-corrosion cracking of components⁶, and also to minimize the transport of radioactive species through the cooling loop, which strongly impacts the radiation dose to workers⁷. The most important basic mechanisms of water radiolysis have been established for over half a century⁸⁻¹¹, but measurements of transients have been made at the ca. 250-350°C operating temperatures of pressurized water reactors only within the last two decades¹²⁻²⁸. 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 energy⁸ in the overall radiolysis process:

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 irradiation²⁹. In the present manuscript we consider only G values for low-LET gamma and electron radiolysis.

A recent review by Elliot and Bartels²⁹ (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^{30,31} and $\cdot\text{OH}$ ³² radical populations as they diffuse and recombine from ca. 1 picosecond 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 concentration³³. Commonly this dependence is expressed as³³

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

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 $\text{H}\cdot$ atom:

These reactions are quite slow in room temperature neutral water, but above 200°C the equilibration occurs even on the microsecond timescale of spur recombination²⁹. It becomes difficult even to define the independent escape yields $G(\text{H}\cdot)$ and $G(\text{e}^-_{\text{aq}})$, because results depend

on the pH, even though their sum is largely pH-independent. The reported yield $G(e_{-aq})$ decreases at high temperature, but $G(H^\bullet)$ increases such that their sum is a nearly linear function of temperature²⁹. Thanks to the fast equilibration, it is actually the sum $G(H^\bullet) + G(e_{-aq})$ that has most importance for the reactor modeling problem.³⁴ Elliot and Bartels²⁹ were forced to use mixed neutral and alkaline data sets in their procedure for estimating $G(H^\bullet)$ 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 uncertainty in $G_{esc}(H^\bullet) + G_{esc}(e_{-aq})$ could be 20% at 300°C.

The present manuscript reports new measurements up to 350°C for the sum $(G(e_{-aq}) + G(H^\bullet))$, 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 $G(ox)$:

$$G(red) = G(e_{-aq}) + G(H^\bullet) + 2G(H_2) = G(\dot{OH}) + 2G(H_2O_2) = G(ox) \quad (5)$$

Equation (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 recommendations²⁹ 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.

II. 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 0.00046M concentration. All experiments included 0.001M NaOH to quickly convert the hydrogen atoms to $(e^-)_{\text{aq}}$ via reaction (-4). The pH is low enough to avoid converting $\cdot\text{OH}$ radicals to the $\cdot\text{O}^-$ radical, which would tend to change the spur recombination kinetics and the corresponding escape yields. The $\cdot\text{OH}$ radicals were scavenged with acetate anion (1 to 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 publications³⁵. Briefly, one or two hplc pumps are used to provide high pressure flow of aqueous scavenger solutions at 6 cc/min flow rate. The solutions pass through a pre-heater to reach the desired temperature and then flow through a tube in front of the 2.5MeV electron beam from a van de Graaff accelerator, which is run in continuous (DC) mode.

In the present experiments both the preheater and irradiation zone were made of Hastelloy 276C high temperature alloy. The effective dwell time of the fluid in the irradiation zone is on the order of one second. Subsequently the solution flows to a constant-temperature bath where the temperature is dropped, and then the pressure drops in a capillary tube.

In the present experiments, irradiated solution was collected for ten minutes (60 ml) and then argon sparging of the sample was initiated. The sparging gas was sampled by leaking some of the flow into a mass spectrometer which was set to observe H_2 , N_2 , and O_2 . Product peaks appeared and decayed within several minutes. These were integrated to produce the relative product yields. A fiber optic was placed directly in front of the sample tube and during the irradiation Cerenkov light generated in the fiber was detected by a photodiode. The light is proportional to the dose incident on the sample and so this provides a secondary dosimeter. Generally three doses (50-300Gy, varied by changing the beam current or dose rate) are used for each data point, and sometimes a blank for high temperature experiments as well to guard against any thermal decomposition reactions on the tubing walls. The slope of the dose dependence is taken as the most precise relative measurement of the yield. Examples of raw data can be found in our previous publication³⁵ and in Section D of the supporting information.

