Estimation of Yields of OH Radicals in Water Irradiated by Ionizing Radiation

Hiroshi YAMAGUCHI*, Yukio UCHIHORI, Nakahiro YASUDA, Masashi TAKADA and Hisashi KITAMURA

Hydroxyl radical /Fricke dosimeter/Electrons/Heavy ions/Spur /Model.

The yield of OH radical induced by ionizing radiation was estimated by an empirical model; a prescribed diffusion model for a spur of single size applying to neutral water. Two representative spur distances were introduced, one for an incident primary charged particle and one for a representative secondary electron, to calculate chemical yields among active species in a spur. The total yield from the track was a combination of these primary and secondary yields. Two coefficients of this combination were the parameters of the present model. Based on an optimization of these parameters by existing experimental Fricke G-values, the present model estimates the yields of OH at the microsecond timescale after an irradiation, in a unified manner from electrons to heavy ions. The predicted yields of OH around the nanosecond timescale after an irradiation may be a relevant basis for a study on the mechanisms of radiation effects. This prediction by the present model was exemplified for electrons, photons and heavy ions (proton, helium, carbon, neon, argon and iron).

INTRODUCTION

In living systems direct radiation action causes molecular alteration in DNA, and indirect action does also through the interaction of reactive species, induced by water radiolysis, with DNA.¹ Several reaction paths to DNA damage by reactive species, radicals from water radiolysis have been studied.² There has been substantial evidence that OH radical is of prime significance in the biological effects of ionizing radiation.³ The importance of strand breaks in DNA caused by OH radical has been emphasized.⁴⁻⁷ The OH radicals produced by low LET radiolysis of cellular water are the source of about 2/3 of the cell deaths and about 2/3 of the DNA strand breaks.⁸ The relevant time scale is about 1.3 nanoseconds for the surviving OH radicals attacking DNA in an environment containing scavengers of the low molecular weight cellular constituents.⁹ Correlations between yields of DNA single strand breaks (ssb) and yields of OH radicals in terms of track structure of electrons and UV photons have been analyzed.¹⁰ Track simulations by Monte Carlo method have been developed including chemical reactions among water radicals.¹⁰⁻¹⁴ This approach has been extensively applied to electrons and photons, because relevant data on interaction cross-section have been available. This type of simulation for heavy ions, however, has been applied very few,¹⁵ because the interaction cross-section data for heavy ions is lacking. For the time being, an alternative approach may still be needed. The present paper deals with an empirical model of deterministic kinetics calculations in order to estimate the yields of OH radical including heavy ions at two representative times, nanoseconds and microseconds after an irradiation. The former may be relevant to the period of formation of DNA initial damage and the latter to the period in which chemical reactions are in equilibrium in a uniform bulk solution.

The deterministic kinetics models have been developed separately for electrons or photons,¹⁶⁻²¹ and for heavy ions,²²,²³ for solving differential equations of diffusion controlled chemical reactions among species in spurs. The latter, the study for heavy ions,²³ however, provides no data on the yields of OH. The present model was developed to be applicable to all radiation in a unified manner.

The experimental Fricke G value is accurately calibrated and widely used for radiation dosimetry (radiation chemical yields are quoted as G values in units of molecules/100 eV or μmole/Joule). The present model regarded the extensive data of the Fricke system as an anchor so that these data should be explained first by the model as to be the yields of microsecond through optimization of parameters of the

*Corresponding author: Phone: 043-206-4032, Fax: 043-251-4531, E-mail: yamag@nirs.go.jp
Space and Particle Radiation Science Research Group, National Institute of Radiological Sciences 9-1, Anagawa 4, Image-ku, Chiba 263-8555 JAPAN.
model, and then the optimized model should estimate the yields of OH radicals at microseconds as well as nanoseconds.

**MATERIAL AND METHOD**

The present model was a prescribed diffusion model applied to neutral water based on the following assumptions. (1) Spurs were produced along the paths of an incident primary charged particle and of an ejected secondary electron (Fig. 1).

(2) The initially produced spur was constant in size and in number of radical species inside the spur. The energy Es to form a spur was 56 eV, equivalent to 1.17 ionizations and 1.24 excitations in the spur on average.  
(3) The distance between successive initial spurs along path of the charged particle varied with radiation quality or track structure. Two spur distances were considered to characterize the main feature of the track structure: one \( Z_{p1} \) was associated with the primary particle, and the other \( Z_{s1} \) was associated with a representative ejected electron of average energy \( T_s \). The optimum distance between spurs \( Z_{s1} \) was here equal to \( E_s \), which was energy necessary to form at least one spur on the secondary.  
(4) Two components of differential yields of \( i \)-th radical were evaluated, one due to primary particle of energy \( T \) and the other secondary electron of energy \( T_s \). The optimum combination of these two components, i.e., the primary particle yields \( g_{p}^{s}(i,T) \) and the secondary electron yields \( g_{s}^{s}(i,T_s) \), was found by fitting to experimental Fricke data.

