Radiolysis of Aqueous Solutions with Pulsed Ion Beams. 4. Product Yields for Proton Beams in Solutions of Thiocyanate and Methyl Viologen/Formate

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The yields of radicals from water decomposition produced in the radiolysis of two types of aqueous solutions, thiocyanate and methyl viologen (MV^{2+}), were determined using proton pulses of 5.2 MeV energy. Aerated thiocyanate solutions in the concentration range of 0.001−0.75 M gave yields of $(SCN)_2^{\bullet -}$, formed from scavenging OH radicals, that were lower than those for high-energy electrons and higher than those for ^{4}He ions of 21 MeV energy. The $(SCN)_2^{\bullet -}$ yield increased with increasing thiocyanate concentration, but the decay of thiocyanate radicals through intratrack reactions appears to be substantial in proton radiolysis. Methyl viologen radical cations ($MV^{\bullet +}$) formed by scavenging e_{aq}^-, H atoms, and OH radicals were measured in deaerated 0.5 mM MV^{2+} solutions containing formate. The $MV^{\bullet +}$ yields agreed with the results of steady-state proton beam radiolysis, which confirms earlier results that this system is a suitable chemical dosimeter for ion beam pulse radiolysis. The yields of $MV^{\bullet +}$ in deaerated MV^{2+} solutions containing formate and formate/tertiary butanol were used to determine the yields of OH radicals and the sum of the e_{aq}^- and H atom yields. Both sets of yields for proton beams were lower than the corresponding ones for high-energy electrons and higher than those for 21 MeV ^{4}He ions. The predicted hydroxyl radical yields for proton beams increase with increasing scavenging capacity and approach the value found for high-energy electron radiolysis. The sum of the e_{aq}^- and H atom yields is about 1.8 molecules/100 eV and nearly independent of the scavenging capacity for OH radical. Intratrack reactions were simulated using a deterministic diffusion kinetic model, and the results qualitatively predict the observed yields in the thiocyanate and the MV^{2+} solutions.

Introduction

A characteristic of water radiolysis with high linear energy transfer (LET = stopping power, $-dE/dx$) radiations is the reduced yields of the radical products such as e_{aq}^-, H atoms, and OH radicals.[1,2] These results are mainly deduced from experiments in which the analysis of stable products using selective solutes are used to infer radical yields. Pulse radiolysis techniques are a great aid in determining the yields of radical products from water decomposition because the transient reactive species can be observed directly. Pulse radiolysis techniques have been used extensively in the high-energy electron radiolysis of water.[3−5] However, only a few experiments using ion beam pulse radiolysis have been reported.[6−15] There are many difficulties in performing pulse radiolysis with ion beams, including the short particle range, low beam intensity, and relatively long pulse duration. The advantage to steady-state ion beam radiolysis is that many more systems are available to probe water decomposition, especially those systems examined comprehensively in high-energy electron pulse radiolysis.

Previous studies have detailed the construction of an ion beam pulse radiolysis system at the HIMAC (Heavy Ion Medical Accelerator in Chiba). Product yields have been reported in three kinds of aqueous solutions, thiocyanate, peroxodisulfate, and methyl viologen containing formate, using 21 MeV helium ion beams.[16−18] Furthermore, it was proposed that the methyl viologen/formate system can be a useful chemical dosimeter for ion beam pulse radiolysis. Proton beams of 5.2 MeV energy were used in the present work to compare with the helium ion results in order to obtain more information on track or LET effects on the radiation chemistry of water. As is well-known, protons have an important role in the radiation effects of neutrons in aqueous system because the main primary process of neutrons is to produce recoil protons. Water is used as a coolant in many nuclear fission reactors, and it is also planned to be used in several nuclear fusion reactors. In D−T fusion reactions, neutrons of 14 MeV as well as ^{4}He ions are released. It is difficult to produce such high-energy neutrons for experimental use. Protons of this energy range are readily made using

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accelerators, so the data obtained using proton beam radiolysis can be a useful alternative for estimating neutron radiolysis.

