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Effect of Formate Concentration on Radical Formation in the Radiolysis of Aqueous Methyl Viologen Solutions

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The yields of methyl viologen radical cation ($MV^{\bullet +}$) in the radiolysis of nitrogen-saturated 0.5 mM methyl viologen (MV^{2+}) solutions containing formate were measured using ^{60}Co γ-rays, ^{1}H ions of 2−15 MeV, and ^{4}He ions of 5−20 MeV. The concentrations of formate were 1, 10, 100, and 1000 mM, which correspond to OH radical scavenging capacities of 3.2×10^6 to 3.2×10^9 s^{-1}. Methyl viologen radical cation yields should be stoichiometrically equivalent to the sum of the hydrated electron, H atom, and OH radical yields. This outcome is found in γ-ray radiolysis except at very high or low formate concentrations. At all formate concentrations, the ^{1}H and ^{4}He ion radiolyses give yields of methyl viologen radical cations that are significantly lower than expected from the results of other aqueous solutions. Possible reasons for the differences are discussed.

Introduction

The track structure induced by heavy, charged particles passing through water differs from that of low linear energy transfer (LET) radiation such as fast electrons and γ-rays. This difference is considered to be the main reason the yields of decomposition products surviving intratrack reactions depend on the kind of radiation.[1,2] One approach to investigate the extent of intratrack processes is to measure the yields of the scavenged intermediates as a function of the scavenger concentration. There have been a few studies of this type using scavengers for e_{aq}^{-} or OH radicals in ion beam radiolysis.[3−6] However, the number of scavengers useful for these studies is limited compared to experiments with low LET radiation. Most studies with heavy particles examine stable end products whereas pulse radiolysis techniques common with low LET fast electrons allow for the examination of short-lived scavenged products or even the direct observation of the transients themselves. Simple and accurate scavenger systems would be immensely helpful in determining the effects of track structure on the fast chemistry in heavy particle tracks. A method for measuring total radical yields would be particularly useful for assessing general track structure and for determining the total water decomposition.

In this study, aqueous solutions of methyl viologen containing formate were used to estimate the sum of the yields of e_{aq}^{-}, H atoms, and OH radicals in heavy particle radiolysis. This system has been studied extensively using pulsed electron techniques,[7,8] and the yield of the reduced methyl viologen (MV^{+}) is thought to be a measure of the total radical yield.[7] The scavenging of e_{aq}^{-} is by the direct reduction of the methyl viologen cation (MV^{2+}) while the H atoms and OH radicals should be scavenged by formate, and the resulting product reduces MV^{2+}. The initial concentration of the methyl viologen was the same for all experiments while the scavenging capacity for H atoms and OH radicals was varied by changing formate concentration. Experiments were performed with γ-rays in order to determine the accuracy of the system for estimating total radical production and to elucidate any possible limitations of the system. Irradiations with protons of 2−15 MeV and helium ions of 5−20 MeV were performed with similar solutions as with γ-rays. The observed dependences of product yields on particle energy and LET and formate concentration are presented.

Experimental Section

Particle irradiations were carried out with ^{1}H and ^{4}He ions using the FN Tandem Van de Graaff of the Nuclear Structure Laboratory at the University of Notre Dame. The window assembly and irradiation procedure were the same as reported earlier.[9,10] Particle energy was determined by magnetic analysis, and the energy loss to windows was determined from standard stopping power tables.[11] Absolute dosimetry was performed by collecting and integrating the charge from the sample cell and exit windows in combination with the particle energy. Beam current and total doses were approximately 1 nA and 1×10^{19} eV (50 Gy), respectively.

The radiolysis cells had an irradiation zone of Pyrex with a titanium or mica window (∼4−6 mg/cm^2) which was connected in series to a gas bubbler and a 1 cm quartz optical cuvette. Each cell contained a glass-enclosed magnetic stirrer that circulated the solution through the irradiation zone, bubbler, and cuvette. The total volume of the solutions was ∼33 mL. Dissolved oxygen was removed by passing ultrahigh-purity nitrogen through activated charcoal traps and bubbling through the solution throughout the radiolysis.