Our method makes measurements of the product yields at elevated temperatures relative to a dosimetry standard at room temperature. An implicit assumption is that the dose distribution from the electron beam is independent of temperature, even though the water density changes from ca. 0.98 g/cc at room temperature, to ca. 0.65 g/cc at 350°C. Simulations of the dose distribution in our cylindrical metal tube were carried out using the GEANT4 toolkit^{36,37} version 9.5. The dose decreases approximately 50% from the front side to the back side of the 3.2mm o.d./2.0mm i.d. tube, almost entirely due to scattering of the 2.5 MeV electrons by the steel.

Energy of the electrons penetrating the water is still in excess of 1 MeV. We confirmed that a 40% change in water density vs. temperature makes less than 1% change to the integrated dose distribution. Dose is defined in terms of energy/mass, so the relative amount of product produced must still be normalized by the water density at each temperature, as described in previous publications³⁵.

To calibrate the relative yields of the high temperature experiments, the $G(N_2)$ and $G(H_2)$ values for three N_2O solutions were measured using ^{60}Co gamma radiolysis at room temperature with a dose rate of 33 Gy/min. The solutions are: (a) water solution of 0.002 M sodium acetate + 0.001 M NaOH saturated with 2% N_2O/Ar mixture, (b) water solution of 0.01 M phenol saturated with 10% N_2O/Ar mixture and (c) water solution of 0.01M ethanol saturated with 10% N_2O/Ar mixture. The latter two solutions have been used in the earlier work of Janik, et al³⁵ and were used in initial experiments of the present study. To remove air and saturate samples with the N_2O/Ar mixture the apparatus shown in figure 1 was used. A glass U-tube containing 10.0 ml of sample was connected to the tubing using O-ring compression fittings and placed on the gamma source sample platform. The sample was saturated by the N_2O/Ar mixture (valves in position A) and then lowered into the radiation area of the source. After irradiation (200 or 300 Gy) the sample was elevated, gaseous products (H_2 and N_2) were sparged with pure argon and this carrier gas was sampled by the mass spectrometer (valves in position B).

Calibration of the mass spectrometer was done with a 20% $H_2/80\%$ N_2 mixture injected periodically into the carrier gas through a septum with a gas-tight syringe. Precise calibration of the dose made use of a Fricke dosimeter⁸ having density of 1.025 g/cm³ (0.8 N H_2SO_4 was used). The Fricke dosimeter solution was irradiated in the same glass vessel, volume and conditions as the N_2O solutions. The concentration of Fe^{3+} ions was determined spectrophotometrically at 304

nm, using extinction coefficient $2194 \text{ M}^{-1} \text{ cm}^{-1}$ and assuming the radiolytic yield of Fe^{3+} ions is equal to 15.45 molecules/100 eV.^{8,38}

Figure 1. Apparatus used for N_2O calibration yield experiments at room temperature.

The estimated errors in ^{60}Co measurements are below $\pm 2.2 \%$ for nitrogen and below $\pm 4.2 \%$ for hydrogen. The errors in electron radiolysis experiments are $\pm 2.1\%$ and $\pm 5.6\%$ respectively for N_2 and H_2 .

Table 1. G-values (molecules/100 eV) for three aqueous N_2O dosimeter solutions at 25°C

Dosimetry solutions	Yields (molecules/100 eV)	
	G(N_2)	G(H_2)
2mM NaOAc /1mM NaOH /0.48mM N_2O	3.06 ± 0.06	0.48 ± 0.02
10mM EtOH/2.4mM N_2O	2.79 ± 0.06	1.04 ± 0.03
10mM PhOH/2.4mM N_2O	2.87 ± 0.06	0.43 ± 0.02

III. Results

The room temperature yields measured for the N₂O dosimeter solutions are presented in Table 1. In the 10% N₂O solutions (i.e. 2.4mM concentration) with ethanol or phenol, G(N₂) should represent G(e_{-aq}) because H atoms are scavenged by the alcohol. The measured numbers are slightly higher than expected for G_{esc}(e_{-aq}) because the scavenging rates in excess of 1 x 10⁷ s⁻¹ interfere with the spur chemistry (see Supporting Information for a discussion of this issue). The G(N₂) numbers measured here are very close (within 2%) to those calculated by Janik et al using a stochastic model.³⁵