Among radical products of water radiolysis, e_{aq}^- and the OH radical are the major reducing and oxidizing species, respectively. Direct observation of e_{aq}^- is easier than that for the OH radical because it has a large absorption in the visible range.[4,19] However, the shortest pulse available at the HIMAC is 1 μs, which makes it difficult to determine the e_{aq}^- yield directly. Burns et al. measured e_{aq}^- yields directly using nanosecond proton pulse radiolysis.[6,7] Pulse radiolysis studies at longer times require the use of a scavenger for the e_{aq}^- that gives an optically observable product stable for the duration of the experiment. The absorption due to the OH radical is much smaller than that for the e_{aq}^- and in the UV region, so scavenger methods are also necessary. In the present study, the product yields in solutions of thiocyanate and in methyl viologen/formate were determined. The OH radical is the main primary radical for producing the observed products in the former system, while the sum of all radical products of water can be determined in the latter system. Second-order intratrack reactions of radical species may complicate the analysis of the observed results,[16] but these data are still useful for examining the ion beam radiolysis of water.

One principal goal is to determine the dependence of the OH radical yield on the scavenger concentration. This dependence reflects the structure of the radiation track and is needed to estimate the validity of models.[20−22] In the present study, the product yields were measured as a function of the concentration of the OH radical scavengers, thiocyanate or formate. Various features of the intratrack reactions in proton radiolysis are discussed and compared with the data from high-energy electrons and helium ion beams.

Experimental Section

Irradiations were performed using 6 MeV $^1H^+$ beams from the HIMAC at the National Institute of Radiological Sciences in Chiba, Japan. The irradiation system has been described elsewhere.[16] Protons enter the sample solution with 5.2 MeV energy after being degraded by passing through the vacuum windows. The irradiation depth of interest is 100 μm, which is defined by the width of the probe argon ion laser that passed across the face of the entrance window and orthogonal to the ion beam. Proton energy after penetrating 100 μm of the solution is 4.3 MeV, so the average LET in the measurement area is 8.5 eV nm^{-1}. Therefore, the yields measured in this work are track segment yields as opposed to track average yields determined in the complete stopping of the incident particles. Pulses of 5 μs were used for methyl viologen system, and pulses of 20 or 30 μs were used for the thiocyanate solutions. The absorbed dose was proportional to the pulse duration, and the conversion factor was 3.7 Gy per μs duration. The absolute doses were determined from beam currents and the intensity profile as described previously.[16]

Methyl viologen dichloride was obtained from Tokyo Kasei, potassium thiocyanate was from Koso Kagaku, and sodium formate and tertiary butanol were from Wako. These chemicals were reagent grade and used without further purification. All the solutions were made with water prepared using an ion-exchange resin and a Millipore ultrapure water system. In the radiolysis of methyl viologen solutions, dissolved oxygen was removed by bubbling nitrogen gas before irradiation.

Results and Discussion

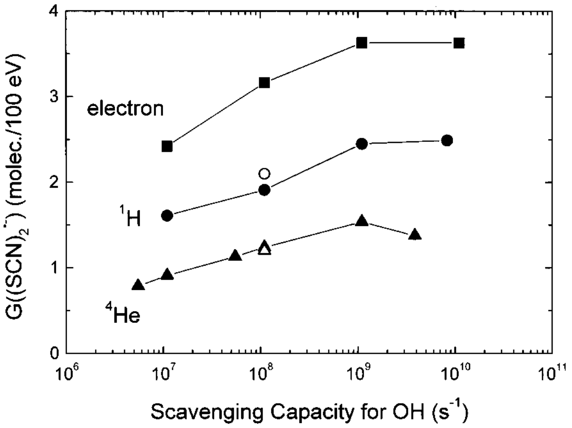

Figure 1. Yield of $(SCN)_2^{\bullet-}$ in the radiolysis of SCN^- solutions as a function of OH radical scavenging capacity: (●) ^{1}H, this work; (■) electrons and (▲) ^{4}He, ref 16; (○) ^{2}H and (△) ^{4}He, ref 12.