(5) Reactions and rate constants among reactive species were assumed as shown in Table 1.  
(6) The geometrical size of the spur and the initial yields of species were assumed at 10\(^{-12}\) sec as shown in Table 2.  
(7) The estimated yields at 10\(^{-6}\) sec were regarded to be the yields in bulk that was comparable with experimental data.

![Fig. 1. Spurs along the incident primary particle path and representative secondary path. Spheres represent spurs of constant size.](image)

**Table 1.** Chemical reaction in neutral water.

| Reactions | \( \times 10^{10}(\text{M}^{-1}\text{S}^{-1}) \) |
|-----------|---------------------------|
| (1) \( e_{aq}^{-} + e_{aq}^{-} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^{-} \) | 0.55 |
| (2) \( e_{aq}^{-} + \text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}^{-} \) | 2.5 |
| (3) \( e_{aq}^{-} + \text{H} \rightarrow \text{H} \) | 2.3 |
| (4) \( e_{aq}^{-} + \text{OH} \rightarrow \text{OH}^{-} \) | 3 |
| (5) \( e_{aq}^{-} + \text{H}_2\text{O} \rightarrow \text{OH}^{-} + \text{OH} \) | 1.1 |
| (6) \( \text{H} + \text{H} \rightarrow \text{H}_2 \) | 0.78 |
| (7) \( \text{H} + \text{OH} \rightarrow \text{H}_2\text{O} \) | 2 |
| (8) \( \text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH} \) | 0.009 |
| (9) \( \text{H}^{+} + \text{OH}^{-} \rightarrow \text{H}_2\text{O} \) | 14.3 |
| (10) \( \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \) | 0.55 |

**Table 2.** Diffusion constants, initial radii and yields of species in a spur.

| Species | \( D \times 10^{2}(\text{cm}^2\text{s}^{-1}) \) | \( r_0(\text{nm}) \) | \( G_0(100\text{eV}^{-1}) \) |
|---------|-----------------|-------------|----------------|
| 1. \( e_{aq}^{-} \) | 4.5 | 6.0 | 4.78 |
| 2. \( \text{H} \) | 7 | 4.0 | 1.32 |
| 3. \( \text{H}^{+} \) | 9 | 4.0 | 4.78 |
| 4. \( \text{OH} \) | 2.8 | 4.0 | 6.1 |
| 5. \( \text{OH}^{-} \) | 5 | 4.0 | 0 |
| 6. \( \text{H}_2\text{O} \) | 2.2 | 4.0 | 0 |
| 7. \( \text{H}_2 \) | 8 | 4.0 | 0.15 |

The followings were mathematical statements of the assumptions. The combined differential yields \( G(i,T) \) of the incident primary particle of energy \( T \) and the representative secondary electron of energy \( T_s \) was calculated as follows.

\[
G(i,T) = A_1 \left[ g_p(i,T) + A_2 f g_s(i,T_s) \right] \quad (1)
\]

\[
f = \frac{\text{LET}_A}{\text{LET}_{inf}} \quad (2)
\]

where \( g_p(i,T) \) and \( g_s(i,T_s) \) were the differential yields of \( i \)-th species induced by the primary of energy \( T \) and secondary of the average energy \( T_s \), respectively. \( \text{LET}_A \) was the restricted LET of the cutoff energy of \( \Delta \) (here \( \Delta = 100 \text{ eV} \)), \( \text{LET}_{inf} \) was the infinite \( \text{LET} \) of the primary particle. \( A_1 \) and \( A_2 \)
were the adjustable parameters of the present model when fitting the model to the experimental Fricke data.

The concentration $C_i$ of the $i$-th species (here we assigned species numbers as follows. $e_{aq}^{-1}$, H$^\pm$, H$_2$O$^\pm$, OH$^-$, OH$^-$, H$_2$O$_2$, $H_3$O$^+$), was obtained by the differential equations for diffusion controlled chemical reactions,

$$\frac{dC_i}{dt} = D_i \nabla^2 C_i - \sum k_{ij} C_i C_j + \sum k_{ji} C_j C_i$$

(3)

where $D_i$ is the diffusion constant, $k_{ij}$ is the rate constant between species $i$ and $j$. With the assumption of Gaussian distribution for the species inside the spur (prescribed), the eq (3) reduces to the differential equations for number of species $N_i$ inside the spur,

$$\frac{dN_i}{dt} = - \sum j k_{ij} N_j f_j + \sum k_{ji} N_j N_k f_{jk}$$

(4)

$$f_j = [1 + (\pi (b_j^2 + b_j^2)^{1/2})]/Z_i][\pi (b_j^2 + b_j^2)^{3/2}]$$

(5)

where $Z_i$ is the average distance between successive spurs along the primary particle or the secondary electron, $b_j^2$ is the time-dependent parameter of width of distribution (Gaussian), $b_j^2 = b_{0j}^2 + D_j t$, where $b_{0j}$ is the initial radius of the species $i$-th. The average distance $Z_i$ (=$Z_p$ or $Z_{aq}^{-1}$) was assumed to be,