Results for the acetate solution should closely approximate the room temperature escape yields, but a correction can be made. Assuming G(H)=0.55 as reported by Elliot, et al³⁹ and Spinks and Woods⁸, then based on the known rate constants, 4% of this yield should be scavenged by acetate rather than hydroxide ion, and G(H₂) will be enhanced by 0.02 units, while G(N₂) will be smaller by the same amount. In this case the corrected G_{esc}(H₂) yield is 0.46±0.02, identical to accepted values. The corrected G_{esc}(e_{-aq} + H) yield is 3.08±0.06, lower than the number (3.35) found in the E&B review, as expected on the basis of scavenging power. Bartels and coworkers³⁰ suggested on the basis of transient absorption measurements, calibrated against G(e_{-aq})=2.7/100eV for scavenging power 10⁷ s⁻¹, that the limiting room temperature G_{esc}(e_{-aq}) should be 2.5/100eV. A similar number was implicit in the stochastic simulations used by Janik et al³⁵ to (successfully) calculate the other N₂O dosimeter yields in table 1. Using this number and adding the H atom yield of 0.55, we have good agreement within the experimental error of about 2%. We can conclude that our gamma radiolysis measurements quantitatively agree with previous work, and these solutions may be used as relative dosimetry standards for the high temperature measurements.

Preliminary high temperature experiments were carried out to check the effect of changing N₂O and acetate concentrations. The effect of changing acetate concentration in a 10% N₂O/.001M hydroxide solution is illustrated in Figure 2 for several temperatures. At 100°C, there is no effect on the N₂ yield of changing acetate concentration from 1 to 10 mM. (A marginal increase is noted in the H₂ yield at 10 mM acetate because some H atoms are scavenged.) Unexpectedly, there is an increase in G(N₂) for lower acetate concentrations at 250°C. No corresponding change in the H₂ yield was found at this temperature.

We ascribe this increased N₂ yield at low acetate concentration to a chain reduction of N₂O as was found in previous studies using alcohol scavenger³⁵. The free radical formed from acetate, $\cdot\text{CH}_2\text{COO}^-$, cannot reduce N₂O. However, the product of acetate recombination (reaction 7) is succinate, $-\text{OOCCH}_2\text{CH}_2\text{COO}-$. Reaction of $\cdot\text{OH}$ radicals at the methylene groups of succinate (reaction 8) occurs with higher rate constant than with the acetate methyl group. (At room temperature, k_8 is⁴⁰ $3.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, while k_6 is⁴¹ $8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, but we have no information on the relative rates above 200°C.) The carbon-centered succinate radical might very well reduce N₂O, giving N₂, $\cdot\text{OH}$ radical, and the conjugated unsaturated product butenedioate (reaction 9). The regeneration of the $\cdot\text{OH}$ radical in reaction 9 completes the chain reduction mechanism.

To avoid this chain reaction it is necessary to avoid reaction (8). This will occur naturally if very little succinate is ever formed in reaction (7) relative to the initial concentration of acetate. The chain will be avoided at high initial acetate concentration and low total dose. This qualitatively explains the result in figure 2, where high enough acetate concentration produces a constant N_2 yield.

Figure 2. $G(\text{N}_2)$ vs. acetate concentration at several temperatures.

Based on the preliminary studies using 20ml sample volumes, it was realized that quite low total dose would be necessary and the S/N ratio for H_2 would be less than desired. A new sample collection tube was prepared to collect 60ml samples (ten minute collections). Acetate

concentration was increased to 2 mM as a compromise to avoid reaction 7, even though some $\text{H}^\bullet$ atoms will be converted to H_2 product. The maximum dose was limited to convert less than 5% of the acetate in any irradiation, i.e. succinate should always be less than 100 μM concentration. Above 250°C even this proved insufficient, as we measured N_2 yields higher than expected from the literature. In figure 3 we show $G(\text{N}_2)$ vs. the acetate concentration, but now with small dose fixed at ca. 55 Gy. Superimposed are the 2mM acetate experiments with yield taken from the slope of dose dependence (our standard practice). It is clear that above 250°C, the G value reaches a limiting value (at 55Gy) only for 5mM and higher acetate concentrations. These values are accepted as the correct sum of $G_{\text{esc}}(\text{e}^-)_{\text{aq}}$ and $G_{\text{esc}}(\text{H})$ which we desire.