Thiocyanate. Aqueous KSCN solutions with concentrations of 1, 10, 100, and 750 mM were irradiated with 20 or 30 μs proton pulses under air-saturated conditions. The absorbed doses of 20 and 30 μs pulses were 74 and 111 Gy per pulse, respectively. Transient absorption was observed at 488 nm, which is well-known to be due to $(SCN)_2^{\bullet-}$, with an extinction coefficient of 7300 M^{-1}cm^{-1}.[16,23] The yield of $(SCN)_2^{\bullet-}$ derived from the maximum absorbance of each time profile was not proportional to the absorbed dose. $(SCN)_2^{\bullet-}$ is not stable and disappears during the pulse duration by second-order reactions. The decrease of the yield due to these reactions was evaluated by analyzing the time profile, and the true $(SCN)_2^{\bullet-}$ yields were determined as described previously.[16] The results are shown in Figure 1 as a function of the scavenging capacity for OH radicals. The unit of the radiation chemical yield, the *G*-value, is the number of radicals produced per 100 eV energy absorbed. The scavenging capacity is the pseudo-first-order rate coefficient for the disappearance of the OH radical in the scavenging reaction and is equal to the product of the rate coefficient for this reaction and the scavenger concentration. Figure 1 shows that the $(SCN)_2^{\bullet-}$ yield increases with increasing OH radical scavenging capacity and levels or even decreases above 10^9 s^{-1}. The time scale of scavenging OH radicals is approximately given by the reciprocal of the scavenging capacity. The yield of $(SCN)_2^{\bullet-}$ corresponds to the yields of OH radicals which survive the reactions in the track until they are scavenged by SCN^-. It can be seen that on the nanosecond−microsecond time scale OH radicals are undergoing a considerable amount of track reactions with 5.2 MeV protons, suggesting that their tracks contain relatively high concentrations of water decay products even to these long times.

In the radiolysis of KSCN solutions, the OH radical is scavenged by SCN^- to form $(SCN)_2^{\bullet-}$. A series of subsequent reactions is reported to occur as follows:[24−26]

$$OH + SCN^- \rightarrow SCNOH^{\bullet-} \quad k_1 = 1.1 \times 10^{10}\ M^{-1}\,s^{-1} \tag{1}$$

$$SCNOH^{\bullet-} \leftrightarrow {}^{\bullet}SCN + OH^- \quad K_2 = 3.2 \times 10^{-2}\ M \tag{2}$$

$${}^{\bullet}SCN + SCN^- \leftrightarrow (SCN)_2^{\bullet-} \quad K_3 = 2 \times 10^5\ M^{-1} \tag{3}$$

In aerated solutions, e_{aq}^- is converted by oxygen into $O_2^{\bullet-}$, which does not produce $(SCN)_2^{\bullet-}$. The scavenging capacity for this reaction is 4.8×10^6 s^{-1}, so it does not lead to cooperative effects that would increase the apparent OH radical yields. Thus, the yield of $(SCN)_2^{\bullet-}$ should be equivalent to the OH radical yield.