$$Z_i = E_s / L_{1\delta}$$

(6)

where $E_s$ was the energy to produce a spur and $L_{1\delta}$ was the restricted local energy loss of the primary particle due to other than the secondary electrons of energy higher than $\delta$. $L_{1\delta}$ was calculated using either the Rutherford formula for ionization cross section for heavy ions ($Z_p$) or the Moeller formula for electrons ($Z_{aq}^{-1}$) by the method of ref. (26), which is specific in taking into account soft collision due to small energy transfer $Q$ in addition to the usual hard collisions. According to the method developed for electron of ref. (26) $\text{LET}_{\text{inf}} = L_1 + L_2 + L_3 + ...$., where $L_1$, $L_2$, $L_3$ are the energy loss by primary electron, secondary-, thirdly- order of ejected electrons, respectively. The local energy loss $L_{1\delta}$ was calculated on this $i\delta_1$. The different settings, $\delta = 56$ eV in eq.(6), while $\Delta = 100$ eV in eq.(2), come from this difference between $L_1$ and $\text{LET}_{\text{inf}}$ ($\Delta$ was logically equal to 2Es, but a conventional $\Delta$ was used, because results were little difference). An approximation was made here that when relative incident velocities $\beta$ were the same between an electron and a heavy ion, $Q$ dependence of the soft collision would be the same between them. With these settings eq.(4) were numerically solved to obtain the yields of $g_s(i,T)$ or $g_s(i,T_s)$ at the time of $10^{-6}$ sec and finally $G(i,T)$ for the incident particle in eq (1). The estimated G-value $G(\text{Fe}^{3+})$ of the Fricke system was obtained by the material balance.27

$$G(\text{Fe}^{3+}) = 3G(e_{aq}^{-1}) + 3G(H) + G(OH) + 2G(H_2O_2)$$

(7)

In comparisons of the calculated results by eq (7) with experimental $G(\text{Fe}^{3+})$ the values of $A_1$ and $A_2$ in eq (1) were optimized. For heavy ions experimental data are reported as differential yields, while for electrons or photons many cases of experimental data reported are the integral yields. In the cases of integral yields the yields calculated by the first term of eq (1) should be further integrated with the energy degradation spectrum and the initial spectrum of electron energy.19,21) Strictly speaking these spectra depend on experimental condition such that how much extent the charged particle equilibrium is held. Since the present model was not meant to give absolute values, but to give reasonably practical estimates, these integrals were not performed. It was found, however, that the parameter $A_1$ enabled the calculated results by eq (1) practicably comparable with experimental integral yields of electrons or photons. Hereafter the yields given by eq.(1) was called simply "yields" for electrons or photons and "differential yields" for heavy ions.

For heavy ions, calculation of $L_{1\delta}$ for the primary ion was based on that of proton $L_{1\delta}$ and effective charge $Z_{\text{eff}}$ of the heavy ion.28,29)

$$L_{1\delta} = Z_{\text{eff}}^2 L_{1\delta\alpha}$$

(10)

$$Z_{\text{eff}}^2 = Z_0^2 [1 - \exp (- 125\beta Z_0)^{-(2/3)}]$$

(11)

where $Z_0$ is the atomic number and $\beta$ the relative velocity of the incident heavy ion.

RESULTS

Radical OH yields from radiation were calculated as a combination from the primary particle plus a contribution from a secondary electron. In both parts the same concept of spur and the differential equations of diffusion controlled radical reactions were applied to the solution of neutral water. The combination of these two yields was adjusted so that the calculated values fit comprehensively with the experimental Fricke G-value $G(\text{Fe}^{3+})$. Then the present model predicted $G(\text{OH})$ at microseconds and nanoseconds for electrons , photons and as well as for heavy ions. In Table 3 values of these adjustment parameters $A_1$ and $A_2$ in the eq.(1) and the largest relative differences between present estimates and experiments in this paper were summarized.

Figure 2 shows the yields $G(\text{Fe}^{3+})$ for photons.30–33) Difference between the present model and experiments was largest (15.8%) at the energy of 2 - 4 keV. The present model agreed reasonably well with experiments by the single normalization at the $G(\text{Fe}^{3+})$ of $\gamma$-rays (A1 = 0.812). Comparisons of $G(\text{Fe}^{3+})$ were made for $\beta$-rays from radionuclides $^3T$, $^3S$, $^3P$ and $^90Y$ with normalization of calculated results at the data of $^3T$ $\beta$-rays (A1 = 0.812). The difference between two was largest (7.7%) for the case of $^3P$ (not shown here). From the coincidence of the value of $A_1$ between photons and $\beta$-rays and difference in $A_1$ from heavy ions (Table 3) $A_1$ was meant to adjust the calculated results by eq (1) to integral yields. The present model was possible
to calculate the integral yields of electrons or photons, but these adjustments were accepted within the present approximation of ignorance of facts that the chemical reactions associated with OH in the Fricke solution differ from those in neutral water, and that even in neutral water the yields of OH differ depending on concentration of dissolved oxygen.

