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**Scavenging of “dry” electrons prior to hydration by azide ions:
Effect on the formation of H₂ in the radiolysis of water by ⁶⁰Co γ -rays
and tritium β -electrons**

By

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Abstract:

In this study, we use Monte Carlo track chemistry simulations to show that “dry” secondary electrons, precursors of the “hydrated” electron (e^-_{aq}), can be scavenged on the sub-picosecond time scale prior to hydration, by a high concentration ($>0.1\text{--}1\text{ M}$) of azide ions (N_3^-) in water irradiated with ^{60}Co γ -rays and tritium β -electrons at $25\text{ }^\circ\text{C}$. This is a striking result, as N_3^- is known to react very slowly with e^-_{aq} . These processes tend to significantly reduce the yields of H_2 as observed experimentally. For both energetic Compton electrons (“linear energy transfer”, $LET \sim 0.3\text{ keV}/\mu\text{m}$), which are generated by the cobalt-60 γ -rays, and ^3H β -electrons ($LET \sim 6\text{ keV}/\mu\text{m}$), our H_2 yield results confirm previous Monte Carlo simulations, which indicated the necessity of including the capture of the precursors to e^-_{aq} . Interestingly, our calculations show no significant changes in the scavenging of “dry” electrons at high azide concentrations in passing from γ -radiolysis to tritium β -radiolysis (*i.e.*, with LET). This led us to the conclusion that the higher H_2 yield observed experimentally for ^3H β -electrons compared to ^{60}Co γ -rays is mainly explained by the difference in the radiation track structures during the chemical stage ($>1\text{ ps}$). The higher LET of tritium β -electrons leads to more molecular products (H_2 in this case) in tritium radiolysis than in γ -radiolysis. Finally, a value of $\sim 0.5\text{ nm}$ was derived for the reaction distance between N_3^- and the “dry” electron from the H_2 yields observed in ^{60}Co γ -radiolysis at high N_3^- concentrations.

Keywords: Liquid water, azide ion (N_3^-) solutions, radiolysis, linear energy transfer (LET), cobalt γ -rays, tritium β -electrons, secondary electrons, “dry” electron scavenger, mobility, H_2 yield, Monte Carlo track chemistry simulations.

1. Introduction

The radiation chemistry of liquid water¹⁻³ is of fundamental importance for a variety of practical applications, particularly in the nuclear power industry, where radiolysis products cause corrosion and activity transport,^{4,5} and in radiation biology,⁶⁻⁹ where living cells and tissues consist mainly of water (~70%–85% by weight). Exposed to ionizing radiation, water is the site of ionizations and direct excitations:

which result, on the picosecond time scale, in a cascade of events leading to the formation of free radicals and molecular products along the track of the incident radiation. In pure water radiolysis, they essentially comprise the “hydrated” electron (e^-_{aq}), $\text{H}^\bullet$, $^\bullet\text{OH}$, H_2 , H_2O_2 , and $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$ ($\text{p}K_{\text{a}} \approx 4.8$ at 25 °C). Among these radiolysis products, one of the most interesting is molecular hydrogen, largely due to the questions it raises about the mechanism(s) by which it is formed or the nature of its precursor(s). Studies of a variety of scavenger systems at high concentrations using computer simulations in conjunction with available experimental data¹⁰⁻¹² have suggested that the majority of the total H_2 “primary” yield¹³ in ^{60}Co γ -radiolysis involves reactions of the short-lived, low-energy (“dry”) secondary electrons prior to trapping and hydration,¹⁴ *during the sub-picosecond physicochemical stage*. These reactions include^{15,16}

- *The geminate recombination of the “dry” electron with its short-lived H_2O^{*+} parent cation (or “hole”) due to their Coulomb attraction, which tends to draw them back together:*

followed by the *dissociation of the excited water molecule*^{17,18}

where $\text{O}(^1\text{D})$ is the oxygen atom in its singlet ^1D (non-radical) first excited state. Note that reaction (3) *must* take place before the H_2O^{*+} cation (whose lifetime has recently been estimated at 46 ± 10 fs)¹⁹ undergoes proton transfer to a neighboring water molecule

to give the hydronium cation H_3O^+ and the hydroxyl radical $\cdot\text{OH}$. In fact, this recombination affects only the “dry” electrons which are formed *in the vicinity of the parent water cation* and occurs in the first steps of their random walk, *i.e.*, in times as short as a few femtoseconds.²⁰

- The “dissociative electron attachment” (or DEA) involving the resonant capture of a low-energy, “dry” electron by a water molecule²¹⁻²⁵

followed by the reaction of the hydride anion with a second water molecule via instant proton transfer