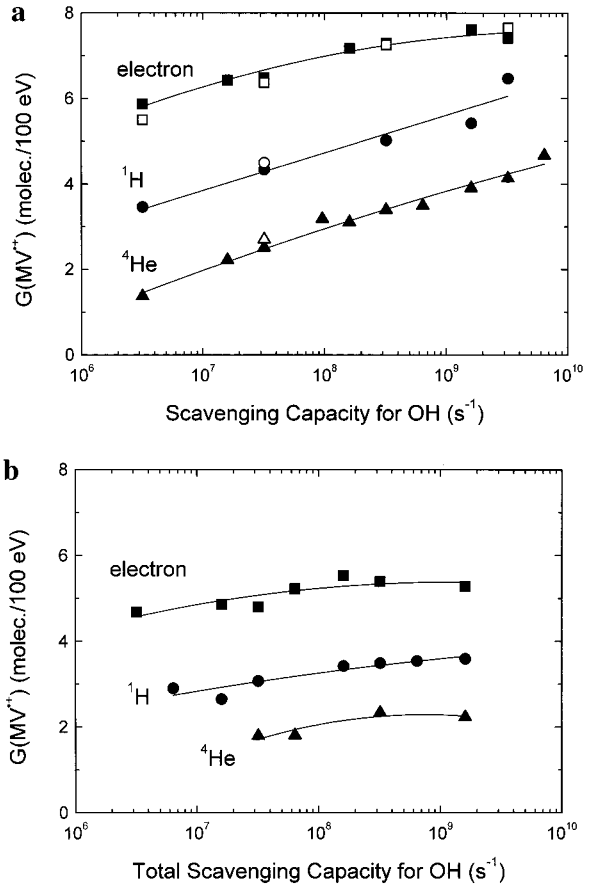

Figure 2. Yield of MV$^{\bullet+}$ in the radiolysis of 0.5 mM methyl viologen solutions containing formate as a function of scavenging capacity for OH radicals. Solid symbols are the results from pulse radiolysis, and open symbols are the results with continuous beams, ref 30: (●) ^{1}H, this work; (■) electrons and (▲) ^{4}He, ref 18. (a) Solutions with no added *t*-BuOH. (b) Solutions with both formate and *t*-BuOH, with the latter at a concentration five times that of the former.

There is good agreement between the present results and those obtained at the same LET in a different pulse radiolysis study by Sauer et al.[12] This agreement suggests that dosimetry and other considerations have been accounted for properly in the present study. The reported values of $(SCN)_2{}^{\bullet-}$ yields with high-energy electrons and 21 MeV ^{4}He ions (LET = 35 eV nm^{-1}) are also shown in Figure 1.[16] The yields for proton beams are lower than those for electrons and higher than those for ^{4}He ions throughout the measured scavenging capacity range. Decreased OH radical yields at higher LET are due to a larger amount of OH radical reaction with the other species produced by water radiolysis before being scavenged by SCN$^-$. The leveling off of $G((SCN)_2{}^{\bullet-})$ at higher scavenging capacity is observed with all three particle beams and even decreases for ^{4}He ion beams. If the initial yield of the OH radical does not depend on the radiation type, the yields for the ion beams would approach the same value as one for electron beams at higher scavenging capacity. The reason the yields are lower than expected is because of reactions of the secondary radicals, $^\bullet$SCN and $(SCN)_2{}^{\bullet-}$, in the radiation track.[16] Helium ions show the largest decrease in $G((SCN)_2{}^{\bullet-})$ because they have the densest track of reactive species. It can be seen in Figure 1 that the decrease in $G((SCN)_2{}^{\bullet-})$ above 10^9 s^{-1} with proton beam radiolysis is not as large as that with ^{4}He ions but still large enough that it cannot be ignored. The consequence of this problem is to restrict the ability of this system to predict OH radical yields, as further discussed below.

Methyl Viologen/Formate. Aqueous solutions of 0.5 mM MV^{2+} containing various concentrations of formate were irradiated with 5 μs proton pulses under deaerated conditions. The absorbed dose was 19 Gy per pulse. Transient absorption due to MV$^{\bullet+}$ was measured using the 515 nm line of the argon ion laser as the analyzing light. The extinction coefficient at 515 nm is 4100 M^{-1}cm^{-1}.[27] In oxygen-free solutions, MV$^{\bullet+}$ is quite stable. Hydrogen peroxide reacts with MV$^{\bullet+}$ on the time scale of several hours, so the decay due to this reaction can be ignored.[28,29] In practice, it is difficult to remove all the oxygen from the solution and traces of oxygen remained to oxidize the MV$^{\bullet+}$. This reaction occurred on the time scale of hundreds of microseconds in the present configuration. Therefore the true yields of MV$^{\bullet+}$ can be derived from the maximum absorbance, which appeared approximately at the end of the pulse. Figure 2a shows G(MV$^{\bullet+}$) as a function of the formate scavenging capacity for the OH radical. A datum from a previous study using a continuous proton beam is shown in the same figure.[30] The value plotted is the track segment yield calculated from the measured track averaged yields at 2 and 5 MeV. The result agrees well with the present study.