The cuvette was placed in a diode array spectrophotometer (Hewlett-Packard, HP8453), and the sample cell was not moved during the irradiation and the following optical measurements. This arrangement minimized random variations in the absorption measurements and allowed for rapid analysis following radi-

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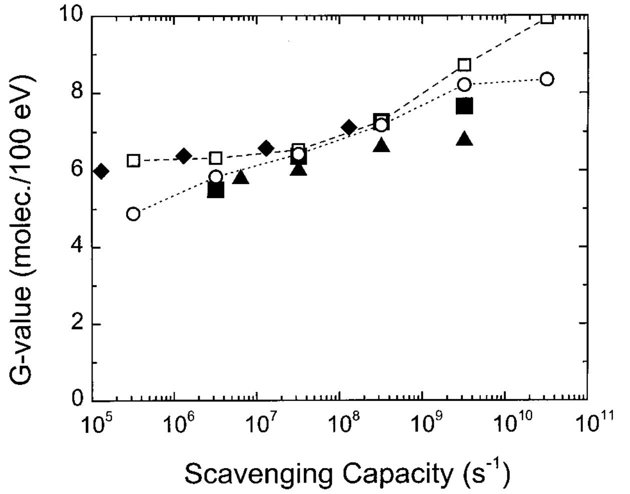

Figure 1. Production of $MV^{•+}$ in the γ-radiolysis of 0.5 mM methyl viologen and formate solutions as a function of formate scavenging capacity for OH radicals: (■) this work and (▲) ref 7. The appropriate sum of the ferrous sulfate and formic acid product yields are (◆).The results of simulations are (□) for the total scavengable radical yield and (○) for $MV^{•+}$ in the methyl viologen and formate system.

olysis. Product yields were determined by measuring the amount of reduced methyl viologen cation at 605 nm using the extinction coefficient of 13 100 M^{-1} cm^{-1}.[7]

Radiolysis with γ-rays was performed using a Gammacell 220 ^{60}Co γ-ray source at the Radiation Laboratory of University of Notre Dame. The sample cell was of Pyrex and contained a cuvette for optical measurements. Ultrahigh-purity nitrogen was bubbled through the sample during the irradiation and absorption measurements. The absorbed dose was typically 37 Gy obtained by a 2 min irradiation. Dosimetry was performed with the Fricke dosimeter assuming a ferric ion yield of 15.45 ions/100 eV.[12] At 1 M formate the density of the solution is only about 1% greater than that for pure water, and no additional correction was made in the dosimetry. Similarly, effects due to the direct radiolysis of formate were assumed to be negligible.

Methyl viologen dichloride and sodium formate of Aldrich reagent grades were used as received. All solutions were 0.5 mM in methyl viologen dichloride and 1, 10, 100, or 1000 mM in formate. Solutions were made with water from a Millipore Milli-Q UV system.

Results and Discussion

γ-ray Radiolysis. The absorption spectra obtained after irradiation have two peaks at 395 and 605 nm, which are attributed to the spectrum of the reduced methyl viologen cation, $MV^{•+}$.[13] It is reported that in the absence of oxygen $MV^{•+}$ decays on the time scale of several hours by the reaction with H_2O_2.[14] A slow decay of $MV^{•+}$ was also observed in this work. However, the low doses and dose rates kept the decay slow enough to be ignored in the determination of yields. Linearity of the yield of $MV^{•+}$ with dose was observed.

The production of $MV^{•+}$ in the radiolysis of 0.5 mM MV^{2+} solutions containing 1, 10, 100, or 1000 mM formate is shown in Figure 1 as a function of the formate scavenging capacity for OH radicals. Radiation chemical yields are expressed in the units of G-value, which is the number of product molecules produced per 100 eV energy absorbed. The scavenging capacity is the pseudo-first-order rate constant obtained by the product of the rate constant and scavenger concentration. The data of Buxton and Wood are also shown in Figure 1.[7] They used aqueous solutions of 0.2 mM MV^{2+} and pulsed radiolysis techniques. The two sets of data agree well, showing the negligible contribution of side reactions beyond a few microseconds that could lead to a decrease in yields with the long time measurements. With increasing scavenger concentration one is sampling intratrack chemistry at earlier times. The increasing yield of $MV^{•+}$ with increasing scavenging capacity gives an indication of the amount and the time scale of intratrack reactions of the products of water radiolysis.

The reactions to produce $MV^{•+}$ in aqueous solutions of methyl viologen and formate have been reported as follows.[8,13–16]

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

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

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

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

The yield of $MV^{•+}$ is considered to be equivalent to the sum of the yields of e_{aq}^{-}, H atom, and OH radical. At a concentration of 0.5 mM methyl viologen the scavenging capacity for e_{aq}^{-} is 2.5×10^7 s^{-1}. The scavenging capacities for H atoms and OH radicals depend on the formate concentration. However, the reaction of formate with H is slower than that with OH by an order of magnitude, and G(H) is much smaller than G(OH). Therefore, the effect of formate concentration can be considered as solely due to the scavenging of OH radicals.