Figure 3 shows the decay of G(eaq–) and G(OH) as a function of time for the electrons of 20MeV. The estimated yields were compared with those of experiments with the same electron parameters of A1 and A2 as Fig. 2. The optimization for other quantities was made for that these decay patterns depended on the value of reaction rate constants, diffusion constants, the parameters of the initial yields G0(eaq–) and G0(OH), and most of all on the initial radius of the spur (Table 2). The optimized radius of spur was resulted in larger about 10 times than that of previous studies. The optimized radius in effect adjusted bulky macroscopic nature of the reaction rate constants kij (Table 1) being applicable at a proper time in the spur of microscopic volume, which was about the same as the width of the hydrated electron thermalization distribution in water.15) These good agreements for the decay kinetics were most important, because this optimization affected accuracy of the prediction of the yields of OH at nanosecond.

Figure 4 shows the differential yields G(Fe3+) for heavy ions. The parameter A1 was equal to one for all heavy ions studied here, which was due to that the present estimates corresponded to the differential yields and that the experimental data were the differential yields. The parameter A2, however, was different among heavy ions (Table 3). The overall fit of the present model was reasonably good. The difference between the model and experiments was as much as about 35% for lower energy than 1000 keV/amu of carbon ions. Since for those low energy ions more complex track structure was expected than was assumed by the present model, the predictions from eq. (1) were poorer (as discussed below). At energies higher than 1000 keV/amu the present model explained reasonably well (within 10%) the experimental yields of heavy ions considered here. The present model was also reasonable for the experimental yields modified with respect to fragmentation of the incident particles (carbon-, neon- and argon- ions).44) Though no data of G(Fe3+) for iron ions is available, the estimates were shown as an example, since these data were important for space research. The experimental data on G(Fe3+) for iron in larger about 10 times than that of previous studies.18–21) The optimized radius in effect adjusted bulky macroscopic nature of the reaction rate constants kij (Table 1) being applicable at a proper time in the spur of microscopic volume, which was about the same as the width of the hydrated electron thermalization distribution in water.15) These good agreements for the decay kinetics were most important, because this optimization affected accuracy of the prediction of the yields of OH at nanosecond.

Figure 3 shows the decay of G(eaq–) and G(OH) as a function of time for the electrons of 20MeV. The estimated yields were compared with those of experiments with the same electron parameters of A1 and A2 as Fig. 2. The optimization for other quantities was made for that these decay patterns depended on the value of reaction rate constants, diffusion constants, the parameters of the initial yields G0(eaq–) and G0(OH), and most of all on the initial radius of the spur (Table 2). The optimized radius of spur was resulted

### Table 3. Results of the present calculations.

| Radiation | parameter in eq (1) | the largest relative difference (%) between the model and experiments |
|-----------|---------------------|-----------------------------------------------------------------------|
| Electrons | A1 0.812, A2 1      | G(Fe3+) 7.7, G(OH) 3.5                                               |
| Photons   | A1 0.812, A2 1      | G(Fe3+) 15.8, G(OH) 8.6                                               |
| Protons   | 1                   | G(Fe3+) 9.3, G(OH) 15.0                                              |
| He- ions  | 1, 0.5              | G(Fe3+) 16.7, G(OH) 35.0                                             |
| C- ions   | 1, 0.6              | G(Fe3+) 34.6, G(OH) 21.2                                             |
| Ne- ion   | 1, 1                | G(Fe3+) 5.9, G(OH) 18.9                                              |
| Ar- ions  | 1, 1.2              | G(Fe3+) 8.3, G(OH) 24.0                                              |
| Iron- ions| 1                   | G(Fe3+) –, G(OH) –                                                  |

Fig. 2. Ferric ions produced in aerated solutions: the yields G(Fe3+) (0.1 μmol/J) as a function of initial photon energy. The energies and yields of photons were those of experiments. The solid line is the G(Fe3+) calculated for photons by the present model normalized to the experimental yield (16.0/0.1 μmol/J, A1 = 0.812) of 60Co γ-rays.

Fig. 3. Time-dependent decay kinetics of OH and eaq–. The solid line for OH and dotted line for eaq– were the predictions by the present model for the 20 MeV electrons. The picosecond pulse radiolysis experiments are OH(\(\sim\))36) eaq–(\(\sim\)).35,37) Inverse Laplace transform of the scavenger concentration data are OH(\(\sim\))38) and eaq–(\(\sim\)).39)
Yields of OH Radical by Electrons and Heavy Ions

Figure 5 shows the differential \( G(\text{OH}) \) for heavy ions at microsecond. The parameters of the model were the same as those for \( G(\text{Fe}^{3+}) \) in Fig. 4. The present model agreed reasonably well with experiments, though the present model tended to predict smaller values for higher specific energies than those of the experiments. This underestimation was due to two things. (1) The average energy of secondary electron was less than 1 keV (0.1 keV < \( T_s < 0.524 \text{ keV} \)) for the ions (incident energy of \( 10^2 - 10^6 \text{ keV/amu} \)), and (2) the present model predicted lower yields of OH in this energy region of electrons (as discussed below).

