J. Phys. Chem. A **1999,** *103,* 4769−4774

Radiolysis of Aqueous Solutions with Pulsed Helium Ion Beams. 3. Yields of OH Radicals and the Sum of e_{aq}^- and H Atom Yields Determined in Methyl Viologen Solutions Containing Formate

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Received: October 27, 1998; In Final Form: April 12, 1999

The production of methyl viologen radical cation ($MV^{•+}$) in the radiolysis of aqueous solutions of 0.5 mM methyl viologen (MV^{2+}) containing formate and tertiary butanol (t-BuOH) was studied using fast electron (integral yields) and 21 MeV ^{4}He ion beam pulses (track segment yields). The formate concentration was varied in the range of 10^{-3}−2 M. It was confirmed that $MV^{•+}$ is formed within microseconds and that it is stable in the measured time regions if the solution contains neither t-BuOH nor oxygen. Tertiary butanol radical formed through the scavenging of OH radical or H atom by t-BuOH reacts with $MV^{•+}$, and this rate constant was determined as $(8 \pm 2) \times 10^8$ M^{-1} s^{-1}. The effect of formate concentration on the yield of methyl viologen radical cation was measured in deaerated or N_2O-saturated solutions. The radical yields in deaerated solutions agreed well with those measured by continuous ion beam radiolysis, which confirmed that this system can be used as a chemical dosimeter for ion beam pulse radiolysis. The yields of OH radicals were derived from the yields of $G(MV^{•+})$ in the presence and the absence of t-BuOH. In the radiolysis with low linear energy transfer (LET) radiations, the calculated OH radical yields agree well with the values determined by other OH radical scavengers, formate and formic acid, except at high scavenging capacity. In ^{4}He ion beam radiolysis, the yields have a discrepancy in the measured scavenging capacity range. The sum of the contributions of e_{aq}^- and H atoms to form $MV^{•+}$ was also determined. This value was lower than the yields estimated from other studies with ^{4}He ion beams. Yields are highly dependent on the nature of the solutes and combination of solutes because of intratrack reactions of the products.

Introduction

The radiolysis of aqueous solutions with γ-rays or fast electrons has been studied extensively under a variety of conditions.[1−3] In contrast with low linear energy transfer (LET) radiations, most data obtained using ion beam radiolysis were in acid solutions because of use of the Fricke dosimeter for its convenience and usefulness. However, information in neutral solutions is necessary to understand the biological effects of radiation. Previous papers have reported an ion beam pulse radiolysis system at HIMAC (Heavy Ion Medical Accelerator in Chiba) and the yields of scavenged hydrated electron and OH radical as a function of the scavenger concentrations.[4,5] Pulse radiolysis is widely used for low LET radiations and the technique enhances the number of available chemical systems. In ion beam radiolysis, however, it was found that the intratrack reactions of the secondary products are more important than in low LET radiolysis and that a scavenger which produces less reactive secondary species must be used to measure the scavenged yield at high scavenging capacity.

Methyl viologen has been well studied and it is known to be reduced easily to form radical cation, $MV^{•+}$.[6−9] Since the radical is stable and has a large absorption in the visible region,[7−13] it is expected to be well suited to measure the yield of the primary scavenged radical. Methyl viologen is also reduced by formate radical anion, $COO^{•-}$, so that aqueous solutions of methyl viologen and formate can be used to estimate the sum of the yields of e_{aq}^-, H atoms, and OH radicals.[14] In a previous study, we used this system with continuous radiation and reported that the yields of $MV^{•+}$ are equal to the values predicted from the use of other scavengers in γ-ray radiolysis.[15] In proton and ^{4}He ion beam radiolysis, however, $G(MV^{•+})$ values were substantially lower than expected. In that study, only the yields of radicals which remained after a few minutes, irradiation could be measured, so it is interesting and necessary to investigate the same system using an ion beam pulse technique. Here, pulsed electron beams were first used to confirm the reaction kinetics reported in this system. Then the dependence of the radical cation yield on the formate concentration was measured using both electron and ^{4}He ion beam pulses.

Another purpose of this study is to check the accuracy of the dosimetry with pulsed ion beams. No chemical dosimeter has

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10.1021/jp9842401 CCC: $18.00 © 1999 American Chemical Society
Published on Web 05/29/1999

been established for ion beam radiolysis, and because of the difference in geometry the dosimetry in pulse radiolysis is more difficult than in continuous radiolysis. Aqueous solutions of methyl viologen and formate would make a good chemical dosimeter for ion beam pulse radiolysis, because of the stability and the large absorption coefficient of $MV^{\bullet+}$. The yields of stable $MV^{\bullet+}$ are expected to enable a comparison of pulse and steady state experimental systems.