It is desirable to know the accuracy of the methyl viologen and formate system to predict the total radical yield in the radiolysis of water. Therefore, the simulation of the intraspur reactions in this system was performed with a deterministic diffusion kinetic model. The method of simulation was described elsewhere.[17] Although such a model gives a simplistic physical view of the radiolytic process, it can quite accurately reproduce scavenger yields for a number of different systems. The model predictions give an indication of how the methyl viologen and formate system compares to the results obtained using other scavengers. The first of the model calculations was performed on neat water, i.e., no added methyl viologen or formate, and the predicted total yields of scavengable e_{aq}^{-}, H atoms, and OH radicals are shown as open squares in Figure 1. Experimental and simulated values agree at 10 and 100 mM formate, but the former is lower than the latter at higher and lower formate concentrations.

No other single scavenger system has been used to determine the total yield of radicals in the radiolysis of water. The sum of $G(e_{aq}^{-})$ and G(H) yields can be estimated as half the difference in the yields of ferric ions in aerated and deaerated acidic ferrous sulfate solutions.[1] Formic acid solutions have been used extensively to determine the scavenging capacity dependence of OH radicals in γ-radiolysis.[18] In this system, the production of carbon dioxide in aerated solutions is equivalent to OH radical yields. The rate constant for OH radical scavenging by formic acid is about an order of magnitude smaller than that for formate[16] so the scavenging capacities will be similarly shifted at the same concentrations of scavengers. The appropriate summation of the results from the ferrous sulfate and formic acid systems should be equivalent to the total radical yield in the radiolysis of water. The agreement is good as shown in Figure 1.

To gain a better understanding of the methyl viologen and formate system, it was modeled directly by adding eqs 1−4 and the following to those for pure water in the previous model calculations.[8,16,19,20]

$$OH + MV^{2+} \rightarrow MV(OH)^{2+} \qquad k_5 = 2.5 \times 10^8\ M^{-1}\,s^{-1} \tag{5}$$

$$H + MV^{2+} \rightarrow \text{product} \qquad k_6 = 6.0 \times 10^8\ M^{-1}\,s^{-1} \tag{6}$$

$$COO^{\bullet -} + MV^{\bullet +} \rightarrow \text{products} \qquad k_7 = 1 \times 10^9\ M^{-1}\,s^{-1} \tag{7}$$

$$COO^{\bullet -} + COO^{\bullet -} \rightarrow \text{products} \qquad k_8 = 6.5 \times 10^9\ M^{-1}\,s^{-1} \tag{8}$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad k_9 = 2.7 \times 10^7\ M^{-1}\,s^{-1} \tag{9}$$

$$MV^{\bullet +} + H_2O_2 \rightarrow \text{product} \qquad k_{10} = 6.7\ M^{-1}\,s^{-1} \tag{10}$$

It can be seen that the predictions for the yields of $MV^{\bullet +}$ (open circles in Figure 1) are much closer to the experimentally observed values. The model suggests that reactions of H_2O_2 with $MV^{\bullet +}$ and OH are too slow to be of any consequence in γ-radiolysis. At low formate concentrations part of the OH radicals that normally would be scavenged by the formate are found to react with MV^{2+} and thereby lower the yield of $MV^{\bullet +}$. At high formate concentrations the scavenging reactions occur on a very short time scale, and the concentrations of $COO^{\bullet -}$ and $MV^{\bullet +}$ are relatively high. For a short time, the second-order reactions 7 and 8 are significant, and they lower the expected yield of $MV^{\bullet +}$. The concentration of $MV^{\bullet +}$ in the bulk solution is much smaller than that of MV^{2+} under the conditions of these experiments, so reaction 7 would predominately occur between the radicals produced in a single spur.

Contributions from reactions 5−9 lead to a decrease in the observed yields of $MV^{\bullet +}$ and thereby severely limit the usage of this system for probing the scavenger capacity dependence of total radical yield. Only at scavenging capacities of about 10^8−10^9 s^{-1} are the measured $MV^{\bullet +}$ yields expected to realistically represent total radical yields. Nevertheless, total radical yields can give such valuable information about track processes that this system was used to probe heavy ion tracks.