Figure 6 shows the predicted yields of species produced by radiolysis of water with electrons or photons as a function of initial energy at different times, nanoseconds (solid lines) and microseconds (dotted lines). Some results at microseconds were compared with those of experiments which estimated the integral yields using inverse Laplace transforms of the scavenger concentrations for electron irradiation, and subtraction of integral yields from two different dosimetric solutions by photons. It was noted that the yields of OH and hydrated electrons overwhelmed the yields of other species more at nanoseconds than at microseconds. More experimental data were needed to test the present model.

Figure 7 shows the predicted yields of species due to radiolysis of water as a function of initial energy at nanoseconds produced by proton (solid lines) and carbon ions (dotted lines). Proton and carbon ion of the same specific energy (keV/amu) travels in the same velocity. It was seen that dependences of the yields of species on specific energy were different between proton and carbon ion even though they traveled in the same velocity.

Figure 8 shows the prediction of \( G(\text{OH}) \) at the time of nanoseconds for ionizing particles considered in this study. The predictions for electrons (open circles) were those of the same velocity as ions (plotted by equivalent specific energy to the ions). The yields of OH by electrons were the highest of all at nanoseconds. That is, if the velocity of charged particles was the same, electrons produced OH radical most on a track segment. Main difference of the yields between electrons and protons were due to the difference of contributions from the secondary electrons. In the ionizing particles (Figs. 6–8) the yields of \( G(\text{OH}) \) at nanoseconds were mean that when a primary incident particle passed by a DNA molecule within a distance of spur radius, OH radicals of \( G(\text{OH}) \times 56/100 \) were relevant in molecular level as the possible agents to DNA molecule, where 56 was the average spur size in eV.

In summary, the present model estimated yields of active species as a function of time induced by ionizing radiation through the optimization of the model with existing \( G \)-value of Fricke system. The optimization was the adjustment of combination in two represented yields of the primary and the secondary path. The practical applicability of the present model was exemplified for the data of electrons, photons and heavy ions of low atomic number with respect to the yields \( G(\text{Fe}^{3+}) \) of resulted difference in (15.8–35%) and \( G(\text{OH}) \) of

\[ G(\text{Fe}^{3+}) \]
resulted difference in (25–35%) at the time of microseconds, and for the data of decay kinetics from picoseconds to microseconds of the yields $G(OH)$ and $G(e_{aq}^-)$ induced by the electrons. The present model may estimate $G(OH)$ at the time of nanoseconds within the similar accuracy as those of microseconds, which may be most relevant to the DNA damages.

**DISCUSSIONS**

Folford *et al* determine the dependence of the yields of OH radicals for photons of energies from 0.28 keV to 1.25 MeV using plasmid DNA as a probe. The plasmid DNA is irradiated in the presence of 0.66 mmol dm$^{-3}$ Tris, a fixed concentration for OH radicals to become homogeneously distributed, and to be a mean life time of the OH radicals equivalent to microseconds. Fig. 9 showed the ratio of ssb yields, but not the estimated OH yields, for different radiations to that determined for $^{60}$Co $\gamma$ radiation in comparison with the present results (dotted line). The present results showed some difference from that of ssb, while the estimates ($\circ$) by Watanabe *et al* with a full scale of Monte Carlo track simulation including explicitly dissolved oxygen agree very well. It suggested that the reactions associated with dissolved oxygen should be taken into account in the present model. The ratio of OH yields for different photons to that for $^{60}$Co $\gamma$ radiation at nanosecond estimated by the present model (solid line) agreed with that ($\tilde{\gamma}$) by Watanabe *et al* better than that of microseconds. The ssb data with a higher concentration of scavengers of the OH radicals being a mean life time of the OH radicals equivalent to nanoseconds would test calculations including the present model at nanoseconds.

The present model has problems. Those are (1) the method obtaining the differential yields may not hold for electrons of energy < 100 eV, and (2) the integral yields of OH for electrons of energy less than 1 keV may be largely affected by these differential yields of electrons of energy < 100 eV through processes of energy degradation by second-
ary electrons. This may be shown in comparison with the present results with those from the full scale of Monte Carlo track simulations\(^\text{13,55}\) (Fig. 10). The Monte Carlo results are the integral yields. The Monte Carlo method differs depending on the chemical reactions and their reaction rate constants assumed. Those of Meesungnoen \textit{et al}\(^\text{55}\) are almost the same chemical reactions as the present model, while those of Watanabe \textit{et al}\(^\text{13}\) are different in explicit inclusion of dissolved oxygen in solution. Large discrepancies among three estimates were observed at energy below 1 keV. An integral yields of OH calculated using the present differential yields (only \(g_p(i,T)\) in eq.(1) ) and a known electron energy degradation spectrum\(^\text{19}\) was not improved so much from the present results (Fig. 10) in comparison with those of Monte Carlo simulations (results are not shown). Large discrepancy of the present model for energy < 1 keV was attributed to the differential yields of energy < 100 eV. The lower energy of heavier incident particle of < 1000 keV/amu, however, the more complex overlapping of spurs would appear. The present assumption of dealing this overlap with only between nearest two spurs would be much oversimplification of the reality. Probably overlapping over several spurs along path should be included. Doubly differential interaction cross-section on energy and ejected angle of secondary electrons from the primary ion path are key data to study this overlapping. As there is little data available on these for ions heavier than helium ions, it makes a Monte Carlo track simulation difficult to be applied and also the present model difficult to evaluate dependence of the soft collision of \(L_{p1}\) on charge of the incident ion. It was the circumstance that the parameter \(A_2\) in eq.(1) was empirical and that the resulted values of \(A_2\) (Table 3) appeared no intuitive trend among heavy ions.