Experimental Section

The ion beam irradiations were performed using 24 MeV $^4He^{2+}$ ions from HIMAC at the National Institute of Radiological Sciences. The system has been described in a previous paper.[4] The energy of ions entering the solution is 21 MeV after the energy loss at the window, and the area with 100 μm depth was measured with narrowed laser light. After 100 μm, the energy of the ^{4}He ions is about 17 MeV. The differential LET of 21 and 17 MeV ^{4}He ions are 32 and 37 eV nm^{-1}, respectively, and the average LET in the measured area is 35 eV nm^{-1}. The yields measured in this work are therefore track segment yields. Normal low LET pulse radiolysis with electrons or γ-ray radiolysis measures track-averaged or integrated yields. Previous work[15] with heavy particles used track-averaged LET and measured track-averaged yields. Pulses of 5 and 10 μs duration were used, and the absorbed doses were 150 and 300 Gy/pulse, respectively.

The irradiations with electron beams were done at the LINAC facility at the Nuclear Engineering Research Laboratory, the University of Tokyo, using 10 ns pulses with an energy of 35 MeV. Details of the system have been described elsewhere.[16] The sample supply system was similar to the one used in ^{4}He ion beam radiolysis, where the solution was stocked in the reservoir vessel with a gas bubbling system and flowed through Pyrex glass tube into a quartz cell. For dosimetry, 0.01 M KSCN solutions saturated with N_2O were used with $G\epsilon$ value of 51 000 M^{-1} cm^{-1} (100 eV)$^{-1}$ at 472 nm for $(SCN)_2^{\bullet-}$.[17] Absorbed dose was typically 20 or 30 Gy/pulse.

Methyl viologen dichloride was obtained from Tokyo Kasei, and sodium formate, tertiary butanol, ethanol, and 2-propanol were from Wako Co. Ltd. These chemicals were reagent grade and used as received. All the solutions were made with water which was prepared through ion-exchange resin and Millipore equipment. Deaeration by nitrogen bubbling or saturation with N_2O was carried out before irradiation.

Results and Discussion

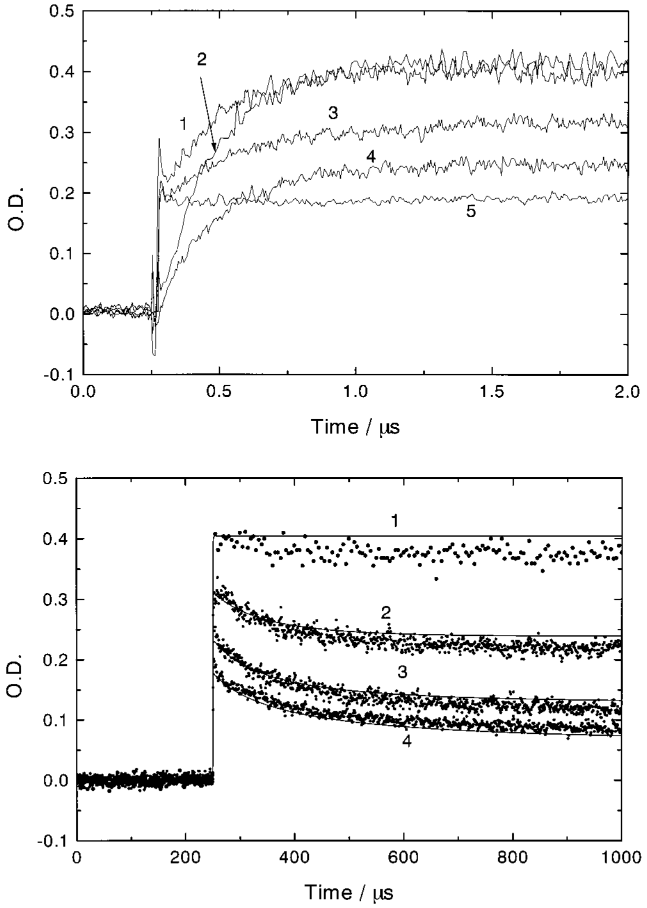

Figure 1. Formation and decay of $MV^{\bullet+}$ observed in the electron beam pulse radiolysis. The samples were the aqueous solutions of 0.5 mM methyl viologen containing either 10 mM formate or 50 mM tertiary butanol or both of them. (a, top) curve 1, deaerated solution containing formate; 2, N_2O saturated and containing formate; 3, deaerated and containing formate and t-BuOH; 4, N_2O saturated and containing formate and t-BuOH; 5, deaerated and containing t-BuOH. (b, bottom) curve 1, deaerated and containing formate; 2, deaerated and containing formate and t-BuOH; 3, N_2O saturated and containing formate and t-BuOH; 4, deaerated and containing t-BuOH. The dots are experimental results, and the solid lines are the simulated results using $k_9 = 8 \times 10^8$ M^{-1} s^{-1}.