Chemical dosimeters for ion beam pulse radiolysis are not well established. The thiocyanate system discussed above is commonly used with high-energy electrons, but second-order reactions may make it unsuitable for use with heavy ion beams. It was proposed that deaerated methyl viologen solutions containing formate could be a promising system for dosimetry based on the data using ^{4}He ion beams at an LET of 35 eV nm^{-1}. The present study confirms the suitability of this system for proton beams. The G-value of MV$^{\bullet+}$ at 10 mM formate was determined to be 4.3 ± 0.4 for proton beams with LET of 8.5 eV nm^{-1}.

The mechanism to produce MV$^{\bullet+}$ in aqueous solutions of methyl viologen containing formate has been reported as follows:[5,29,31-33]

$$e_{aq}{}^{-} + MV^{2+} \rightarrow MV^{\bullet+} \qquad k_4 = 5 \times 10^{10}\ M^{-1}\,s^{-1} \tag{4}$$

$$OH + HCOO^{-} \rightarrow COO^{\bullet-} + H_2O \qquad k_5 = 3.2 \times 10^{9}\ M^{-1}\,s^{-1} \tag{5}$$

$$H + HCOO^{-} \rightarrow COO^{\bullet-} + H_2 \qquad k_6 = 2.1 \times 10^{8}\ M^{-1}\,s^{-1} \tag{6}$$

$$COO^{\bullet-} + MV^{2+} \rightarrow MV^{\bullet+} + CO_2 \qquad k_7 = 1 \times 10^{10}\ M^{-1}\,s^{-1} \tag{7}$$

The yield of MV$^{\bullet+}$ is considered to be equivalent to the sum of the yields of $e_{aq}{}^-$, the H atom, and the OH radical. Formate concentration mainly affects the scavenging capacity for OH radical because the scavenging of H atom is slower by an order of magnitude, and the yield of H atom is much smaller than that of the OH radical. The scavenging capacity for $e_{aq}{}^-$ is 2.5 × 10^7 s^{-1} at the MV^{2+} concentration of 0.5 mM. Cooperative effects on the OH radical yield due to the scavenging of the $e_{aq}{}^-$ is expected to be minimal and only occur at the lowest OH scavenging capacities. [34-36]

As shown in Figure 2a, G(MV$^{\bullet+}$) increases with increasing OH radical scavenging capacity because of the time dependence of the intratrack radical reactions. Figure 2a also contains the data of previous studies using γ-rays, electron pulses, and continuous and pulsed ^{4}He ion beams (LET = 35 eV nm^{-1}).[18,30] The yields for proton beams are lower than those for low LET radiations and higher than those for ^{4}He ion beams throughout the formate concentration range used here. The trend of the results on particle type is the same as that observed with SCN^- solutions and shows the increased importance of intratrack reactions at higher LET.

Figure 2b shows the yield of $MV^{\bullet+}$ in deaerated solutions of 0.5 mM MV^{2+} containing both formate and tertiary butanol (*t*-BuOH). The pulse duration was 5 μs, providing 19 Gy per pulse. The plotted values were determined from the peak absorbance in each time profile. Reaction of the $MV^{\bullet+}$ with the tertiary butanol radical occurs on the time scale of several tens of microseconds at the dose used in this experiment, and decay of the $MV^{\bullet+}$ signal during the pulse was ignored. In this chemical system, *t*-BuOH reacts with OH radicals and H atoms in competition with formate[5]

$$OH + C(CH_3)_3OH \rightarrow {}^{\bullet}CH_2C(CH_3)_2OH + H_2O \qquad k_8 = 6.0 \times 10^8\ M^{-1}\ s^{-1} \quad (8)$$

$$H + C(CH_3)_3OH \rightarrow {}^{\bullet}CH_2C(CH_3)_2OH + H_2 \qquad k_9 = 1.7 \times 10^5\ M^{-1}\ s^{-1} \quad (9)$$