The remainder of the radiolytic formation of H_2 is due to the following three radical-radical combination reactions of the hydrated electron and $\text{H}^{\cdot}$ atom in the tracks as they expand by diffusion during the nonhomogeneous chemical stage on the ps- μs time scale:^{15,16,26}

and, but to a much lesser extent,

with the corresponding rate constants (k) taken from the compilation of Elliot and Bartels.²⁷

Since no real-time studies on H_2 formation have been performed, the temporal dependence of the radiolytic H_2 yield is usually investigated by varying the concentration of appropriate scavengers for e^-_{aq} and the $\text{H}^\bullet$ atom, which are the two main free radical precursors of H_2 *within the diffusing radiation tracks*. In a previous paper¹² that explored the basic radiation chemical mechanisms underlying the “self-radiolysis” of tritiated water, we used Monte Carlo track chemistry simulations to investigate the scavengeability of the molecular H_2 yield produced in water irradiated by cobalt γ -rays and tritium β -electrons (maximum kinetic energy of 18.6 keV) by azide anions (N_3^-). This particular scavenger was chosen because it has very different reactivities towards e^-_{aq} and $\text{H}^\bullet$ atoms, reacting very slowly with the hydrated electron and very quickly with the hydrogen atom. Our work revealed significant chemical changes in the H_2 scavengeability by N_3^- when passing from γ - to tritium β -electron radiolysis, which can be explained by *differences in the electron track structures*, namely:

- In the case of the energetic (~ 1 MeV) Compton electrons generated by low-LET ^{60}Co γ irradiation, the track structure is initially formed by well-separated clusters of radiolytic species (or “spurs”)^{28,29} that are approximately spherical in shape.

- The low-energy, higher-LET β -electrons of tritium, on the other hand, deposit their energy mainly as dense, continuous (roughly cylindrical) columns of species (referred to as “short tracks” in the terminology of the Mozumder-Magee model³⁰ of energy deposition). In contrast to the spur geometry, this short-track geometry favors radical-radical combination reactions involving e^-_{aq} and $\text{H}^\bullet$ atoms, which leads to a

clear increase in the H_2 yield for tritium β -electrons compared to ^{60}Co γ -rays. This agrees very well with the experimental data³¹⁻³³ over a large range of N_3^- concentrations.¹²

However, at azide concentrations higher than $\sim 0.1\text{--}1\text{ M}$, our calculations¹² of the H_2 yields from ^{60}Co γ -radiolysis failed to reproduce the sharp decrease observed experimentally (e.g., for 5 M N_3^- , the H_2 yield is decreased to about one-third of its original value³¹). For the ^3H β -radiolysis, there was no clear evidence of such a sharp decrease in $G(\text{H}_2)$ in solutions with high N_3^- concentrations due to a relatively large dispersion in the experimental data.³²⁻³⁴ Nevertheless, based on recent work^{10,11} on the influence of scavengers of the precursors to e_{aq}^- on the yield of “non-scavengeable” H_2 formation,³⁵ we decided to include *the ultra-fast capture of these precursors* (thereafter referred to as e_{pre}^-) by N_3^- (Fig. 1) in our simulation model for the two types of radiation considered.

2. Simulation model

A) Monte Carlo track-chemistry simulations: The IONLYS-IRT code

The experimentally observed yield value for molecular hydrogen is a composite value to which each of the H_2 production processes contributes. Adding a scavenger that competes with these processes to varying degrees changes the relative amount that each process contributes to the total yield. In this work, we use our Monte Carlo track-chemistry computer code, called IONLYS-IRT,³⁶ to simulate the radiolysis of water containing various concentrations of N_3^- scavengers. This code is described in detail elsewhere.^{12,15,36,37} Only a brief overview of its most essential features is given below.

Our code first models *the early physical and physicochemical stages of the radiation action up to $\sim 1\text{ ps}$ in the track development* in a 3D geometric environment