Reaction Kinetics. The absorption spectrum of $MV^{\bullet+}$ has two peaks at 395 and 605 nm, and the reaction kinetics of $MV^{\bullet+}$ was investigated by observing the transient absorption at 605 nm. Several values between 6000 and 15 000 M^{-1} cm^{-1} were reported as the absorption coefficient of this peak.[7−11,14] The smaller one, approximately 6000 M^{-1} cm^{-1},[8] was measured in the presence of oxygen, so part of the radicals would have reacted with oxygen. The others are around 13 000 M^{-1} cm^{-1}, and in the present research, 13 100 M^{-1} cm^{-1} was taken from the latest report to calculate the yields.[14] Figure 1a shows the time profiles observed in the radiolysis with electron pulses. In the present research, the concentration of methyl viologen was always 0.5 mM and those of formate and t-BuOH were varied. The formation of $MV^{\bullet+}$ has two components in deaerated solutions containing formate, curve 1, and the rise time of the fast component is less than 50 ns and that of slow one is approximately 300 ns. The reactions to produce $MV^{\bullet+}$ in solutions of methyl viologen and formate have been reported as follows.[6,8,13,18,19]

$$e_{aq}^{-} + MV^{2+} \rightarrow MV^{\bullet+} \qquad k_1 = 5 \times 10^{10}\ M^{-1}\ s^{-1} \quad (1)$$

$$OH + HCOO^{-} \rightarrow COO^{\bullet-} + H_2O \qquad k_2 = 3.2 \times 10^{9}\ M^{-1}\ s^{-1} \quad (2)$$

$$H + HCOO^{-} \rightarrow COO^{\bullet-} + H_2 \qquad k_3 = 2.1 \times 10^{8}\ M^{-1}\ s^{-1} \quad (3)$$

$$COO^{\bullet-} + MV^{2+} \rightarrow MV^{\bullet+} + CO_2 \qquad k_4 = 1 \times 10^{10}\ M^{-1}\ s^{-1} \quad (4)$$

The expected rise times of reactions 1 and 4 are 40 and 200 ns, respectively, which agree well with the two components of the observed time profiles. When the formate concentration was changed, the fast component did not change and the height of the slow one increased with increasing formate concentration. In N_2O-saturated solutions, hydrated electrons would be converted to OH radicals.[19,20] The scavenging capacity for e_{aq}^{-} is different when N_2O is present, and this will affect the kinetics and yields, as discussed later.

$$e_{aq}^{-} + N_2O \rightarrow N_2 + O^{\bullet -} \qquad k_5 = 9.1 \times 10^9\ M^{-1}\ s^{-1} \quad (5)$$

$$O^{\bullet -} + H_2O \rightarrow OH + OH^- \qquad k_{5a} = 1 \times 10^6\ M^{-1}\ s^{-1} \quad (5a)$$

The observed time profile (Figure 1a, curve 2) shows that the fast component decreased nearly to zero and that the total production yield of $MV^{\bullet +}$ is almost the same as in the deaerated solutions. These results support the above kinetics.

Tertiary butanol reacts with H atom and OH radical.[19]

$$OH + C(CH_3)_3OH \rightarrow {}^{\bullet}CH_2C(CH_3)_2OH + H_2O$$

$$k_6 = 6.0 \times 10^8\ M^{-1}\ s^{-1} \quad (6)$$

$$H + C(CH_3)_3OH \rightarrow {}^{\bullet}CH_2C(CH_3)_2OH + H_2$$

$$k_7 = 1.7 \times 10^5\ M^{-1}\ s^{-1} \quad (7)$$

The radical, produced in reactions 6 and 7, does not lead to the formation of $MV^{\bullet +}$. This nonreactivity was confirmed by the time profile observed in the solutions of methyl viologen and t-BuOH, curve 5 in Figure 1a, which has the fast component with the same height as curves 1 and 3 and does not have the slow component. When both formate and t-BuOH are present in the solution, they compete to scavenge OH radicals. Curves 3 and 4 in Figure 1a were obtained in the solutions of 10 mM formate and 50 mM t-BuOH saturated with nitrogen and N_2O, respectively. The scavenging capacities for OH radical of formate and t-BuOH are approximately the same, and half of OH radicals react with t-BuOH and do not lead to the formation of $MV^{\bullet +}$. The scavenging of H atom by t-BuOH is slow and most of H atoms should react with formate. The reaction between e_{aq}^{-} and t-BuOH is also slow ($k < 4 \times 10^5\ M^{-1}\ s^{-1}$)[19] and would not have any effect on the observed kinetics.

It is reported that $MV^{\bullet +}$ is rather stable in the absence of oxygen and reacts with H_2O_2 on the time scale of several hours.[12,13] As shown in Figure 1b, the observed decay in solutions free of t-BuOH is small and is probably due to a trace of oxygen remaining (on the order of micromoles). In solutions containing t-BuOH, $MV^{\bullet +}$ decays in several hundreds of microseconds by the reaction with tertiary butanol radicals.

Transient yields of $MV^{\bullet +}$ were simulated to estimate the rate constant of the reactions between $MV^{\bullet +}$ and tertiary butanol radical. The primary yields of e_{aq}^{-}, H atom, and OH radical used in the simulation were 3.0, 0.6, and 3.2, respectively,[21] which were chosen considering the scavenging capacity for each radical. The formation of $MV^{\bullet +}$ and tertiary butanol radicals was simulated using the reactions 1−7, and it was assumed that the two reactions 8 and 9 are the predominant cause of the decay.[22]

$$2\,{}^{\bullet}CH_2C(CH_3)_2OH \rightarrow \text{products} \qquad k_8 = 7.0 \times 10^8\ M^{-1}\ s^{-1} \quad (8)$$

$$MV^{\bullet +} + {}^{\bullet}CH_2C(CH_3)_2OH \rightarrow \text{products} \qquad k_9 \quad (9)$$