Recent experiments suggest a revision of the initial yield of hydrated electron from the conventional 4.8 ± 0.3 per 100 eV (Table 2) to 4.0 ± 0.2 per 100 eV\(^\text{56,58}\) and theoretical study on this re-evaluation of the yield of hydrated electron results in 4.4~4.5 per 100 eV\(^\text{57}\). Inclusion of this revision and changes in the initial yields of other species associated with this revision would result in different predictions from those of the present calculations. In any case the present model would deal this revision with applying different set of \(A_1\) and \(A_2\).

For heavy ions of lower energy the present model has other problems. Current setup was that the spur distance \(Z_{p1}\) in eq.(6) was measured at the time around \(10^{-15}\) sec, while their volumes were expanded to those up to the time around \(10^{-12}\) sec (Table 2) and species distributed spatially with Gaussian (Fig. 1). Spur distance \(Z_{p1}\) would hold for energy of even lower where \(Z_{p1}\) becomes smaller than the average distance of water ~0.27 nm, since each water has a volume (sphere of radius around 0.1 nm), and moves around average position due to thermal fluctuation\(^\text{59}\). The lower energy of heavier incident particle of < 1000 keV/amu, however, the more complex overlapping of spurs would appear. The present assumption of dealing this overlap with only between nearest two spurs would be much oversimplification of the reality. Probably overlapping over several spurs along path should be included. Doubly differential interaction cross-section on energy and ejected angle of secondary electrons from the primary ion path are key data to study this overlapping. As there is little data available on these for ions heavier than helium ions, it makes a Monte Carlo track simulation difficult to be applied and also the present model difficult to evaluate dependence of the soft collision of \(L_{p1}\) on charge of the incident ion. It was the circumstance that the parameter \(A_2\) in eq.(1) was empirical and that the resulted values of \(A_2\) (Table 3) appeared no intuitive trend among heavy ions.

Recent experiments suggest a revision of the initial yield of hydrated electron from the conventional 4.8 ± 0.3 per 100 eV (Table 2) to 4.0 ± 0.2 per 100 eV\(^\text{56,58}\) and theoretical study on this re-evaluation of the yield of hydrated electron results in 4.4~4.5 per 100 eV\(^\text{57}\). Inclusion of this revision and changes in the initial yields of other species associated with this revision would result in different predictions from those of the present calculations. In any case the present model would deal this revision with applying different set of \(A_1\) and \(A_2\).

The present model used two \(L_{1\beta}\) in eq.(1) as descriptive variables for the primary and the secondary particles, which were basis to describe dependence of the yields of G(Fe\(^{3+}\)) or G(OH) on radiation quality. Study was in progress within

\begin{align*}
\text{Fig. 9.} & \quad \text{Estimated yields of the OH radicals, as a ratio of that for } \ ^{60}\text{Co }\gamma\text{ radiation, using yields of ssb induced in a presence of a fixed concentration of OH scavenger Tris. The symbol (\(\bullet\)) shows the results at the time equivalent to microsecondsestimated from the data of ssb,}\(^\text{54}\) \text{ dotted line shows the prediction by the present model and the symbol (\(\circ\)) shows the results from a full scale of track simulation.}\(^\text{13}\) \text{ The predictions at nanosecond (solid line) by the present model was compared with that (\(\triangledown\)) of the full scale of the track simulation.}\(^\text{13}\)
\end{align*}

\begin{align*}
\text{Fig. 10.} & \quad \text{Comparison of yields of G(OH) at microseconds calculated by the present model (solid line) and by the track simulations (\(\Delta, \bullet\)) for electrons.}\(^\text{13,55}\)
\end{align*}
the present approach that an effective spur distance $Z_{eff} = f Z_{sp} + (1-f) Z_{ol}$ would be an unified descriptive variable for radical yields applicable to all ionizing radiation of low and high LET, where $f$ was the factor in eq. (2), $Z_{sp}$, $Z_{ol}$ were the spur distance of the primary and the representative secondary electron, respectively. The present dealing the yields of secondary electron with the factor $f$ in eq. (2) but not with the factor $(1-f)$ as Chatterjee and Magee\(^{15}\) does was meant that one of the spur of the pair of spurs on the secondary path would stay on the primary path (Fig. 1) as the probably dominant case. We believe that something like $Z_{eff}$ would be better descriptive variable than $(MZ^2/E)$ which is proposed by the study using the track simulation for heavy ions,\(^{15}\) where $M$ is the mass, $Z$ the charge and $E$ the energy, and hence $(MZ^2/E)$ is essentially the same as $(Z^2/p^2)$.