("IONLYS" program). In the case considered here, we have modified this program to take into account the interaction of azide anions in concentrated N_3^- solutions with the initially formed "dry" electrons (*vide infra*). In the absence of dose-rate effects, the chemical effects of irradiation can be represented as the sum of the separate effects of individual (non-overlapping) tracks. Therefore, the history of only a single track needs to be considered. Note that the IONLYS program consists of two modules. One is used to transport the incident charged particle under consideration (called either TRACEPR for an impacting primary electron or TRACPRO/TRACION for an incident energetic proton/ion). The other (called TRACELE) is for transporting all of the "dry" secondary electrons resulting from the ionization of the water molecules until they are hydrated. To mimic the effects of ^{60}Co γ /fast electron-radiolysis, we simulated short segments of ~ 300 MeV ($\text{LET} \sim 0.3 \text{ keV}/\mu\text{m}$) irradiating proton tracks, using the TRACPRO module of IONLYS. Tritium- β primary electron ("effective" initial energy of $\sim 7.8 \text{ keV}$; mean LET in water: $\sim 6 \text{ keV}/\mu\text{m}$)³⁷ track structures were simulated using the TRACEPR module of IONLYS. However, as explained below, we found it advantageous to use the TRACPRO module to mimic tritium β -radiolysis by simulating short track segments of ~ 7 MeV incident protons that have a similar track structure and LET ($\sim 6 \text{ keV}/\mu\text{m}$)³⁸ to those of the ^3H β -electrons (Fig. 2A). In addition, we neglected the "direct" action of ionizing radiation on the solute. This is a good approximation for N_3^- concentrations up to $\sim 1\text{--}2 \text{ M}$ (in the latter case, approximately 2–4% of the total energy is absorbed directly by the azide anions). In the presence of $3 \text{ M } \text{N}_3^-$ (the highest N_3^- concentration considered in this work given the limitations of our computing capacities), the proportion of direct effects is relatively greater ($\sim 7\%$) but can reasonably be ignored.

The complex spatial distribution of the reactants of the considered track system at the end of the physicochemical stage is provided as an output of the IONLYS program.

It is then used directly as *the starting point for the subsequent chemical stage, which is covered by the “IRT” component of the code (> 1 ps)*. This program describes the resulting diffusion and chemical reactions of the various radical and molecular products of radiolysis with each other or in competition with dissolved solutes (N_3^- in the case studied here) present in the solution at the time of irradiation. It uses the “independent reaction times” or IRT method,³⁹⁻⁴¹ a computationally efficient stochastic simulation technique that can simulate reaction times without having to follow the trajectories of the diffusing species. Its implementation has previously been described elsewhere.⁴¹ The ability of this method to give accurate time-dependent chemical yields over a wide range of irradiation conditions has been well validated by comparison with full random flights Monte Carlo simulations^{42,43} that follow the reactant trajectories in detail.

B) The physicochemical stage: Modeling “dry” electron scavenging by azide ions

As mentioned above, we modified the step-by-step IONLYS program to include the possibility of azide anions scavenging the short-lived precursors (e^-_{pre}) to the hydrated electron, which are involved in the ultrafast formation of H_2 . *We used a simulation model consisting of a right circular cylindrical volume of water containing the studied azide concentration (Fig. 2B).* Protons of either 300 MeV (LET $\sim 0.3 \text{ keV}/\mu\text{m}$) or 7 MeV (LET $\sim 6 \text{ keV}/\mu\text{m}$) (mimicking irradiation by ^{60}Co γ or ^3H β rays, respectively), or by 7.8-keV (LET $\sim 6 \text{ keV}/\mu\text{m}$) tritium β -electrons, are generated at the center of the front circle of the cylinder and penetrate perpendicular to this surface. In this cylindrical geometry, the proton tracks, which are essentially rectilinear trajectories, run along the cylinder axis and consist mainly of aligned, well-separated “spurs”.^{12,37} For the ^3H β -electron irradiation, the “short-track” trajectories are not linear, but rather have

a more or less tortuous shape due to the successive angular deflections experienced by the primary electrons (Fig. 2). Compared to proton irradiations, this non-linearity of electron trajectories has two main disadvantages: 1) from a computational point of view, it significantly increases computer times, and 2) the simulated electron trajectories have a non-negligible probability of crossing the limits of the model cylinder used, resulting in irregularities in the yield calculations. To avoid this, *we used 7-MeV incident protons here to simulate the tritium β -radiolysis of azide solutions.*

In preliminary simulations we varied the secondary electron energy above which we could neglect the capture of the “dry” electron by N_3^- , and showed that *only the electrons in the region of subexcitation energy (i.e., those with kinetic energies lower than ~ 7.3 eV, the first electronic excitation threshold of water)^{20,30,44,45} could most efficiently be captured by N_3^- scavengers.* Taking into account the track structures and the previously calculated low-energy secondary electron penetration ranges in water⁴⁶ enabled us to set appropriate values for the parameters of the cylinder. The length of the cylinder (i.e., the track length of the incident protons) was chosen to vary between 100 μm (for 10^{-4} – 0.1 M N_3^-), 60 μm (for 1 M N_3^-), and 40 μm (for 2 and 3 M N_3^-). The energy and LET of the protons were well defined over these simulated track segments. With regard to the radius of the circular base of the cylinder, we chose a value of 15 nm in accordance with our electron thermalization distance results reported in *ref. 46.*⁴⁷

Note that, in the computer simulations reported here, the number of individual proton “histories” (~ 100) was chosen to ensure only minor statistical fluctuations in the computed average H_2 yields while maintaining acceptable computer time limits.