Calculations were carried out by a numerical differentiation method using FACSIMILE code.[23] The time profiles predicted by these simulations are also shown in Figure 1b. They well reproduce the yields of $MV^{\bullet +}$ for all the data. The rate constant of the reaction 9 is estimated as $k_9 = (8 \pm 2) \times 10^8\ M^{-1}\ s^{-1}$ to give the best fitting curves. We have carried out further simulation using various values for the rate constant k_8. It was found that the results are not sensitive to k_8 because t-BuOH has lower concentration than $MV^{\bullet +}$ and is consumed faster. Variation of k_8 in the same order causes merely small change of k_9 (within error). Primary yields of e_{aq}^{-}, H atom and OH radical predominantly determine the peak yields of $MV^{\bullet +}$. The values chosen in this paper can reproduce the experimental results well and change of the primary yields does not give a good determination of k_9 or fit to the data.

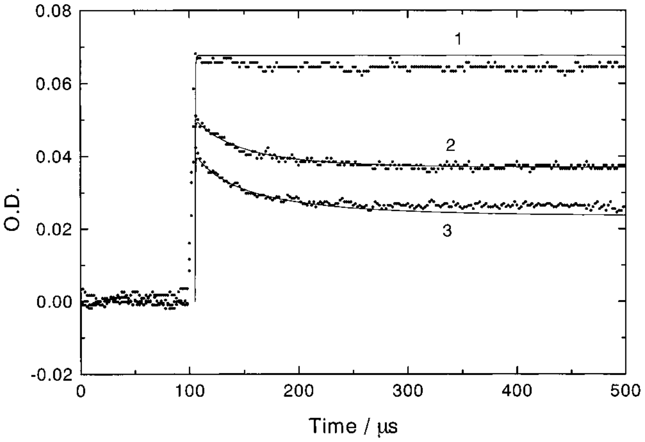

Figure 2. Transient absorption signals of $MV^{\bullet +}$ observed in the ^4He ion beam pulse radiolysis. The samples were aqueous solutions of 0.5 mM methyl viologen and 10 mM formate either free of t-BuOH or containing 50 mM t-BuOH: curve 1, deaerated solution containing formate; 2, deaerated and containing formate and t-BuOH; 3, N_2O saturated and containing formate and t-BuOH. The dots are experimental results, and the solid lines are the simulated ones.

In ^4He ion beam pulse radiolysis, transient absorptions were measured using the 515 nm line of the argon ion laser as the analyzing light. The absorption coefficient of $MV^{\bullet +}$ at 515 nm is 4100 $M^{-1}\ cm^{-1}$.[14] Figure 2 shows the time profiles observed in three kinds of 0.5 mM methyl viologen solutions: deaerated solution containing 10 mM formate(curve 1), deaerated solution containing both 10 mM formate and 50 mM t-BuOH (curve 2), and N_2O-saturated solutions containing both 10 mM formate and 50 mM t-BuOH (curve 3). Because pulse durations were 5 μs, the formation of the radical could not be investigated. In the solution free of t-BuOH(curve 1), the decrease of the absorbance was negligible and no apparent decay was observed at other formate concentrations. This result suggests that the yield of $MV^{\bullet +}$ can be measured by both pulsed and continuous ion beam experiments. In the solutions containing t-BuOH, the absorbance decreased and approached a plateau within a few hundred microseconds. Figure 2 contains the results of the simulation for each solution, which are mentioned below.

In this chemical system, the role of formate is to convert H atoms and OH radicals into the species which reduce MV^{2+}. In order to make a further check of the methyl viologen systems, ethanol and 2-propanol were used instead of formate because $CH_3C^{\bullet}HOH$ and $(CH_3)_2C^{\bullet}OH$ radicals are expected to reduce MV^{2+}. Deaerated solutions of 0.5 mM MV^{2+} containing either 15 mM ethanol or 20 mM 2-propanol were irradiated. The reduction of $MV^{\bullet +}$ by each alcohol radical was confirmed using both electron and ^4He ion beams; however, the yields of $MV^{\bullet +}$ were lower than in formate solutions. The lower yields can be explained if it is assumed that approximately 15% of the products formed through the reaction of the alcohols and OH radicals are not the radicals described above and will not lead to the formation of $MV^{\bullet +}$.[24] These results agree with the study of Mulazzani et al. in which aqueous solutions of methyl viologen and 2-propanol were irradiated with electron pulses.[18]

