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COMMENTS

Comment on “Experimental Determination of the Dependence of OH Radical Yield on Photon Energy: A Comparison with Theoretical Simulations” by Fulford et al. (*J. Phys. Chem. A* 1999, *103,* 11345−11349)

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Recently, Fulford et al.[1] have determined experimentally the dependence of the “primary” yield of $^{\bullet}$OH radicals ($G_{^{\bullet}\mathrm{OH}}$), a major transient species produced in water radiolysis,[2,3] on photon energy of incident radiation using aqueous solutions of plasmid DNA as a probe to sample the number of hydroxyl radicals present at the spur expansion completion (or homogenization) time, that is, $\sim 10^{-6}$ s, after the initial deposition of energy. These authors[1] measured the yield of single-strand breaks (ssb) induced within the DNA probe when irradiated with photons varying in energy from 0.28 keV (C_K X-rays) to 1.25 MeV (^{60}Co γ-rays). The data, when normalized relative to the yield of ssb for ^{60}Co γ-rays, were then used as a measure of $G_{^{\bullet}\mathrm{OH}}$ (taking $G_{^{\bullet}\mathrm{OH}} \approx 2.80$ molecule/100 eV [that is, 0.29 μmol/J in SI units; for conversion of yield values into SI units, 1 molecule/100 eV $\approx 0.103\,64$ μmol/J] for ^{60}Co γ radiation at $\sim 10^{-6}$ s). As the photon energy decreases from $\sim$1.25 MeV to 1.5 keV, the values of $G_{^{\bullet}\mathrm{OH}}$ so obtained decrease from $\sim$2.80 to 0.695 molecule/100 eV, whereas there is a steep upturn in $G_{^{\bullet}\mathrm{OH}}$ with a further decrease in photon energy from 1.5 to 0.28 keV; for this latter energy, $G_{^{\bullet}\mathrm{OH}}$ reaches a value of $\sim$2.48 molecule/100 eV.[1] Several theoretical calculations (using both analytical models and stochastic simulations) for electrons[4−6] or photons[6,7] predicted such a general shape for the $G_{^{\bullet}\mathrm{OH}}$ vs particle energy curve, with a minimum $^{\bullet}$OH radical yield occurring between 0.1 and 1 keV, in partial agreement with Fulford et al.’s experimental data.[1] Using simulated electron track structures, Pimblott and LaVerne[8] also found a turnaround in $G_{^{\bullet}\mathrm{OH}}$ for electrons of an initial energy lower than $\sim$1 keV.

In support of the experimental data of Fulford et al.,[1] we present in this comment the results of our Monte Carlo calculations of $G_{^{\bullet}\mathrm{OH}}$ as a function of incident electron energy in the range of 0.05−150 keV. A detailed description of our computational modeling of the radiolysis of liquid water, the cross sections employed to describe the various physical processes, and the “independent reaction times” (IRT) simulation methodology used to model the nonhomogeneous chemistry of diffusing and reacting spur species up to $\sim 10^{-6}$ s has been given previously.[9−12] In the simulations reported here, the tracks of transported primary electrons are selected so that the difference between the initial energy of those electrons and the energy deposited along the corresponding tracks is equal to $\sim$5 eV. These primary electrons are also assumed to move in straight paths, with simulated path lengths varying from $\sim$0.004 to 470 μm for the incident electron energy range considered, in reasonably good agreement with the electron ranges recommended in ICRU 16 for liquid water.[13,14] The number of different primary electron histories ($\sim$50−500, depending on the initial electron energy) is chosen so as to ensure only small statistical fluctuations when calculating average yields, while keeping acceptable computer time limits. The energy dependence of our calculated values of $G_{^{\bullet}\mathrm{OH}}$ at 10^{-6} s is shown in Figure 1, along with the measurements of Fulford et al.[1] (after converting experimental photon energies to electron energies, using ref 15). The simulated $^{\bullet}$OH radical yields obtained by Hill and Smith[5,17] and by Pimblott[6] are also included for comparison. As can be seen, there is a substantial similarity between the shapes of the different curves, though there are some differences in the yields and in the positions of the minimum. Our values of $G_{^{\bullet}\mathrm{OH}}$ are very close to those calculated by Pimblott[6] and are generally closer to experiment than those determined by Hill and Smith;[5,17] in particular, they match the