Since there are no experimental data on the reactivity of N_3^- towards e^-_{pre} , *we considered the ($N_3^- + e^-_{pre}$) reaction distance (R_{react}) as an adjustable parameter.* Using the ^{60}Co γ -radiolysis case of 1 M N_3^- solutions as a reference, we varied R_{react}

using a trial-and-error approach until a good fit was obtained between our calculated $G(\text{H}_2)$ value and the corresponding experimental value^{31,32} of ~ 0.3 molecule/100 eV (Fig. 3A). This was achieved for $R_{\text{react}} \sim 0.5$ nm, a value that can simply be viewed as the sum of the reaction radius of the azide anion (~ 0.26 nm)⁴⁸ and the spatial extent of the “dry” electron if we assume it has the same value as that for the hydrated electron (~ 0.245 nm).⁴⁹⁻⁵²

An estimate of the scavenging rate constant (k) of e^-_{pre} can be obtained from the Smoluchowski equation:^{53,54}

$$(11) \quad k = 4\pi N_A \left[D(\text{N}_3^-) + D(e^-_{\text{pre}}) \right] R_{\text{react}},$$

where N_A is Avogadro's constant, $D(\text{N}_3^-)$ and $D(e^-_{\text{pre}})$ are diffusion coefficients, and R_{react} is the reaction distance. Of course, eq. (11) – which is often used to evaluate diffusion-controlled rate constants – can only be given approximately here, since the low-energy “dry” electron scavenging by N_3^- is presumably not controlled by diffusion. An additional factor is the Coulomb repulsion between N_3^- and e^-_{pre} ,⁵⁵ which makes it somewhat more difficult for these two reactive species to approach each other closely. Using $R_{\text{react}} = 0.5$ nm obtained in this work and the $(\text{N}_3^- + e^-_{\text{pre}})$ rate constant proposed by Harris and Pimblott¹¹ ($k \sim 10^{12} \text{ M}^{-1} \text{ s}^{-1}$) in their studies on the effect of azide-ion concentration on the yield of H_2 in ^3H β -particle and ^{60}Co γ radiolysis readily yields $D(\text{N}_3^-) + D(e^-_{\text{pre}}) = 2.64 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. Since $D(\text{N}_3^-) = 1.84 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$,¹² we then deduce that $D(e^-_{\text{pre}}) \sim 2.62 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, i.e., a value 54 times greater than the diffusion coefficient of the hydrated electron at 25 °C $D(e^-_{\text{aq}}) = 4.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.⁵⁶

An estimate of the mobility of e^-_{pre} , $\mu(e^-_{\text{pre}})$, can be derived from the Einstein formula, which relates the diffusion coefficient and mobility: $\mu(e^-_{\text{pre}}) = e D(e^-_{\text{pre}}) / k_B T$, where $e = 1.6 \times 10^{-19} \text{ C}$, k_B is Boltzmann's constant ($1.38 \times 10^{-23} \text{ J/K}$) and $T = 298 \text{ K}$. Using $D(e^-_{\text{pre}}) \sim 2.62 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, one finds $\mu(e^-_{\text{pre}}) \sim 0.1 \text{ cm}^2/\text{V s}$, a value that is

approximately 8 to 10 times higher than the highest mobilities reported for solvated electrons in weakly polar liquids, such as *n*-propylamine ($1.3 \times 10^{-2} \text{ cm}^2/\text{V s}$), dimethylsulfide ($1.36 \times 10^{-2} \text{ cm}^2/\text{V s}$) or dimethyl ether ($10^{-2} \text{ cm}^2/\text{V s}$).⁵⁷

C) The chemical stage: The reaction mechanism

The reaction scheme and rate constants for the radiolysis of pure liquid water at 25 °C are the same as used previously (see Table 1 of [ref. 37](#)). This series of reactions, initially compiled in [refs. 36 and 41](#), now includes some newly measured or recently re-assessed reaction rates.²⁷ The complete reaction scheme describing the radiolysis of aerated aqueous solutions containing azide anions has been reported elsewhere.¹² Below we briefly give *the reactions of N_3^- with the radiolytic species formed in the water of the irradiated solutions that we added to the IRT program*. These reactions compete with the reactions of pure water radiolysis.