Table 2. Temperature Dependence of Radiation Yields

Temperature [°C]	This work		Reviewed data ²⁹	
	Measured Yields (molecules/100 eV)		Escape yields (molecules/100 eV)	
	$G(\text{N}_2)$	$G(\text{H}_2)$	$G(\text{e}^-_{\text{aq}}) + G(\text{H})$	$G(\text{H}_2)$
25	3.08 ±0.06	0.46 ±0.03	3.35	0.44
100	3.57 ±0.07	0.49 ±0.03	3.81	0.47
150	3.88 ±0.08	0.51 ±0.03	4.11	0.49
200	4.35 ±0.09	0.55 ±0.03	4.40	0.51
250	4.67 ±0.10	0.57 ±0.03	4.69	0.56
300	4.85 ±0.10	0.61 ±0.04	4.99	0.64
350	5.23 ±0.11	0.81 ±0.04	5.30	0.76

Figure 3. $G(N_2)$ vs. acetate concentration. Low dose (55Gy) data are open symbols connected by lines. Filled symbols are measured via dose dependent signal at 2mM acetate.

Final results for the yield of N_2 in the acetate/.001M OH $^-$ /.00048M N_2O scavenger system is shown vs. temperature in figure 4. The numbers are listed in Table 2. A polynomial fit to the data (t in $^{\circ}C$) is

$$G_{esc}(H^{\bullet} + e^{-}_{aq}) = 2.868 + 7.573 \times 10^{-3} t + 2.500 \times 10^{-6} t^2 \quad (9)$$

The values recommended for $G(e^{-}_{aq}) + G(H^{\bullet})$ by Elliot and Bartels²⁹ are superimposed for comparison. As expected, the $G_{esc}(H + e^{-}_{aq})$ in the lower temperature regime is below the review values because E&B made use of $G(e^{-}_{aq})$ data with (room temperature) scavenging power greater

than $10^7 \text{ M}^{-1} \text{ s}^{-1}$. The $G_{\text{esc}}(\text{H} + \text{e}_{\text{aq}}^-)$ above 200°C is quite similar to the values recommended in the review, but the present determination is much more firmly grounded than any previous measurement.

Figure 4. Escape yield of reducing radicals, measured as $G(\text{N}_2)$ using alkaline N_2O /acetate scavenger system. The present measurements are compared with values (dashed line) recommended by Elliot and Bartels²⁹.

The $G(\text{H}_2)$ measured in the alkaline N_2O /acetate system is shown in figure 5 and listed in Table 2, also in comparison with the E&B review recommendation²⁹. The present numbers are slightly scattered due to the S/N ratio afforded by the low dose used here, but are in excellent overall agreement with previous measurements. Moreover, the H_2 yield is expected to be slightly higher than the $G_{\text{esc}}(\text{H}_2)$ in pure water, just as shown in the plot, because some small fraction of the $\text{H}^\bullet$ atoms are scavenged by acetate anion. In light of the good agreement, we recommend retaining the formula given by Elliot and Bartels:

$$G_{\text{esc}}(\text{H}_2) = 0.419 + 8.721 \times 10^{-4} t - 4.971 \times 10^{-6} t^2 + 1.503 \times 10^{-8} t^3 \quad (10)$$

Figure 5. Yield of molecular H₂ measured in the alkaline N₂O/acetate system. The dashed line is the formula given by Elliot and Bartels.²⁹

IV Discussion

The careful simultaneous measurement of $G(\text{H}^\bullet + \text{e}_{\text{aq}}^-)$ and $G(\text{H}_2)$ vs. temperature reported here has great utility in establishing mass balance for the overall radiolysis mechanism of water. The necessary constraint between yields of the various species is set forth in equation 5. It must be true at any given time in development of the track and spur chemistry, but because most independent measurements have effectively used different “times” (inverse scavenging powers), it is difficult to demonstrate that mass balance is achieved. Only by considering long-time limiting escape yields (effectively $t = \infty$) is it reasonable to expect that equation 5 should constrain the measured G values from different experiments.