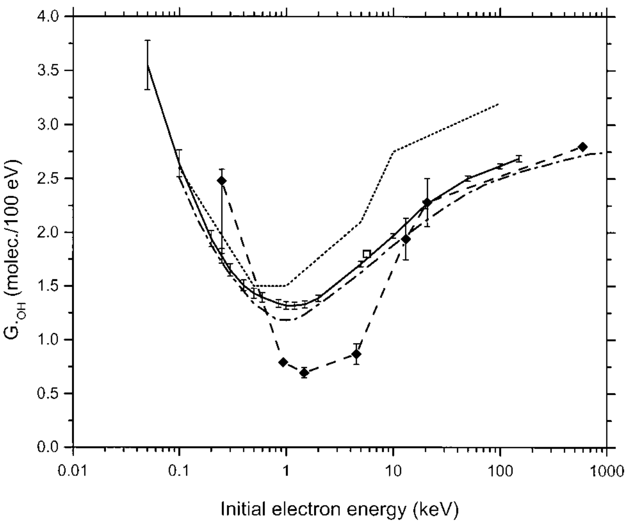

Figure 1. Variation of the primary yields of $^{\bullet}$OH radicals produced by electron radiolysis of pure liquid water at 25 °C as a function of incident electron energy: —, present work (the error bars show the 95% confidence intervals of our simulation results); ···, Monte Carlo electron simulations of Hill and Smith (ref 5); − - −, Monte Carlo electron simulations of Pimblott (ref 6); − ◆ −, experimental data of Fulford et al. (ref 1). We should note that the experimental variation of $^{\bullet}$OH yield is based on photon energy, not electron energy. However, for the sake of comparison, those experimental photon energies have been converted to electron energies, using ref 15. □, experimental value of $G_{^{\bullet}\mathrm{OH}}$ at neutral pH for ^{3}H β-rays (average energy $\sim$5.67 keV; corresponding dose-average linear energy transfer (LET) $\sim$9.48 keV/μm; refs 15 and 16).

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TABLE 1: Effect of Electron Energy on the Initial and Primary $^{\bullet}$OH Radical Yields (Expressed in molecule/100 eV) and on the Extents $\Delta G_{^{\bullet}\mathrm{OH}}$ of the Main Spur Reactions that Contribute to the Decay and Formation of $^{\bullet}$OH Radicals in Our Monte Carlo Simulations of the Electron Radiolysis of Liquid Water (See Text)

initial electron energy (keV)	0.1	1	10	150
initial $^{\bullet}$OH radical yield[a]	6.015	5.827	5.804	5.761
$\Delta G_{^{\bullet}\mathrm{OH}}$ ($^{\bullet}\mathrm{OH} + \mathrm{e^-_{aq}} \rightarrow \mathrm{OH^-}$)	−1.855	−2.289	−2.055	−1.660
$\Delta G_{^{\bullet}\mathrm{OH}}$ ($^{\bullet}\mathrm{OH} + {}^{\bullet}\mathrm{OH} \rightarrow \mathrm{H_2O_2}$)	−1.409	−2.076	−1.657	−1.315
$\Delta G_{^{\bullet}\mathrm{OH}}$ ($^{\bullet}\mathrm{OH} + \mathrm{H^{\bullet}} \rightarrow \mathrm{H_2O}$)	−0.515	−0.596	−0.529	−0.462
$\Delta G_{^{\bullet}\mathrm{OH}}$ ($^{\bullet}\mathrm{OH} + \mathrm{OH^-} \rightleftarrows \mathrm{O^-} + \mathrm{H_2O}$)	−0.106	−0.191	−0.124	−0.097
$\Delta G_{^{\bullet}\mathrm{OH}}$ ($\mathrm{H_2O_2} + \mathrm{e^-_{aq}} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{OH^-}$)	0.098	0.251	0.189	0.134
$\Delta G_{^{\bullet}\mathrm{OH}}$ ($\mathrm{H^+} + \mathrm{O^-} \rightarrow {}^{\bullet}\mathrm{OH}$)	0.067	0.110	0.075	0.059
$G_{^{\bullet}\mathrm{OH}}$ (at $\sim 10^{-6}$ s)	2.641	1.318	1.969	2.687