Heavy Particle Radiolysis. The yields of $MV^{\bullet +}$ in the radiolysis of 0.5 mM methyl viologen and 10 mM formate solutions are shown in Figure 2 as a function of the initial ion energy. The particles were completely stopped in the solution so the measured *G*-value is the track-averaged yield. There is an increase in $G(MV^{\bullet +})$ with increasing ion energy for both protons and helium ions. The slope of the curve for protons decreases at high energy, while the increase is almost linear for helium ions in the measured range. The yield with 15 MeV protons is 4.6, which is considerably lower than the value of 6.4 found with γ-rays. Previous studies with the Fricke dosimeter would suggest that at these energies the results with protons and γ-rays should be very similar.[9]

No accurate diffusion kinetic models exist for predicting the expected yields for the heavy ion radiolysis of the methyl viologen and formate system. The sum of the total yield of e_{aq}^- and H atoms obtained from acidic ferrous sulfate solutions[9] and the yields of scavenged OH radicals from formic acid solutions[21] are shown in Figure 2 to be considerably higher than the measured yields of $MV^{\bullet +}$. This procedure worked well for γ-radiolysis, but the reason for the discrepancy with heavy ions is not known. It is possible that use of a stoichiometric determination for the sum of e_{aq}^- and H atoms gives too high values. In aerated ferrous sulfate solutions the H atom is scavenged by oxygen with a scavenging capacity of about 5×10^6 s^{-1} while in deaerated solutions the direct reaction of H atoms with ferrous ions is about 7×10^4 s^{-1}. In addition, the scavenging capacity of methyl viologen for the hydrated electron is about 2.5×10^7 s^{-1}. The yields of radicals are not changing quickly on these time scales in γ-radiolysis, and agreement between the different probes was good. Matching the times at which radicals are scavenged may be important in heavy ion radiolysis depending on their temporal variation. Extensive track chemistry on the same time scale as the scavenging reaction makes it much more difficult to compare the results using two different probe solutes. However, track reactions are expected to be nearly complete with these particles on the time scales examined here, and it is unlikely that the previous results

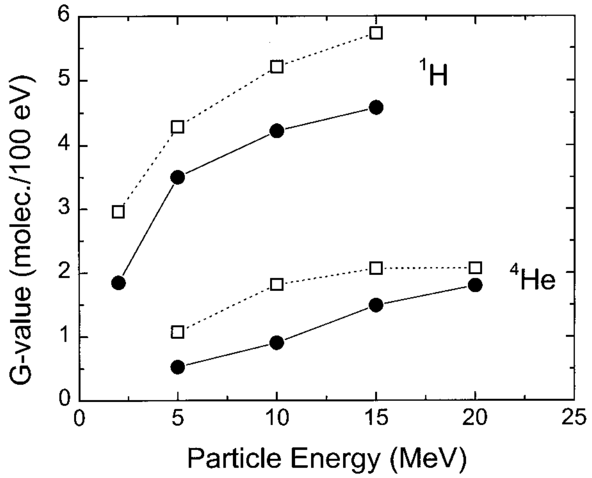

Figure 2. Yield of $MV^{\bullet +}$ in the ^1H and ^4He ion radiolysis of 0.5 mM methyl viologen and 10 mM formate solutions as a function of initial particle energy, (●) this work. The appropriate sums of the ferrous sulfate and formic acid product yields are (□).

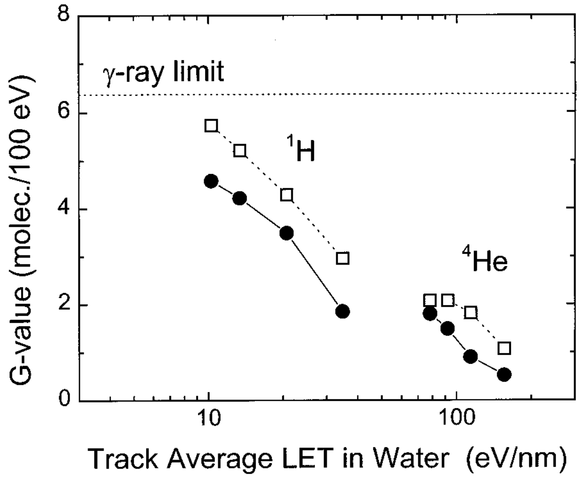

Figure 3. Yield of $MV^{\bullet +}$ in the ^1H and ^4He ion radiolysis of 0.5 mM methyl viologen and 10 mM formate solutions as a function of track average LET, (●) this work. The appropriate sums of the ferrous sulfate and formic acid product yields are (□).