The concentration of *t*-BuOH was kept 5 times as large as that of formate in order for the scavenging capacities for OH radicals to be identical. The ${}^{\bullet}CH_2C(CH_3)_2OH$ radical does not lead to $MV^{\bullet+}$ formation. Consequently, half of the OH radicals are converted to $MV^{\bullet+}$. Scavenging of H atoms by *t*-BuOH is slow, and most of the H atoms should react with formate. The reaction between e_{aq}^- and *t*-BuOH is also slow ($k < 4 \times 10^5\ M^{-1}\ s^{-1}$)[5] and will not have any effect on the kinetics of the OH radical.

As shown in Figure 2b, the yield of $MV^{\bullet+}$ increases with increasing OH radical scavenging capacity. The total scavenging capacity for OH radicals is defined as the sum of the scavenging capacity of the formate and *t*-BuOH. The slope of each curve is smaller than the corresponding one in Figure 2a because only half of the OH radicals are contributing to $MV^{\bullet+}$ formation. Figure 2b also shows the results for high-energy electrons and ^4He ion beams. As expected, the data of the present study with protons are between these two series; the lower yields are observed with higher LET radiation.

Yields of Primary Radicals. Reactions 4−8 stoichiometrically provide the yield of $MV^{\bullet+}$ in the absence and presence of *t*-BuOH in the following equations:

$$G(MV^{\bullet+})_{free} = G(e_{aq}^-) + G(H) + G(OH) \qquad (I)$$

$$G(MV^{\bullet+})_{t-BuOH} = G(e_{aq}^-) + G(H) + G(OH)/2 \qquad (II)$$

The yield of OH and the sum of e_{aq}^- and H atom yields can be derived from these two equations:

$$G(OH) = 2[G(MV^{\bullet+})_{free} - G(MV^{\bullet+})_{t-BuOH}] \qquad (III)$$

$$G(e_{aq}^-) + G(H) = 2G(MV^{\bullet+})_{t-BuOH} - G(MV^{\bullet+})_{free} \qquad (IV)$$

The validity of this method is influenced by the accuracy of the rate constants, k_5 and k_8. We already used this method for low LET radiations in the previous paper, and the derived values well agreed with the OH radical yields widely accepted.[18] The results calculated for OH radicals from equations (III) using the data of Figure 2a,b are shown in Figure 3. Data for high-energy electrons and ^4He ions are also contained in the figure.[18] For all the beams, *G*(OH) increases with increasing OH radical scavenging capacity, which indicates larger amount of OH radicals are scavenged at earlier times. The yields for electron and proton beams are approximately equal at the highest scavenging capacity of $10^9\ s^{-1}$, while the yields for ^4He ion beams are the lowest over the entire scavenging capacity range examined here.

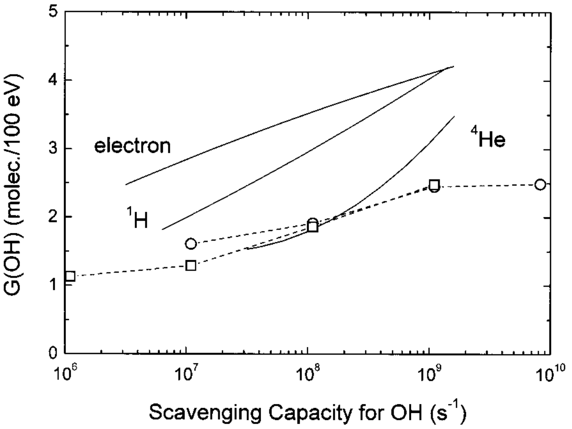

Figure 3. Yields of OH radicals as a function of its scavenging capacity. Solid lines are OH radical yields calculated from eq III and the data in Figure 2a,b. Open circles denote OH radical yields determined in the proton beam radiolysis of SCN^- solutions, this work, and open squares denote track average OH radical yields for a 10 MeV proton, ref 37.