[a] At $\sim 10^{-13}$ s, after taking into account "contact" reactions (see refs 10 and 11).

observed yields quite well for electrons of energy above ∼10 keV. Moreover, the position of the minimum of our computed $G_{^{\bullet}\mathrm{OH}}$ values occurs at ∼1.2 keV, in very good agreement with the experimental value at ∼1.5 keV.[1] However, the minimum $^{\bullet}$OH radical yield that we obtain (∼1.32 molecule/100 eV) remains somewhat higher than that found experimentally (0.695 molecule/100 eV).[1]

We should point out explicitly here that the calculations reported in this work are for electrons, and the experiment by Fulford et al.[1] is done with photons. According to the latter authors (ref 1 and personal communication), "some differences in yields between photons and electrons of a given energy are to be expected when the photon interaction results in two electrons (photon and Auger) of lower energies." Pimblott,[6] who performed both electron and photon track structure simulations in water, predicted "significant differences between the yield for photons and that for electrons for energies greater than 1 keV". His simulated values of $G_{^{\bullet}\mathrm{OH}}$ at the minima of the curves near 1 keV (Figure 2 of ref 6) are equal to ∼1.19 and ∼1.02 molecule/100 eV for electrons and photons, respectively, whereas the minimum $^{\bullet}$OH radical yield found experimentally is 0.695 molecule/100 eV.[1] Judging from those results, the difference is not large between the calculated $G_{^{\bullet}\mathrm{OH}}$ values for electrons and photons and could not be discerned from the experimental data. At present, we have no explanation to offer on the differences that exist in the range of ∼1−10 keV between the various theoretical simulations for electrons or photons and the experimental dependence of $G_{^{\bullet}\mathrm{OH}}$ on photon energy reported by Fulford et al.[1]

The effect of electron energy on the formation and decay kinetics of $^{\bullet}$OH radicals is considered in Table 1. As we can see, the "initial" $^{\bullet}$OH radical yield decreases only slightly (by about 0.25 molecule/100 eV) from 0.1 to 150 keV, with this decrease occurring mainly below ∼1 keV. Those $^{\bullet}$OH radicals, present at $\sim 10^{-13}$ s, mostly originate from ionization and electronic excitation events that take place in the physical and physicochemical stages of the radiolysis of water.[10,11] The energy dependence of $G_{^{\bullet}\mathrm{OH}}$ therefore does not arise from changes in the initial yields of $^{\bullet}$OH radicals but rather from the reactions that are involved in their formation or decay in the nonhomogeneous chemical stage. Table 1 also shows the effect of increasing incident electron energy on the extent, expressed as a cumulative $\Delta G_{^{\bullet}\mathrm{OH}}$ value, of the main reactions of $^{\bullet}$OH radicals in the spurs as they expand by diffusion in the time interval $\sim 10^{-13}$−10^{-6} s. As can be seen, the extents of the reactions that contribute to the decay of $^{\bullet}$OH radicals all have a pronounced maximum (in absolute value) at ∼1 keV. In other words, there are less $^{\bullet}$OH radicals surviving spur reactions at this energy, which in turn readily explains the observed minimum in the variation of $G_{^{\bullet}\mathrm{OH}}$ with incident electron energy.

A detailed report on the effect of initial electron energy on all primary free-radical and molecular yields of liquid water radiolysis will be published elsewhere.

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(17) In our Figure 1, we have used the primary $^{\bullet}$OH yield values given in Figure 10b of the original paper of Hill and Smith (ref 5).