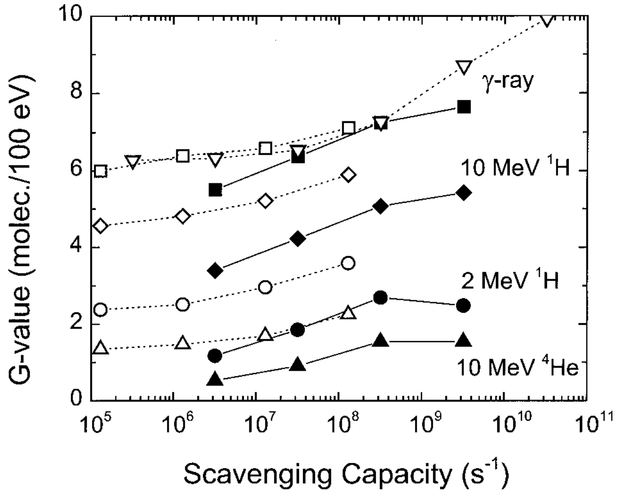

Figure 4. Production of $MV^{\bullet+}$ in the radiolysis of 0.5 mM methyl viologen and formate solutions as a function of formate scavenging capacity for OH radicals: (■) γ-rays, (◆) 10 MeV ^{1}H, (●) 2 MeV ^{1}H, and (▲) 10 MeV ^{4}He. The appropriate sums of the ferrous sulfate and formic acid product yields for heavy ions are given as open symbols. The results of simulations are (▽) for the total scavengable radical yield with γ-rays.

for radical formation are in such large error. It is more probable that one or more transient species are interfering with the mechanism for the production of $MV^{\bullet+}$.

The yields of $MV^{\bullet+}$ are plotted as a function of track-averaged LET in water in Figure 3. As expected, the total yield of scavengable radicals decreases as the LET increases because of the greater amount of intratrack reactions. The total amount of radicals at 100 eV/nm is only about 15% of the low LET γ-ray limit. These results show the greatly enhanced importance of intratrack reactions in heavy particle tracks. There does not seem to be any logical variation in the expected yields and the measured yields of $MV^{\bullet+}$ with protons and helium ions. This result suggests that there may be more than one process responsible for the discrepancy.

The yields of $MV^{\bullet+}$ as a function of scavenging capacity are shown in Figure 4 for protons of 2 and 10 MeV and helium ions of 10 MeV. The yields increase with increasing scavenging capacity and level off at high scavenging capacity. Second-order reactions of $COO^{\bullet-}$ and $MV^{\bullet+}$ are the likely cause for lower $MV^{\bullet+}$ yields at high scavenging capacity. These reactions may also be responsible for the slightly lower than expected yields of $MV^{\bullet+}$ with heavy particles at lower scavenging capacities. Another species that can react with $MV^{\bullet+}$ is H_2O_2. The yield of H_2O_2 is only slightly larger in high LET radiation, but it is produced at early times and its concentration in the track may be substantial. Reactions of H_2O_2 with e_{aq}^- are believed to occur with particles of these LETs,[22] and this reaction may compete with scavenging by methyl viologen in the track. At high LET, HO_2 may also be involved in reducing the $MV^{\bullet+}$ yield, but little is known about this reaction.[20] Further experiments and accurate track calculations will eventually elucidate the chemistry of this system.

Conclusions

Caution must be exercised in the use of any scavenging system to probe for individual radicals or for total radical yields. The reduction of the methyl viologen cation in deaerated formate solutions is seen to have limitations for estimating the total yield of radicals. At very high or low concentrations of formate inaccurate predictions can be obtained in γ-radiolysis because of competing scavenging reactions or secondary bimolecular reactions. It appears that even for heavy particles at relatively low LET the production of $MV^{\bullet+}$ is not equivalent to the total yield of radicals from water decomposition. The $MV^{\bullet+}$ is a strongly absorbing species, and it is mainly produced within the microsecond time scale. These characteristics make this system interesting to examine using pulsed techniques. Time-resolved measurements would give more information about the behavior of $MV^{\bullet+}$ in heavy particle tracks, and such experiments are now in progress.

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