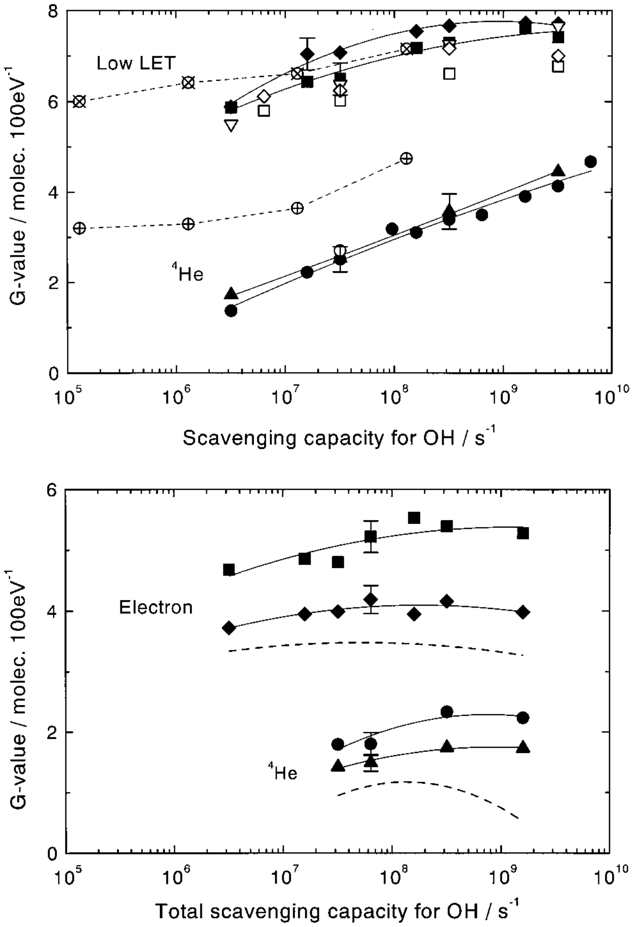

Figure 3. Yield of $MV^{\bullet +}$ in the radiolysis of 0.5 mM methyl viologen and formate solutions as a function of scavenging capacity for OH radical. Solid symbols are the results of the present work: (■) deaerated solutions with electrons, (◆) N_2O-saturated solutions with electrons, (●) deaerated solutions with ^{4}He, (▲) N_2O saturated solutions with ^{4}He. Typical error range is shown for each series of data. (a, top) Solutions do not contain t-BuOH. Open symbols are the data of the references: (▽) γ-rays and (○)^{4}He in deaerated solutions, ref 15; (□) in deaerated and (◇) in N_2O-saturated solutions with electron pulses, ref 14. The yields predicted from the results of the ferrous sulfate solution and HCOOH are shown as (⊗) for γ-rays and (⊕) for ^{4}He ion beams. (b, bottom) Solutions contain both formate and t-BuOH with the latter at a concentration 5 times as large as that of formate. Broken lines are the sums of the e_{aq}^- and H atom yields calculated using eq III with the data of deaerated solutions for ^{4}He ion and electron beams.

Yields of Methyl Viologen Radical Cation. Figure 3a shows $G(MV^{\bullet +})$ in solutions of 0.5 mM MV^{2+} containing various concentrations of formate as a function of the scavenging capacity for OH radical. The units of *G* is the number of radicals produced per 100 eV energy absorbed. Note that the low LET yields are track-averaged yields, while the high LET data are track segment (21−17 MeV) yields. Scavenging capacity is defined as the product of the rate constant and the scavenger concentration. Formate mainly affects the scavenging capacity for OH radical, because the scavenging of the H atom is slower by an order of magnitude and the yield of H atom would be much smaller than that of OH radical. The $MV^{\bullet +}$ yields increased with increasing the scavenging capacity in all four sets of data. The average lifetime of the scavenged radical is equal to the reciprocal of the scavenging capacity. Thus the lower yields at the lower scavenging capacity represent the decay of OH radical by the reactions with water decomposition products in the track. The data of the previous study using γ-rays and continuous ion beams in deaerated solutions are also shown in the figure.[15] This yield for ^{4}He ion beams is the track segment yield calculated from the data of the particle energy at 15 and 20 MeV. Virtually the same yield is obtained when a polynomial fit to a plot of *GE* vs *E* is differentiated, where *E* is the initial particle energy. The results agree well with the present measurements both for low LET and ^{4}He ion beams. Buxton and Wood measured $G(MV^{\bullet +})$ by electron beam pulse radiolysis using 0.2 mM MV^{2+} solutions.[14] The results are in good agreement with the others, though they suggest a small dependence on the MV^{2+} concentration.

Accurate dosimetry is a major problem in ion beam pulse radiolysis. In this research, dose was calculated from the beam charge of each pulse measured by the oscilloscope and the spatial distribution of the beam intensity measured by the absorption change of CTA (cellulose triacetate) film.[25] The dosimetry would be more accurate in continuous irradiation, because the charge of the particles can be collected and consideration of spatial distribution is not necessary. The yields agree well between pulse and continuous radiolysis, which suggests that the method to evaluate the dose in this research is sufficiently correct. As shown in Figure 1, $MV^{\bullet +}$ is formed within several microseconds and is stable for long times if no oxygen is present. The absorption coefficient is large, and the effect of oxygen is not important on the time scales of pulsed irradiation. Thus this system could be a promising chemical dosimeter in ion beam pulse radiolysis. The *G* value of $MV^{\bullet +}$ at 10 mM formate was determined as 2.5 ± 0.2 for ^{4}He ion beams of LET 35 eV nm^{-1}.