For comparison with our new estimate of $G_{\text{esc}}(\text{red})$, we consult the data reviewed by Elliot and Bartels²⁹ for the yields of oxidizing species $G(\cdot\text{OH})$ and $G(\text{H}_2\text{O}_2)$. Several studies have made measurements of $G(\text{H}_2\text{O}_2)$ up to around 100°C, and the results are consistent within ± 0.1 molecule/100eV. The study of Elliot et al³⁹ made use of $5 \times 10^{-4}\text{M}$ acrylamide to scavenge all radicals with reasonably low scavenging power. Their measurements agree with others where larger scavenging powers were used, so we can probably accept these numbers as representing the $G_{\text{esc}}(\text{H}_2\text{O}_2)$. $G(\text{H}_2\text{O}_2)$ numbers at temperatures higher than 100°C are much less reliable due to the instability of H_2O_2 , which catalytically decomposes on oxide surfaces. In fact the extrapolated linear behavior recommended in the E&B review²⁹ represents little more than a guess based on expectations.

The only reliable temperature-dependent yields presented for $\cdot\text{OH}$ radical (up to 300°C) come from scavenging of carbonate anion to produce the $\cdot\text{CO}_3^-$ radical in pulse radiolysis experiments carried out at AECL Chalk River Laboratories^{29,39}. The scavenging power for $\cdot\text{OH}$ was below $1 \times 10^6 \text{ s}^{-1}$ at room temperature. Oxygen from air saturation was used to scavenge the $\text{H}\cdot$ atoms and $(\text{e}^-)_{\text{aq}}$. The scavenging power of ca. $4 \times 10^6 \text{ s}^{-1}$ for hydrated electron at room temperature compares favorably with the low scavenging power used in the present study, so we can reasonably expect the carbonate radical yield to represent $G_{\text{esc}}(\text{OH})$. However, before we use the $G(\text{OH})$ numbers recommended by Elliot and Bartels²⁹, we need to correct two flaws in the data analysis of the $\cdot\text{CO}_3^-$ results. The review presented transient spectra of $\cdot\text{CO}_3^-$ radical vs.

temperature. The spectra are slightly shifted and broadened at elevated temperature, as also reported by Wu, et al⁴². The standard assumption was made that the absorption spectrum integrated over photon energy (oscillator strength) should be conserved^{43,44}, so that the peak extinction coefficient at 600nm could be corrected for change in temperature. Use of this corrected extinction coefficient demonstrably improved the mass balance between the oxidizing and reducing species²⁹. However, in condensed phase it is the product of oscillator strength times refractive index that must be conserved⁴³⁻⁴⁵. Refractive index of water near 600nm decreases with temperature⁴⁶ on the order of 7% between room temperature and 350°C. As a result we now realize that the extinction coefficient was over-corrected at high temperature, and the actual G-values for $\cdot\text{OH}$ should be somewhat lower than given in the E&B review²⁹.

Figure 6. G value for dissociation of water (molecules/100eV) calculated from the reducing equivalents with the data of this paper (circles), or with the oxidizing equivalent formulas recommended in reference ²⁹ (dotted line). Also shown are corrected and uncorrected yields for G(OH) inferred from $\cdot\text{CO}_3^-$ radical transient absorbance data.

The second correction involves the room temperature escape yield of $\cdot\text{OH}$ radical and extinction coefficient of the $\cdot\text{CO}_3^-$ radical. Elliot and Bartels²⁹ use a G(OH) value of 2.7 molecules/100eV at 25°C to interpret the $\cdot\text{CO}_3^-$ absorption data, yielding extinction coefficient of 2000 M⁻¹ cm⁻¹. In contrast, the limiting escape yield for $\cdot\text{OH}$ radicals at room temperature was most recently found by Laverne⁴⁷ to be approximately 2.5 molecules/100eV at scavenging powers of formate ion and formic acid below 10⁶ s⁻¹. The G(OH)=2.7 number is found in the textbook of Spinks and Woods⁸, and is probably influenced heavily by the higher G-values

reported many years ago by Draganic, et al^{10,48} for the same formate/formic acid scavenger system investigated by Laverne⁴⁷. This value for $G(\text{OH})$ was necessary in the E&B review to balance the room temperature value for $G(\text{e}^-)_{\text{aq}}$, which came from experiments³⁵ with scavenging powers admittedly too high²⁹. If we accept Laverne's escape yield result we can re-evaluate the $\dot{\text{CO}}_3^-$ radical extinction coefficient upward by the ratio 2.7/2.5 before we correct for the refractive index change. In figure 6 we plot both the original uncorrected $G(\text{OH})$ proposed by E&B, and the values inferred after these two corrections of the $\dot{\text{CO}}_3^-$ radical extinction coefficient.