The azide ion reacts very fast with $\text{H}^\bullet$ atoms and very slowly with e^-_{aq}

In contrast, its protonated form, HN_3 ,

$$k_{14} \text{ (forward)} \approx 10^9\text{--}10^{10} \text{ M}^{-1} \text{ s}^{-1},$$

is highly reactive towards e^-_{aq} but it reacts more slowly with $\text{H}^\bullet$

Note, however, that under the neutral pH conditions in this work, HN_3 occurs almost entirely as an anion and should therefore not significantly affect the H_2 yield.

The azide ion can also react with $\cdot\text{OH}$ to produce the azide radical $\text{N}_3\cdot$

In this case, we need to consider the following reactions:

The rather slow reaction of azide with e^-_{aq} practically excludes any effect of N_3^- on reactions involving e^-_{aq} in the spurs or tracks. In fact, since the H_2 yield is measured in irradiated *aerated* ($2.5 \times 10^{-4} \text{ M O}_2$) azide solutions, oxygen will scavenge e^-_{aq}

on the $\sim 0.1 \mu\text{s}$ time scale, *i.e.*, before reaction (13) can occur (even in a 3 M N_3^- solution where the scavenging time⁵⁸ of e^-_{aq} by N_3^- is $\geq 0.2 \mu\text{s}$). Experimentally, the presence of oxygen prevents, at long times, the reactions of e^-_{aq} with itself and with water in the bulk of the solutions. Interestingly, $\text{N}_3\cdot$ is inert to O_2 , but may react with the superoxide anion radical

to reform N_3^- .

We also introduced the effect of ionic strength of the solutions on all reactions between ions (with the exception of the peculiar bimolecular self-recombination of e^-_{aq} for which there is no evidence of an ionic strength effect⁵⁹) in the IRT program. The correction of the reaction rate constants was carried out as described in [refs. 60 and](#)

61. Finally, the values of the diffusion coefficients at room temperature used for the various reactive species involved in our IRT simulations of the radiolysis of water are given in Table 6 of ref. 56. The diffusion coefficient for the azide radical $\text{N}_3^\bullet$ in water at 25 °C was assumed to be the same as that of N_3^- ($1.84 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$).¹²

3. Results and discussion

The effect of azide-ion concentration on the yield of H_2 for 300- and 7-MeV incident protons (mimicking ^{60}Co γ -rays or fast electrons, and 7.8-keV ^3H β -electrons, respectively) in the radiolysis of aerated aqueous N_3^- solutions is illustrated in Figs. 3 and 4. The H_2 yields shown in these figures are the limit plateau values of the time profiles of $G(\text{H}_2)$ ¹² corresponding to each considered N_3^- concentration between 10^{-4} and 3 M. As can be seen, our simulated $G(\text{H}_2)$ values, assuming that N_3^- scavenges the low-energy “dry” electrons before they are hydrated (solid lines), agree better with experimental data³¹⁻³³ than our previously reported results (dashed lines),¹² which did not consider the scavenging of the short-lived precursor to H_2 . This applies in particular to γ -radiolysis at high N_3^- concentrations, in which our calculated H_2 yields reproduce the experimentally observed sharp decrease in $G(\text{H}_2)$ well (Fig. 3A). These results confirm previous studies by Harris and Pimblott¹¹ who obtained similar findings in the case of ^{60}Co γ radiolysis on N_3^- scavenging of the short-lived precursor to e_{aq}^- and H_2 on the subpicosecond time scale. In the case of ^3H β -electron radiolysis (Fig. 3B), at high (>0.1 M) azide concentrations, there is a relatively large dispersion/variability of the experimental data^{32,33} which prevents us from observing any clear, continuous lowering of $G(\text{H}_2)$ as with γ irradiation. This experimental error is readily explained by the difficulty to perform experiments with ^3H as a source of β -electrons.^{11,34}