In electron beam radiolysis, $G(MV^{\bullet +})$ was slightly higher in N_2O-saturated solution than in deaerated solution, while they were almost the same in ^{4}He ion beam radiolysis. Higher yields in N_2O-saturated solutions were also reported by Buxton and Wood.[14] In N_2O-saturated solutions, the hydrated electron is converted into OH radical with the scavenging capacity $k[N_2O] = 2.5 \times 10^8\ s^{-1}$,[19] while it is scavenged by MV^{2+} with $k[MV^{2+}] = 2.5 \times 10^7\ s^{-1}$ in deaerated solutions. The higher scavenging capacities will increase $G(MV^{\bullet +})$, though quantitative analysis is difficult because of the cooperative effects of the scavengers.[26−28]

Figure 3a contains the total yields of radicals estimated from other solutions. The sum of $G(e_{aq}^-) + G(H)$ was derived from acidic ferrous sulfate solutions[1,29] and $G(OH)$ from formic acid.[30,31] Details were described in the previous paper.[15] As shown in this figure, these values agree well with $G(MV^{\bullet +})$ at low LET while the former are substantially higher than the latter for ^{4}He ion beams. The difference was also found previously with continuous ion beams and it was considered that the yield of $MV^{\bullet +}$ might decrease after irradiation. In the present research, the yields were measured by pulse radiolysis and no decay of $MV^{\bullet +}$ was observed. These results suggest that the reaction of $MV^{\bullet +}$ is not the reason for the lower yield than determined from ferrous sulfate and formic acid solutions.

The yields of $MV^{\bullet +}$ in the aqueous solutions of 0.5 mM MV^{2+} containing both formate and t-BuOH are shown in Figure 3b. The plotted values were determined from the peak absorbance in each time profile, because $MV^{\bullet +}$ decayed by further reaction with the tertiary butanol radical. In all the solutions the concentration of t-BuOH was kept 5 times larger than that of formate in order that the scavenging capacities for OH radicals are the same. The horizontal axis is the total scavenging capacity for OH radical, the sum of the contributions of formate and t-BuOH. The yields were smaller in N_2O-saturated solutions than in deaerated ones. This lower yield occurs because e_{aq}^- is converted to OH radical by N_2O and, consequently, half of them

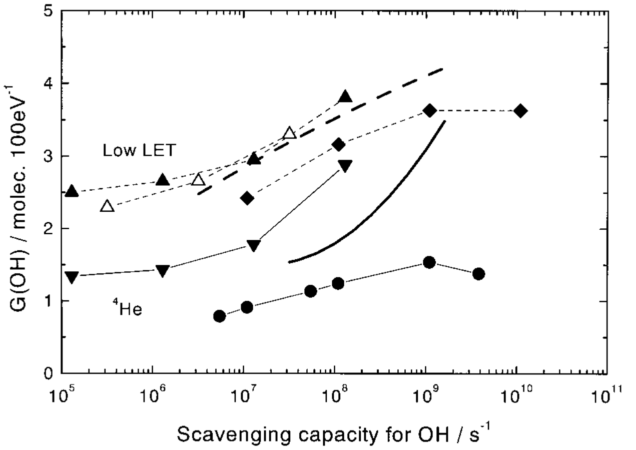

Figure 4. Yields of scavenged OH radicals as a function of scavenging capacity. The solid and broken bold lines are the calculated yields from the data of the present research for ^{4}He ion and electron beams, respectively. Symbols are taken from the references: HCOOH (▲) with γ-ray, ref 30, and (▼) with ^{4}He ion beams, ref 31; SCN$^-$ (◆) with electron, and (●) with ^{4}He ion pulses, ref 4; HCOO$^-$ (△) with γ-rays, ref 33.

are scavenged by t-BuOH. Although the MV$^{\bullet+}$ yields increased with increasing the scavenging capacity, the slopes were smaller than in Figure 3a. The increase in total scavenging capacity would lead to scavenging more OH radicals by formate and give a higher yield of MV$^{\bullet+}$. However, this effect could be reduced through scavenging of OH radicals by t-BuOH.

Yields of Primary Radicals. In solutions free of tertiary butanol, the yield of MV$^{\bullet+}$ can be given stoichiometrically as follows from the reactions 1−4.

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

When t-BuOH is added into the solution, it competes with formate to scavenge OH radical. In the present research the ratio of t-BuOH and formate concentration was kept constant so that half of OH radicals should react with formate. The reactions of t-BuOH with e$_{aq}^-$ and H atom are slow, and these radicals would be scavenged by MV^{2+} and formate, respectively. The scavenging capacity for OH radical is a factor of 2 higher than in the absence of t-BuOH. This leads to a small increase in G(MV$^{\bullet+}$) but this should be accounted for by using the total scavenging capacity in Figure 3b. Therefore, G(MV$^{\bullet+}$) in deaerated solutions of t-BuOH can be given as follows:

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

The sum of hydrated electron and H atom yields can be calculated from eqs I and II.

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

The values were 3.4 and 1.0 for low LET and ^{4}He ion beams, respectively, though they have a little dependence on the scavenging capacity for OH as shown in Figure 3b.

The yield of OH can also be derived from the eqs I and II.

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

The yields of OH radicals calculated from the data of Figure 3 are shown in Figure 4. The data of N$_2$O-saturated solutions were not used because it is difficult to evaluate the effect of converting e$_{aq}^-$ into OH radical.