**ACKNOWLEDGEMENTS**

The author (H. Y.) acknowledges Dr. R. Watanabe for useful discussions.

**REFERENCES**

1. Derlinger, H. and Jung, H. (1970) *Molecular Radiation Biology*. Springer-Verlag New York, Heidelberg, Berlin.
2. Von Sonntag, C. (1987) *The chemical basis of radiation biology*. Taylor & Francis, London - New York - Philadelphia.
3. Alper, T. (1979) *Cellular Biology*, pp97–100, Cambridge Univ. Press, London.
4. Schulte-Frohlinde, D. (1989) Studies of radiation effects on DNA in aqueous solution, ICRU NEWS December, pp.4–15.
5. Milligan, J. K., Aguiler, J. A. and Ward, J. F. (1993) Variation of Single-Strand Yield with Scavenger Concentration for Plasmid DNA Irradiated in Aqueous Solution, Radiat. Res. 133: 151–157.
6. Milligan, J. K., Aguiler, J. A. and Ward, J. F. (1993) Variation of Single-Strand Yield with Scavenger Concentration for SV40 Minichromosome Irradiated in Aqueous Solution, Radiat. Res. 133: 158–162.
7. Price, K. M., Davies, S. and Michael, B. (1993) Evidence for Induction of DNA Double-Strand Breaks at Paired Radical Sites, Radiat. Res., 134: 102–106.
8. Word, J. F., Milligan, J. R. and Fahey, J. R. (1997) Factors controlling the radiosensitivity of cellular DNA, *Microdosimetry- An Interdisciplinary approach* - Eds. D. T. Goodhead, P. O’Neil and H. G. Menzel, The Royal Society of Chemistry, 57–64.
9. Nikkoo, H., O’Neil, P., Goodhead, D. T. and Terrisol, M. (1997) Computational modelling of low-energy electron-induced DNA damage by early physical and chemical events, Int. J. Radiat. Biol. 71: 467–483.
10. Hamm, R. N., Stabin, M. G. and Turner, J. E. (1998) Monte Carlo simulation of diffusion and reaction in water radiolysis - a study of reactant ‘jump through’ and jump distances. Radiat. Environ. Biophys., 36: 229–234.
11. Tomita, H., Kai, M., Kusama, T., Aoki, Y., and Ito, A. (1994) Monte Carlo simulation of DNA strand breaks induced by monoenergetic electrons using higher-order structure models of DNA, Int. J. Radiat. Biol., 66: 669–682.
12. Pimbott, S. M. and Mozumder, A. (1991) Structure of electron tracks in water. 2. Distribution of primary ionizations and excitations in water radiolysis, J. Phys. Chem., 95: 7291–7300.
13. Watanabe, R. and Saito, K. (2001) Monte Carlo simulation of water radiolysis in oxygenated condition for monoenergetic electrons from 100 eV - 1 MeV, Radiat. Phys. Chem., 62: 217–228.
14. Pimbott, S. M. and Laverne, J. A. (1998) Effect Electron Energy on the Radiation Chemistry of Liquid Water, Radiat. Res. 150: 159–169.
15. Pimbott, S. M. and Laverne, J. A. (2002) Effect of track structure on the ion radiolysis of the Fricke dosimeter, J. Phys. Chem., A106: 9420–9427.
16. Mozumder, A. and Magee, J. L. (1966) Model of tracks of ionizing radiations for radical reaction mechanisms, Radiat. Res., 28: 203–214.
17. Magee, J. L. and Chatterjee, A. (1978) The theory of chemical effects of high-energy electrons, J. Phys. Chem. 82: 2219–2226.
18. Schwarz, H. A. (1969) Application of the spur diffusion model to the radiation chemistry of aqueous solution, J. Phys. Chem. 73: 1928–1937.
19. Yamaguchi, H. (1987) A prescribed diffusion model of a many-radical system considering electron track structure in water, Radiat. Phys. Chem. 30: 279–284.
20. Yamaguchi, H. (1989) A Spur diffusion model applied to estimate yields of species in water irradiated by monoenergetic photons of 50 eV - 2 MeV, Radiat. Phys. Chem. 34: 801–807.
21. Yamaguchi, H. (1997) Calculation of G-value of Fricke dosimeter irradiated by photons of 100 eV - 10 MeV, *Microdosimetry- An Interdisciplinary approach* - Eds. D. T. Goodhead, P. O’Neil and H. G. Menzel, The Royal Society of Chemistry, 97–100.
22. Magee, J. L. and Chatterjee, A. (1980) Radiation chemistry of heavy-particle tracks 1. General consideration, J. Phys. Chem. 84: 3529–3536.
23. Chatterjee, A. and Magee, J. L. (1980) Radiation chemistry of heavy-particle tracks 2. Fricke dosimeter system, J. Phys. Chem. 84: 3537–3543.
24. Tabata, Y., Ito, Y., Tagawa, S. (1991) *Handbook of Radiation Chemistry*, USA-CRC press, Boca Raton, FL.
25. Watt, D. E. (1996) *Quantities for Dosimetry of Ionizing Radiations in Liquid Water*, Taylor & Francis, London, Bristol.
26. Pagnamenta, A. and Marshall, J. H. (1986) The track structure of electron in water, Radiat. Res. 106: 1–10.
27. Alpen, E. L. (1998) *Radiation Biophysics*, Academic Press, London Boston New York Sydney Tokyo Tront.
28. Ziegler , J. F., Biersack, J. P. and Lit tmann, U. (1985) *The stopping and range of ions in solids Vol.I Of The stopping and range of ions in Matter*. Ed. by J. F. Ziegler, Pergamon Press.
29. Porter, L. E. (1987) Variations of Projectile Effective Charge in Analysis of Stopping powers for Heavy ions, Radiat. Res. 110: 1–18.
30. Freyer, J. P., Schiliaci, M. E. and Raju, M. R. (1989) Measurement of the G-value for 1.5 keV X-rays, Int. J. Radiat. Biol., 56: 885–892.