Figure 4 shows a *direct* comparison of our calculated $G(\text{H}_2)$ values as obtained from the radiolysis of aerated azide solutions by 300-MeV ($\text{LET} \sim 0.3 \text{ keV}/\mu\text{m}$) and 7-MeV ($\text{LET} \sim 6 \text{ keV}/\mu\text{m}$) irradiating protons as a function of N_3^- concentration. As we can see, our calculations indicate that, over the entire N_3^- concentration range studied, the production of H_2 originating from the higher LET (*i.e.*, ^3H β -electron) radiolysis is always greater than that in the case of 300-MeV protons (*i.e.*, ^{60}Co γ -rays or fast electrons). This result is consistent with the *difference in the structure of radiation tracks*, the “short-track” geometry of ^3H β -electrons (in contrast to spur geometry) favoring radical-radical reactions (8–10) involving hydrated electrons and $\text{H}^\bullet$ atoms¹² and, therefore, leading to more molecular products (H_2 in this case) in tritium β -radiolysis than in γ -radiolysis. It is however interesting to note that this influence of the radiation track structure, which is largest in solutions with low N_3^- concentrations (typically, $<10^{-2}$ – 0.1 M),⁶² decreases continuously as the concentration of N_3^- increases up to 3 M . This is illustrated in Fig. 5, where we show the effect of azide concentration on the fate of e^-_{pre} *during the first picosecond* in the radiolysis of aerated solutions of N_3^- by 300- and 7-MeV irradiating protons, as obtained from our Monte Carlo simulations. As can be seen, at low N_3^- concentrations, the possibility that azide affects $G(\text{H}_2)$ *via* the scavenging of “dry” electrons is highly improbable, if not practically zero, for both types of radiation. At concentrations of N_3^- above $\sim 10^{-2}$ – 0.1 M , the effect of azide anions on $G(\text{H}_2)$ comes mainly from their increasing ability to scavenge e^-_{pre} , thereby reducing considerably the production of hydrated electrons. This continuous decrease in e^-_{aq} indicates that as the N_3^- concentration increases, the influence of the radiation track structure gradually decreases. This explains why the two $G(\text{H}_2)$ vs. N_3^- concentration curves shown in Fig. 4 approach each other more and more at the highest N_3^- concentrations considered.

Finally, for the sake of completeness, we compare in Fig. 6 the extents $\Delta G(\text{H}_2)$ of the various components that contribute to the formation of H_2 in azide solutions irradiated by low-LET 300 MeV and high-LET 7 MeV protons, calculated from our Monte Carlo simulations. As can be seen, the contribution of early time (sub-picosecond) processes (including the prompt DEA, geminate recombination of subexcitation electrons with H_2O^{*+} , and dissociation of directly excited water molecules) is nearly the same for both radiation types, regardless of the azide concentration. Remarkably, this result agrees well with recent experimental data¹⁶ showing relatively small changes in the sub-picosecond presolvated electron scavenging efficiency *versus* LET. In contrast, at N_3^- concentrations lower than ~ 0.2 – 0.1 M, we observe a clear increase in the contribution of track reactions (8)–(10) (in the ps– μs time scale) that produce H_2 in the 7-MeV proton (or 7.8-keV β -electron) radiolysis compared to 300-MeV proton (or ^{60}Co γ -) radiolysis. As discussed above, this result is consistent with the picture of tritium β -radiolysis mainly driven by the chemical action of short tracks of high local LET.¹²

Figure 6 also shows that the production of H_2 from the $(\text{H}^\bullet + \text{e}_{\text{aq}}^-)$ reaction (8) decreases rapidly with increasing N_3^- concentration.¹² This is a clear indicator that N_3^- ions readily scavenge $\text{H}^\bullet$ atoms in the track development on the ps– μs time scale, thus preventing them from contributing to reaction (8). Since azide anions only react very slowly with e_{aq}^- , the formation of H_2 by the $(\text{e}_{\text{aq}}^- + \text{e}_{\text{aq}}^-)$ reaction (9) should be rather unaffected by the presence of N_3^- , at least at low enough N_3^- concentrations. However, the hydrated electrons that have not reacted with $\text{H}^\bullet$ through reaction (8) become now available to participate in reaction (9). Overall, as Fig. 6 clearly shows, there is some compensation between the two contributions involved in the production of H_2 , the contribution from reaction (8) being slightly dominant. It should be

remembered that the ($\text{H}^\bullet + \text{H}^\bullet$) reaction (10) plays a relatively negligible role in the production of H_2 .⁴¹

4. Conclusion

The scavengeability by azide anions of the molecular hydrogen yield, which is generated in the radiolysis of water by cobalt γ -rays and tritium β -electrons, was studied using Monte Carlo track chemistry simulations. Confirming previous work, we demonstrate that low-energy (“dry”) secondary electrons (e^-_{pre}) can be scavenged by a high N_3^- concentration ($> 1 \text{ M}$) on a timescale of less than one picosecond before hydration. This is a remarkable result, as azide is known to be highly unreactive towards the “hydrated” electron. Our calculations of $G(\text{H}_2)$, which include the ultra-fast capture of e^-_{pre} by N_3^- agree very well with experimental data for both γ - and tritium β -radiolysis over the entire range of N_3^- concentrations studied in this work, from 10^{-4} to 3 M .

Interestingly, we do not observe any clear changes in the scavenging of “dry” electrons by N_3^- in passing from γ -radiolysis to tritium β -radiolysis. We concluded, therefore, that the higher H_2 yield observed experimentally for ^3H β -electrons compared to ^{60}Co γ -rays is mainly due to the difference in the radiation track structures during the ps- μs time scale. This is consistent with the short-track geometry of the higher LET tritium β -electrons, which favors radical-radical combination reactions to form more molecular products (H_2 in this case) in tritium radiolysis than in γ radiolysis. However, as the N_3^- concentration increases, the influence of the track structure gradually decreases. This explains why the two curves of $G(\text{H}_2)$ vs. N_3^- concentration come closer and closer at the highest N_3^- concentrations studied.