Transient yields of MV$^{\bullet+}$ in the radiolysis with ^{4}He ion beams were simulated using the primary radical yields determined above. The method of the simulation is the same as with low LET radiolysis except that the primary yields of e$_{aq}^-$, H atom, and OH radical are 0.8, 0.35, and 1.3, respectively. These values were assumed to be constant for all the three kinds of solutions shown in Figure 2, though there should be the small variation of the yields ($\leq$0.1) due to the difference of the scavenging capacity. The rate constant of the reaction 9 was 8 × 10^8 M^{-1} s^{-1}. As is shown in Figure 2, the simulation well reproduced the experimental results.

The sums of e$_{aq}^-$ and H atom yields determined from acidic ferrous sulfate solution are 3.7 and 1.9 for low LET and ^{4}He ion beams, respectively.[1,29] The yield agrees well with the yield determined in the present research at low LET; however, the former is much higher than the latter for ^{4}He ion beams. Two points should be considered when directly comparing these two systems. In the ferrous sulfate solutions the sum of e$_{aq}^-$ and H atom yields are defined as half of the difference of the ferric ion yields under aerated and deaerated conditions. The scavenging capacity for H is about 5 × 10^6 and 7 × 10^4 s^{-1} in aerated and deaerated solutions, respectively. The difference of the scavenging capacity can give the higher yield, as is mentioned in the previous paper.[15] Another reason is that ferrous sulfate was used under acid conditions (0.4 M H$_2$SO$_4$). The proton acts as an e$_{aq}^-$ scavenger in the acid solutions and converts it to H atom. This will lead to the higher yield than in neutral solutions as N$_2$O saturation increases the yield. The difference of the yields between acid and neutral solutions is well-known for low LET; the yields are 3.7 and 3.3 in acid and neutral solutions, respectively.[1,3] Track-averaged yields for ion beams have been reported as a function of initial particle LET: 1.2 (acid) and 0.9 (neutral) at 35 eV/nm.[1,32] The difference between the yields in ferrous sulfate and methyl viologen solutions seems to be higher than estimated from the reports of track averaged yields, so there should be more than one reason.

The most likely cause for the lower yields with ^{4}He ions in the present work is due to the presence of back reactions in this system. A previous examination at high scavenging capacities using low LET radiation found a significantly lower yield of MV$^{\bullet+}$ than expected from other experiments.[15] Calculations suggested that the reaction of the COO$^{\bullet-}$ with itself was significant when it was present at high concentrations.[15] High concentrations of COO$^{\bullet-}$ are expected at high scavenging capacities with low LET and at almost any scavenging capacity at high LET. According to eq III this effect may actually give greater yields of e$_{aq}^-$ + H atom than expected. However, even at low LET and long times reactions 8 and 9 are very noticeable in the systems containing t-BuOH as seen from Figures 1 and 2. A significant contribution of reaction 9 in the dense track at high LET will lead to a decrease in the expected e$_{aq}^-$ + H atom yields according to eq III.

The yields of OH radicals determined by various scavengers are compared with the results of the methyl viologen system in Figure 4.[4,30,31] The data of two other scavengers, formic acid[31] and thiocyanate,[4] were reported in ^{4}He ion beam radiolysis. The rate constants for the scavenging of OH radicals by HCOOH and SCN$^-$ are 1.3 × 10^8 and 1.1 × 10^{10} M^{-1} s^{-1}, respectively.[19] Data using formate as the scavenger are available for low LET radiolysis.[33] Formate was also used for heavy particle radiolysis;[33] however, only the track-averaged yields were reported and are not compared with track segment yields shown in Figure 4.

In low LET radiolysis, the four sets of data agree well, although the yields derived from SCN^- are slightly lower particularly at high scavenging capacity. As was discussed in the previous paper, the lower yield could be because the products can participate in the track reactions at earlier times in the dense track.[4,5] In other words, the species produced through scavenging OH radical, $^\bullet SCN$ and $(SCN)_2^{\bullet -}$, could disappear in track processes. The observed leveling off of the yield derived from thiocyanate can also be explained by the high reactivity of the products. The contribution of the track reactions would be larger in ion beam radiolysis because the species would be distributed with higher density than at low LET. In ^{4}He ion beam radiolysis, however, the other data, methyl viologen and formic acid, have large differences. In these solutions OH radicals are scavenged by formic acid or formate to produce $COO^{\bullet -}$. In formic acid solutions this radical anion is oxidized by oxygen to form CO_2, the yield of which was observed. The rate constant of this oxidizing reaction is 2.0×10^9 M^{-1} s^{-1},[34] so the scavenging capacity for $COO^{\bullet -}$ is 2.4×10^6 s^{-1} in oxygen-saturated solutions ($[O_2] = 1.2$ mM). In methyl viologen and formate systems, $COO^{\bullet -}$ is oxidized by MV^{2+} with the scavenging capacity of 5×10^6 s^{-1}; the conditions are quite similar. As discussed above, a possible reason for the differences is the reaction of the final products in the dense track. Carbon dioxide does not seem to react with $COO^{\bullet -}$, whereas $MV^{\bullet +}$ might react with $COO^{\bullet -}$ at earlier times leading to the lower yield of $MV^{\bullet +}$ than expected.[15] Another possibility is that concentrated HCOOH solution is acid ($k[H^+] = 3 \times 10^8$ s^{-1} at 1 M HCOOH solution) and methyl viologen solution is neutral. The yield might be higher in acid solutions.