The corrected values for $G(\text{ox}) = G(\dot{\text{OH}}) + 2 \times G(\text{H}_2\text{O}_2)$ are plotted in figure 6, together with the sum of our new $G_{\text{esc}}(\text{H}^\bullet + \text{e}^-_{\text{aq}}) + 2 \times G(\text{H}_2)$, which we take as the best estimate of $G_{\text{esc}}(\text{red})$. Also plotted as the dotted line is the original value of $G(-\text{H}_2\text{O}) = G(\text{red}) = G(\text{ox})$ from the E&B review. It can be seen that the new estimate of $G(\text{red})$ from this work is not so very different from that estimated by Elliot and Bartels. The primary difference of 5-10% is found at low temperature because of the use of $G(\text{e}^-)_{\text{aq}}$ from scavenger experiments with too high scavenging power. However, we can see that the correction of $G(\text{OH})$ inferred from the $\dot{\text{CO}}_3^-$ radical absorbance leads to a considerable divergence of $G(\text{ox})$ and $G(\text{red})$ at high temperature.

Two possible reasons for this discrepancy at high temperature can be suggested. The yield of $\dot{\text{OH}}$ radicals, based on the $\dot{\text{CO}}_3^-$ radical absorption, may be too low. Or, the yield of H_2O_2 may be larger than guessed at based on lower temperature measurements.

Regarding the latter point, we note that the escape yield of hydrogen peroxide at high temperature is very difficult to measure, and the function given by Elliot and Bartels is mostly a guess based on linear extrapolation of the low temperature behavior. Good measurements of $G(\text{H}_2\text{O}_2)$ are available from several authors^{39,49,50}, which agree to within 0.1 molecule/100eV up to 100°C. The only high temperature estimate at 275°C is from Kent and Sims, but their overall precision is poor even at room temperature. It is shown by Lin, et al⁵¹ that even in Teflon-coated tubing hydrogen peroxide will quickly catalytically decompose to O_2 and water above 200°C. The general trend of the hydrogen peroxide yield seems to be downward, just as expected if the only source of H_2O_2 is recombination of $\cdot\text{OH}$ radicals in spurs. The same trend is expected of H_2 , but the $G(\text{H}_2)$ increases with temperature nevertheless. So, perhaps the yield of H_2O_2 also increases above 200°C, by some mechanism operating at the early physico-chemical stage of radiolysis? To explain the entire discrepancy between $G(\text{red})$ and $G(\text{ox})$ in figure 6 would require $G(\text{H}_2\text{O}_2)$ of ca. 0.4 at 300°C, essentially unchanged from 200°C.

A more straightforward explanation of the discrepancy illustrated in figure 6 may be that the oscillator strength of the $\cdot\text{CO}_3^-$ spectrum is not in fact conserved. Shkrob⁵² has shown that the carbonate radical absorbance at 600nm is forbidden for the $\text{D}_{3\text{h}}$ symmetry molecule. The absorbance is only possible because the symmetry is broken to $\text{C}_{2\text{v}}$ in aqueous solution. Shkrob further demonstrates that the oscillator strength is a strong function of the distortion away from the $\text{D}_{3\text{h}}$ symmetry. So, it is possible that at elevated temperature, with lower water density, lower dielectric constant, and larger vibrational amplitudes, the molecular geometry shifts on average in the direction of the $\text{D}_{3\text{h}}$ symmetry with its lower oscillator strength. This could cause an underestimate of the $\cdot\text{OH}$ radical yields at high temperature.

While we have focused our attention on the data for $G(\dot{\text{O}}\text{H})$ from the $\dot{\text{C}}\text{O}_3^-$ absorption, there are other measurements of total radical yields, e.g. from transient absorbance of the methyl viologen radical cation MV^+ , which agreed reasonably well with the original $G(-\text{H}_2\text{O})$ estimate, and therefore also reasonably well (c.f. figure 6) with our new measurement of $G(\text{red})$. The estimate for $G(\text{H})$ in the E&B review relied on re-evaluation of archived transient absorption data, which included the $G(\text{OH})$ in the analysis. The overall good result for $G(-\text{H}_2\text{O})$ demonstrated in figure 6 could not have been obtained if $G(\dot{\text{O}}\text{H})$ was low by 20%.