Moreover, a value of $R_{\text{react}} \sim 0.5$ nm was derived for the $(\text{N}_3^- + \text{e}^-_{\text{pre}})$ reaction distance from the H_2 yields observed in ^{60}Co γ radiolysis at high N_3^- concentrations. Using this value of R_{react} and the $(\text{N}_3^- + \text{e}^-_{\text{pre}})$ reaction rate constant of $10^{12} \text{ M}^{-1} \text{ s}^{-1}$ proposed in the literature, we estimated a mobility of e^-_{pre} of about $0.1 \text{ cm}^2/\text{V s}$ at 25°C , a value that is 8 to 10 times higher than the highest mobilities reported for solvated electrons in weakly polar liquids.

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- (13) Due to the random diffusion from their initial positions, the radiolytic species either react within the tracks as they develop over time or escape into the “bulk” solution. The so-called “primary” radical and molecular yields (or “escape” yields), quoted as $g(X)$, are defined as the numbers of species that are formed (or destroyed) per 100 eV of energy absorbed that remain after tracks have dissipated and become available to react with added solutes (if any) at moderate concentrations. For conversion into SI units (mol J^{-1}), 1 molecule per 100 eV $\approx 0.10364 \mu\text{mol J}^{-1}$. For low linear energy transfer (LET) ^{60}Co γ -rays, fast electrons or 300-MeV protons, the escape yield value for H_2 , $g(\text{H}_2)$, is ~ 0.45 molecule per 100 eV at 25 °C.^{1,2}
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dressed with the induced polarization of the surrounding water molecules. The “hydrated” electron is the limiting case where the electron is completely localized in the potential well of nearby strongly polarized water molecules.

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- (62) At these low N_3^- concentrations, the possibility that azide affects $G(\text{H}_2)$ *via* the scavenging of “dry” electrons is highly improbable, if not practically zero, for both types of radiation (see [Fig. 5](#)).

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Figure captions

Figure 1:

(A) The low-energy (“dry”) secondary electron (e^-_{pre}) travels through the N_3^- solution following a tortuous path until it is successively thermalized, trapped, and hydrated (e^-_{aq}).^{30,36}

(B) e^-_{pre} is scavenged by the azide anion (scavenger “S” in the figure) prior to hydration.

Figure 2:

(A) Simulated track histories (projected over the XY plane of the figure) for the following impacting particles: **panel a**: 7.8-keV β -electron (mean LET ~ 6 keV/ μm), **panel b**: 7-MeV proton (LET ~ 6 keV/ μm), and **panel c**: 300-MeV proton (LET ~ 0.3 keV/ μm). The three particles are generated at the origin and start traveling along the Y axis in liquid water at 25 °C. Dots represent the positions of all radiolytic species (e^-_{aq} , $\text{H}^\bullet$, H_2 , $\bullet\text{OH}$, H_2O_2 , etc.) present at ~ 1 ps. **Panels a and b** show the similarity of the “short track” structure of a 7.8-keV electron and the track structure of a 7-MeV proton (under identical LET conditions). The track segment of a 300-MeV proton in **panel c** mimics the irradiation with ^{60}Co γ -rays where Compton electrons predominantly form “spurs” (more or less spherical in shape).

(B) Illustration of the simulation model used in this work, which consists of a right circular cylindrical volume of water containing the studied azide concentration. The front surface of the cylinder is irradiated by protons of either 300 or 7 MeV (mimicking irradiation by ^{60}Co γ or ^3H β rays, respectively), or by 7.8-keV tritium β -electrons that penetrate perpendicular to this surface at its center. In this cylindrical geometry, the proton tracks, which are essentially rectilinear trajectories, run along the cylinder's

axis. The path of a 7.8-keV electron is generally non-linear, and has a more or less tortuous shape due to the successive angular deflections it undergoes. The length of the cylinder (*i.e.*, the track length of the incident particle) was chosen to vary between 100 μm (for 10^{-4} –1 M N_3^-) and 50 μm (for 2 and 3 M N_3^-). The radius of the circular base of the cylinder was set to 15 nm.⁴⁷

Figure 3:

Decrease in the yield of H_2 (in molecule per 100 eV) with the concentration of N_3^- for 300- and 7-MeV incident protons in the radiolysis of air-saturated aqueous azide solutions (neutral pH, 25 °C), calculated from our Monte Carlo simulations over the range of 10^{-4} to 3 M (panels A and B, respectively). Recall that here 300-MeV protons (LET $\sim 0.3 \text{ keV}/\mu\text{m}$) mimic ^{60}Co γ -radiolysis while 7-MeV protons (LET $\sim 6 \text{ keV}/\mu\text{m}$) mimic ^3H β -electron radiolysis (see text). The solid lines show our simulated results under the assumption that N_3^- scavenges the prehydrated (“dry”) secondary electrons (e_{pre}^-) with a scavenging reaction distance $R_{\text{react}} = 0.5 \text{ nm}$. The dashed lines show our results, assuming that N_3^- does not scavenge e_{pre}^- . Experimental data for γ and tritium β -electron irradiations: $\circ$, Peled et al.³¹; $\square$, Christman³²; $\bullet$, Gagnon and Appleby.³³ For comparison, the $G(\text{H}_2)$ values calculated by Harris and Pimblott¹¹ for both types of radiation, with e_{pre}^- scavenging by N_3^- using a $(\text{N}_3^- + \text{e}_{\text{pre}}^-)$ rate constant of $10^{12} \text{ M}^{-1} \text{ s}^{-1}$ (dash-dotted lines) and without “dry” electron scavenging (dotted lines). The concentration of dissolved oxygen used in the simulations was $2.5 \times 10^{-4} \text{ M}$.

Figure 4:

Direct comparison of $G(\text{H}_2)$ (in molecule per 100 eV) as a function of the concentration of N_3^- ions for 300- and 7-MeV incident protons (mimicking ^{60}Co γ -radiolysis and ^3H β -electron radiolysis, respectively), calculated from our Monte Carlo

simulations of the radiolysis of aerated aqueous azide solutions (neutral pH, 25 °C) over the range of 10^{-4} to 3 M. The solid and dashed lines are for 300- and 7-MeV irradiating protons, respectively (they correspond to the solid lines shown in [Fig. 3A and B](#), respectively).

Figure 5:

Fate (in percentage) of e_{pre}^- , the short-lived, low-energy (“dry”) precursor to e_{aq}^- , during the first picosecond following irradiation as a function of azide concentration from 10^{-4} to 3 M, as obtained from our Monte Carlo simulations of the radiolysis of aerated aqueous N_3^- solutions by 300-MeV (^{60}Co γ radiolysis, LET ~ 0.3 keV/ μm) and 7-MeV (7.8-keV ^3H β -electron radiolysis, LET ~ 6 keV/ μm) irradiating protons, at 25 °C. Recall here that the DEA, or “dissociative electron attachment” process corresponds to the resonant capture of e_{pre}^- by a water molecule [reaction (6)]. As can be seen, the recombination of e_{pre}^- with its geminate cation $\text{H}_2\text{O}^{+\bullet}$ [reaction (3)] is more probable than the DEA process, a result in agreement with recent experimental data.¹⁶

Figure 6:

Variation of the extents $\Delta G(\text{H}_2)$ (in molecule per 100 eV) with concentration of N_3^- ions of the different “early-time” and “track” processes that contribute to the yield of H_2 , calculated from our Monte Carlo simulations of the radiolysis of air-saturated aqueous N_3^- solutions, using 300-MeV (LET ~ 0.3 keV/ μm , [panel A](#)) and 7-MeV (LET ~ 6 keV/ μm , [panel B](#)) incident protons over the range of 10^{-4} to 3 M (pH neutral, 25 °C). The solid lines represent the *total* yield of H_2 produced by these two types of processes. H_2 formation from early-time (sub-picosecond) processes include the very fast DEA, geminate recombination of e_{pre}^- with $\text{H}_2\text{O}^{+\bullet}$, and dissociation of directly excited water molecules. Comparison of [panels A and B](#) shows only very small

changes in the H_2 yield contribution from these early-time processes (*i.e.*, in the scavenging efficiency of N_3^- on the subpicosecond time scale) as a function of LET. As for the production of H_2 from track reactions (in the ps– μs time interval), they include the three radical-radical combination reactions, namely, reaction (8) $\text{e}_{\text{aq}}^- + \text{H}^\bullet$ (dash-dot-dot line), reaction (9) $\text{e}_{\text{aq}}^- + \text{e}_{\text{aq}}^-$ (dash-dot line), and reaction (10) $\text{H}^\bullet + \text{H}^\bullet$ (dotted line). The dashed lines show our simulated results assuming that N_3^- does not scavenge the short-lived e_{pre}^- . The concentration of dissolved oxygen used in the simulations was $2.5 \times 10^{-4} \text{ M}$.

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FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6