The yields of OH radicals derived from the proton beam radiolysis of SCN^- solutions are also plotted in Figure 3. These data do not agree with the results of the MV^{2+} system except possibly at the lowest scavenging capacity. An even larger discrepancy was observed with ^4He ion beams.[16,18] The yield of $(SCN)_2^{\bullet-}$ is expected to be low at high scavenging capacities because of the second-order reactions described above. However, agreement between the two systems was expected to be better at the lower scavenging capacities. The only other published data of the scavenger concentration dependence using proton beams are reported for 10 MeV energy by Burns and Sims.[37] These values are track averaged yields, and as shown in Figure 3, they are also lower than the present results. Protons of 10 MeV should give OH radical yields between those of high-energy electrons and the 5.2 MeV protons examined here. However, the experiments of Burns and Sims measured track average yields that are weighted by the contribution due to the relatively high LET track end. There is insufficient data to properly compare the track segment with track average yields for protons of this energy, and further studies will be required to resolve this problem. The true OH radical yields for a 5.2 MeV proton track segment are probably very near to that predicted by the methyl viologen/formate system. Even medium LET particles such as protons produce sufficient concentrations of radicals, and second-order reactions lead to a decrease in $(SCN)_2^{\bullet-}$ yields from thiocyanate solutions.

The sum of the e_{aq}^- and H atom yields as determined from eq IV using the data of Figure 2a,b for proton beam radiolysis is 1.8. The yield is nearly constant over the OH radical scavenging capacity examined here. Note that the scavenging capacity for e_{aq}^- in the methyl viologen/formate systems is constant at about $2.5 \times 10^7\ s^{-1}$. At an OH radical scavenging capacity around $10^7\ s^{-1}$, the values for $G(e_{aq}^-) + G(H)$ are equal to those for *G*(OH) for the proton beam. These results are consistent with the LET dependence of the track averaged yields compiled by Elliot et al.[38]

The yields of Fe^{3+} in the radiolysis of acidic ferrous sulfate solution, Fricke dosimeter, under aerated and deaerated conditions also provide values for $G(e_{aq}^-) + G(H)$.[39] The value of 1.9 for the differential yields of a 5.2 MeV proton radiolysis of the Fricke dosimeter agrees well with the result of the present study. This result reinforces the contention that the methyl viologen/formate system has negligible complications due to secondary reactions for protons and high-energy electrons. At higher LET, the most likely reactions that could lead to a decrease in the yield of $MV^{\bullet+}$ in solutions containing both formate and *t*-BuOH are the following:[5,18,32,40]

$$COO^{\bullet-} + COO^{\bullet-} \rightarrow \text{products} \quad k_{10} = 6.5 \times 10^9\ M^{-1}\,s^{-1} \tag{10}$$

$$MV^{\bullet+} + COO^{\bullet-} \rightarrow \text{products} \quad k_{11} = 1 \times 10^9\ M^{-1}\,s^{-1} \tag{11}$$

$$2^{\bullet}CH_2C(CH_3)_2OH \rightarrow \text{products} \quad k_{12} = 7.0 \times 10^8\ M^{-1}\,s^{-1} \tag{12}$$

$$MV^{\bullet+} + {}^{\bullet}CH_2C(CH_3)_2OH \rightarrow \text{products} \quad k_{13} = 8 \times 10^8\ M^{-1}\,s^{-1} \tag{13}$$

Reactions 10 and 11 give lower yields of $MV^{\bullet+}$ in all the solutions, while reaction 13 gives lower yields of $MV^{\bullet+}$ only in the solutions containing *t*-BuOH. According to eq IV, this reaction may lead to smaller values of $G(e_{aq}^-) + G(H)$. Any possible complications due to reactions 10−13 are expected to occur at LETs higher than those examined here.