It is not clear whether the above points are sufficiently effective to cause the observed variations of the yields. Since the direct measurement of the OH radical yields is difficult even when short pulses are available, the scavenging method is needed to study the behavior of OH radicals. Further work is required to resolve these problems.

Acknowledgment. We thank Dr. Z. Cai, Mr. O. Urabe, and Mr. D. Yoshikawa (University of Tokyo), Dr. T. Kojima and Mr. H. Tachibana (JAERI Takasaki), and the staff of HIMAC for their assistance with the experiment. We also thank one of the referees for valuable suggestions. This research has been carried out as a Research Project with Heavy Ions at NIRS-HIMAC. This is also partly supported by a Grant-in-Aid for Scientific Research (B-074580098), The Ministry of Education, Science, Sports, and Culture, Japanese Government. J.A.L. was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

References and Notes

(1) Allen, A. O. *The Radiation Chemistry of Water and Aqueous Solutions*; Van Nostrand-Reinhold: Princeton, NJ, 1961.

(2) Draganic, I. G.; Draganic, Z. D. *The Radiation Chemistry of Water*; Academic Press: New York, 1971.

(3) Spinks, J. W. T.; Woods, R. J. *An Introduction to Radiation Chemistry*, 3rd ed.; Wiley: New York, 1990.

(4) Chitose, N.; Katsumura, Y.; Zuo, Z.; Domae, M.; Ishigure, K.; Murakami, T. *J. Chem. Soc., Faraday Trans*. **1997**, *93*, 3939.

(5) Chitose, N.; Katsumura, Y.; Domae, M.; Zuo, Z.; Murakami, T. *Radiat. Phys. Chem.*, in press.

(6) Farrington, J. A.; Ebert, M.; Land, E. J.; Fletcher, K. *Biochim. Biophys. Acta* **1973**, *314*, 372.

(7) Thorneley, R. N. F. *Biochim. Biophys. Acta* **1974**, *333*, 487.

(8) Patterson, L. K.; Small, R. D., Jr.; Scaiano, J. C. *Radiat. Res.* **1977**, *72*, 218.

(9) Farrington, J. A.; Ebert, M.; Land, E. J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 665.

(10) Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524.

(11) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

(12) Venturi, M.; Mulazzani, Q. G.; Hoffman, M. Z. *Radiat. Phys. Chem.* **1984**, *23*, 229.

(13) Shiraishi, H.; Buxton, G. V.; Wood, N. D. *Radiat. Phys. Chem.* **1989**, *33*, 519.

(14) Buxton, G. V.; Wood, N. D. *Radiat. Phys. Chem.* **1989**, *34*, 699.

(15) Chitose, N.; LaVerne, J. A.; Katsumura, Y. *J. Phys. Chem. A* **1998**, *102*, 2087.

(16) Kobayashi, H.; Tabata, Y. *Radiat. Phys. Chem.* **1989**, *34*, 447.

(17) Buxton, G. V.; Stuart, C. R. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 279.

(18) Mulazzani, Q. G.; D′Angelantonio, M.; Venturi, M.; Hoffman, M. Z.; Rodgers, M. A. J. *J. Phys. Chem.* **1986**, *90*, 5347.

(19) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

(20) Hickel, B.; Corfitzen, H.; Sehested, K. *J. Phys. Chem.* **1996**, *100*, 17186.

(21) Pimblott, S. M.; LaVerne, J. A. *J. Phys. Chem. A* **1997**, *101*, 5828.

(22) Simic, M.; Neta, P.; Hayon, E. *J. Phys. Chem.* **1969**, *73*, 3794.

(23) Chance, E. M.; Curtis, A. R.; Jones, I. P.; Kirby, C. R. Report AERE-R8775; AERE: Harwell, 1977.

(24) Asmus, K.-D.; Moeckel, H.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218.

(25) Kudoh, H.; Sasuga, T.; Seguchi, T.; Katsumura, Y. *Polymer* **1996**, *37*, 2903.

(26) Draganic, Z. D.; Draganic, I. G. *J. Phys. Chem.* **1972**, *76*, 2733.

(27) Draganic, Z. D.; Draganic, I. G. *J. Phys. Chem.* **1973**, *77*, 765.

(28) LaVerne, J. A.; Pimblott, S. M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3527.

(29) LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 5770.

(30) Hart, E. J. *J. Am. Chem. Soc.* **1954**, *76*, 4312.

(31) LaVerne, J. A. *Radiat. Res*. **1989**, *118*, 201.

(32) Elliot, A. J.; Chenier, M. P.; Ouellette, D. C.; Koslowsky, V. T. *J. Phys. Chem.* **1996**, *100*, 9014.

(33) Burns, W. G.; Sims, H. E. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2803.

(34) Buxton, G. V.; Sellers, R. M.; McCracken, D. R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1464.