Consequently for applications such as modeling nuclear reactor chemistry, or evaluating high temperature pulse radiolysis kinetics data, we recommend that $G_{\text{esc}}(\text{OH})$ be estimated at this time via mass balance relative to the other equations (t in $^\circ\text{C}$):

$$G_{\text{esc}}(\text{H}^\cdot + \text{e}^-_{\text{aq}}) = 2.868 + 7.573 \times 10^{-3} t + 2.500 \times 10^{-6} t^2 \quad (9)$$

$$G_{\text{esc}}(\text{H}_2) = 0.419 + 8.721 \times 10^{-4} t - 4.971 \times 10^{-6} t^2 + 1.503 \times 10^{-8} t^3 \quad (10)$$

$$G_{\text{esc}}(\text{H}_2\text{O}_2) = 0.752 - 1.620 \times 10^{-3} t \quad (11)$$

$$G_{\text{esc}}(\dot{\text{O}}\text{H}) = G_{\text{esc}}(\text{H}^\cdot + \text{e}^-_{\text{aq}}) + 2 \times G_{\text{esc}}(\text{H}_2) - 2 \times G_{\text{esc}}(\text{H}_2\text{O}_2) \quad (12)$$

It should be emphasized again that these equations refer to the limiting escape yields in pure water. In the presence of finite scavenger concentrations, the product yields are likely to be higher.

V. Summary

In the present work we have presented simultaneous measurements of the reducing radical escape yield $G_{\text{esc}}(\text{e}^-_{\text{aq}} + \text{H})$ and the reduced molecular product $G_{\text{esc}}(\text{H}_2)$ in low LET water radiolysis as a function of temperature up to 350°C . The great advantage of this experiment, is

that the mass balance between reducing and oxidizing equivalents (eq. 5) can be rigorously applied. $G_{\text{esc}}(\text{H}_2)$ agrees well with previous experiments. The reducing radical yield is placed on much firmer footing than ever before. The measurements largely confirm the estimate of $G(\text{e}_{\text{-aq}}) + G(\text{H})$ made by Elliot and Bartels²⁹ for temperature above 200°C. At lower temperatures these new measurements conform more closely to the low-scavenging-power limit. We have shown that previous analysis of transient absorbance data for $G_{\text{esc}}(\cdot\text{OH})$ is flawed, and mass balance between reducing and oxidizing species has not been achieved. Nevertheless, previous estimates of $G_{\text{esc}}(\cdot\text{OH})$ cannot be grossly in error. For kinetic modeling studies where mass balance is critical, we recommend that $G_{\text{esc}}(\cdot\text{OH})$ should be calculated from the reducing equivalents, minus twice the $G_{\text{esc}}(\text{H}_2\text{O}_2)$.

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Figure Captions

Figure 1. Apparatus used for N₂O calibration yield experiments at room temperature.

Figure 2. G(N₂) vs. acetate concentration at several temperatures.

Figure 3. G(N₂) vs. acetate concentration. Low dose (55Gy) data are open symbols connected by lines. Filled symbols are measured via dose dependent signal at 2mM acetate.

Figure 4. Escape yield of reducing radicals, measured as G(N₂) using alkaline N₂O/acetate scavenger system. The present measurements are compared with values (dashed line) recommended by Elliot and Bartels²⁹.

Figure 5. Yield of molecular H₂ measured in the alkaline N₂O/acetate system. The dashed line is the formula given by Elliot and Bartels.²⁹

Figure 6. G value for dissociation of water (molecules/100eV) calculated from the reducing equivalents with the data of this paper (circles), or with the oxidizing equivalent formulas recommended in reference ²⁹ (dotted line). Also shown are corrected and uncorrected yields for G(OH) inferred from [•]CO₃⁻ radical transient absorbance data.

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TOC picture

$G(\text{reducing species}) = G(\text{oxidizing species})$