Simulation of Intratrack Reactions. To further examine the scavenging capacity dependence of the primary radical yields, we performed the simulations of intratrack reactions with a deterministic diffusion kinetic model. The method chosen is a numerical approach using the FACSIMILE code.[41] A simple spherical spur and a cylindrical track were assumed for low LET radiations and ion beams, respectively. The parameters for the calculation were taken from the literature.[42,43] Reactions 1−3 and the reactions of the product radicals were considered for SCN^- solutions, and the corresponding rate constants were as reported.[5,12,24−26,44−46] For the MV^{2+} system, reactions 4−13 and the other related reactions as listed in a previous paper were taken into consideration.[30] These simulations are useful in clarifying the characteristics of the reaction kinetics—that is, providing the relative contributions of the different reactions to overall product formation. However, the models are too simplistic in their assumptions on the physical nature of the particle tracks to be able to predict product yields quantitatively.

Figure 4 shows the yield of OH radical yields calculated from eq III using simulated yields of $MV^{\bullet+}$. The yields for electron and proton beams are almost equal at high scavenging capacity, and that for ^4He ion beam is lower than the others. These predictions agree well with observation of the experimental results. The yields of OH radicals determined from the simulations of proton radiolysis of SCN^- solutions are also shown in Figure 4. The predicted yields in SCN^- solutions are considerably lower than G(OH) determined in the methyl viologen/formate system. In SCN^- solutions, the reactions $(SCN)_2^{\bullet-} + (SCN)_2^{\bullet-}$ and $(SCN)_2^{\bullet-} + e_{aq}^-$ (rate constants equal to 1.3×10^9 and $2.0 \times 10^{10}\ M^{-1}s^{-1}$, respectively) have large contributions, leading to a decrease in the observed $(SCN)_2^{\bullet-}$ yields. These latter reactions are more important with increasing LET. Even at 8.5 eV nm^{-1} and low SCN^- concentration, the predicted $(SCN)_2^{\bullet-}$ yields are lower than those for the true OH radical yields. Although this system is widely used as a dosimeter in high-energy electron radiolysis, it must be used with caution at high LET.

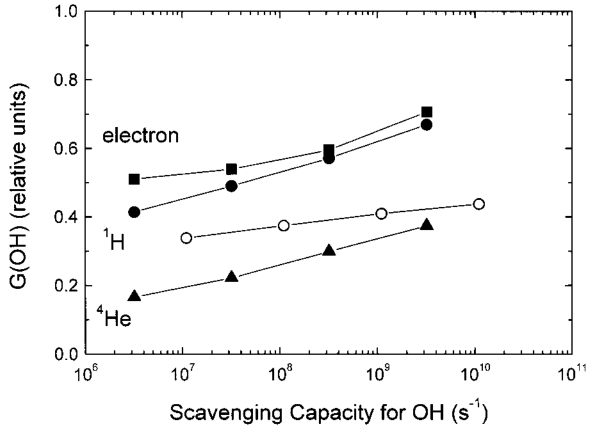

Figure 4. Yields of OH radicals as a function of their scavenging capacity in the simulation of intratrack reactions for spherical spurs (electron) and cylindrical tracks: 8.5 eV nm^{-1} (^1H) and 35 eV nm^{-1} (^4He). Solid symbols are the OH radical yields determined in the MV^{2+} system: (■) electrons, (●) ^1H, and (▲) ^4He. The yields of $(SCN)_2^{\bullet-}$ in the simulation of SCN^- solutions are denoted as ○ for ^1H.

The simulations of the present study are based on a highly simplified physical track model and do not provide accurate absolute values of the product yields. However, the predictions well reproduce the variation of the experimental results between the different types of radiation. A more realistic model that considers a realistic distribution of primary energy deposition events, the effects of secondary electrons, and the reactions and diffusion of radicals and molecules is clearly needed for analysis of the radiolytic effects of high LET particles. The data obtained in the present experiments will be quite useful for the development of more sophisticated track models to further our understanding of the radiolysis of water with high LET particles.

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