31. Hoshi, M., Uehara, S., Yamamoto, O., Sawada, S., Sato, T., Kobayashi, K., Maezawa, H., Furusawa, Y., Hieda, K. and Yama, T. (1992) Iron(II) sulphate (Fricke solution) oxidation yields for 8.9 and 13.6 keV X-rays from synchrotron radiation, Int. J. Radiat. Biol., 61: 21–27.

32. Watanabe R, Usami N and Kobayashi K (1995) Oxidation yields of the ferrous ion in a Fricke solution irradiation with monochromatic synchrotron soft X-rays in the 1.8 - 10 keV region, Int. J. Radiat. Biol., 68, 113–120.

33. ICRU Report 17 (1970) Radiation Dosimetry: X-rays Generated at Potential of 5 - 150 kV, International Commission on Measurements Units and Measurements, Washington D.C.

34. Fregene, A. O. (1967) Calibration of the ferrous sulfate dosimeter by ionometric and calorimetric methods for radiations of a wide range of energy, Radiat. Res. 31: 256–266.

35. Jonah, C. D., Matheson, M. S. and Miller, J. R. (1976) Yields and decay of the hydrated electron from 100 ps to 3 ns, J. Phys. Chem. 80: 1267–1270.

36. Jonah C. D. and Miller, J. R. (1977) Yield and decay of the OH radical from 200ps to 3 ns, J. Phys. Chem. 81: 1974–1977.

37. Jonah, C. D. Miller, J. R. (1985) Picosecond-pulse radiolysis to understand the primary processes in radiolysis, Radiat. Phys. Chem., 26: 485–489.

38. LaVerne, J. A. and Pimbrott, M. (1991) Scavenger and time dependence of radicals and molecular products in the electron radiolysis of water, J. Phys. Chem., 95: 3196–3206.

39. Yoshida, H. (1994) Concentration- and pH-dependent ammonium yields in the reaction of hydrated electrons with glycylglycine, Radiat. Res., 137: 145–151.

40. Hart, E. J., Ramler, W. J. and Rocklin, S. R. (1950) Chemical Yields of Ionizing Particles in Aqueous Solution: Effect of Energy of Proton and Deuterons, Radiat. Res., 4: 378–393.

41. Schiller, M. C., Hart, E. Jr., Naleway, C. A., Jonal, D. and Schmidt, K. H. (1978) Pulse Radiolysis with H and He, Fast and Slow Formation of Fe6 in Acidic Fe5 Solution, J. Phys. Chem., 82: 2246–2248.

42. LaVerne, J. A. and Schuler, R. (1987) Radiation chemical studies with Heavy ions: Oxydation of Ferrous Ion in the Fricke Dosimeter, J. Phys. Chem., 91: 5770–5776.

43. Imamura, M. Matsui, S. and Karasawa, T. (1970) Radiation Chemical Studies with Cyclotron Beams, II. The Radiolysis of an Aqueous Ferrous Ammonium Sulfate Solution with Carbon- and Nitrogen- Ion Radiations, Bull. Chem. Soc. Jpn., 43: 2745–2749.

44. Christman, E. A., Appleby, A. and Jayko, M. (1981) Radiation Chemistry of High-Energy Carbon, Neon, and Argon Ions: Integral Yields from Ferrous Sulfate Solution, Radiat. Res. 83: 443–457.

45. LaVerne, J. A. (1989) The Production of OH Radicals in the Radioysis of Water with 4He Ions, Radiat. Res., 118: 201–210.

46. LaVerne, J. A., Yoshida, H. (1993) Production of Hydrated Electron in the Radiolysis of Water with Helium ions, J. Phys. Chem., 97: 10720–10724.