Track Effects in the Radiolysis of Water: $HO_2^{\cdot}$ Production by 200–800-MeV Carbon Ions[1]

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The production of $HO_2^{\cdot}$ in the radiolysis of ferrous sulfate–cupric sulfate solutions, which provides a sensitive measure of intratrack processes in water, has been determined for carbon ions having energies of 200–800 MeV. The differential yield is found to decrease from 0.047 molecules/100 eV at 200 MeV (linear energy transfer (LET) = 110 eV/nm) to 0.028 molecules/100 eV at 800 MeV (LET = 36 eV/nm). Studies in this energy region permit a direct comparison between the intratrack processes of carbon ions and of protons having the same LET. At the highest carbon ion energy the differential yield of $HO_2^{\cdot}$ is still 40% greater than that found with fast electrons (0.020 molecules/100 eV) but only 60% of that for protons of the same LET. In general, it is found that the yields of $HO_2^{\cdot}$ are similar for carbon ions where the LETs are 3-fold greater than those of protons. This difference reflects the expansion of the track resulting from the greater velocity of the more highly charged particles.

Introduction

Previous studies have shown that the production of $HO_2^{\cdot}$ provides a sensitive measure of the importance of intratrack processes in the radiolysis of water by heavy ions.[2-8] It was found that while the $HO_2^{\cdot}$ yields increase with increasing particle linear energy transfer (LET, equivalent to the stopping power = $-dE/dx$), the LETs required to produce a given yield increased as the charge on the particle increased. For comparison with model calculations, one would like to have information on the dependence of the yields at the same LET obtained with particles having different charges (Z). However, because of experimental limitations, it is difficult to make this comparison directly for particles having charges differing by more than a few units. In the present study we have examined the $HO_2^{\cdot}$ yields produced by 200–800-MeV carbon ions which have LETs in the range 110–36 eV/nm. The LETs of protons range from 85 eV/nm at the Bragg maximum (0.1 MeV) to 36 eV/nm at 0.7 MeV so that a direct comparison of the yields with both particles is possible. The differential yields observed show that in going from protons to carbon ions at a given LET the production of $HO_2^{\cdot}$ within the track core decreases by about a factor of 2. This decreased yield is a manifestation that as Z increases the size of the track critical to intratrack processes also increases significantly.

Experimental Section

Irradiations were carried out with the K500 and the K1200 cyclotrons in the National Superconducting Cyclotron Laboratory (NSCL) at Michigan State University. In the initial experiments, the $^{12}C^{4+}$ ions were accelerated with the K500 to a nominal energy of 30 MeV/nucleon. The energy of the ions, obtained from machine parameters, was 356 MeV with an estimated uncertainty of 2%. The later experiments, with the K1200, utilized carbon ions with nominal energies of 40 and 70 MeV/nucleon. These ions were completely stripped before entering the beam transport system. Magnetic analysis of the beam, with the use of calibrated NMR probes, gave particle energies of 472.9 and 826.1 MeV, respectively, with indicated uncertainties of ~0.3%. The window assembly was similar to that described earlier.[6,8] Energy loss to the exit window (Ti, 3.6 mg/cm^2), air (0.8 mg/cm^2), and the sample cell window (mica, 6–8 mg/cm^2) was determined from the TRIM91 stopping power compilation.[9] Appropriate corrections for energy loss in the window system were respectively 0.7, 0.4, and 0.1% at 30, 40, and 70 MeV/nucleon. Particle energies were also attenuated with aluminum absorbers whose thicknesses were determined from the weight of foils of known cross sections. Energy loss in the absorbers was calculated as described below.

The sample cells used in these experiments were similar to those used in previous studies.[4-8] They contained magnetically coupled stirrers, a total sample volume of 30–40 mL, and were sufficiently long to stop the beam within the water. Absolute energy deposition was determined from the energy of the ions after passing the window system and any added absorbers and the integrated beam current taking into account the measured backscattering of electrons from the exit window. This latter correction was 1% at the two higher energies and 8% at the lowest energy. The correction for 30 MeV/nucleon carbons is greater because of the use of incompletely stripped ions. The vacuum in the beam transport system was sufficiently low ($<5 \times 10^{-7}$ Torr) to ensure integrity of the particle charge. Particle currents used were about 1 nA charge, and the total energy deposited was typically (1–2) $\times 10^{19}$ eV (average dose 4–10 krad).

The solutions were 1 mM in ferrous ammonium sulfate and 10 mM in cupric sulfate in 0.01 N sulfuric acid. Water was triply distilled and stored in quartz vessels until use. As suggested by Hart for fast electrons[10,11] and used in our previous heavy ion experiments,[4-8] O_2 production in these solutions is assumed to be a measure of the production of $HO_2^{\cdot}$. Oxygen production was determined by continuously purging the sample cell with helium. The gas stream was then passed through a Hersch electrolytic cell capable of measuring the $\sim 10^{-8}$ mol of O_2 produced in these studies.[12] In the earlier experiments at 30 MeV/nucleon the output of the Hersch cell was measured with an integrating strip chart recorder. The more recent experiments had an added A/D converter connected to a personal computer which permitted direct integration of the O_2 signals. Calibration of the Hersch cell was with an electrolysis cell placed upstream of the radiolysis cell. Probable error in oxygen analysis is estimated to be ~1%.

Results and Discussions

Because the initial energies are accurately known and the window corrections are small, the yields for $HO_2^{\cdot}$ production in the absence of added absorber should be quite accurate. The G_0 yields measured at 356, 473, and 826 MeV are respectively 0.065, 0.058, and 0.046 molecules/100 eV with error limits of ~1% as primarily reflected in the uncertainty in the chemical measurements. However, because our interest here is mainly to intercompare yields for different particles at a given LET and to provide data for comparison with model calculations, it was necessary to determine differential or track segment yields. This objective in turn requires measurement of the yields as a function of incident particle energy (E_0) so that the differential yields (G_i) can be determined from the slope of plots of G_0E_0 as a function of energy, i.e.

$$G_i = d(G_0E_0)/dE_0 \quad (1)$$

Limitations in beam time and the long times (hours) needed to adjust cyclotron and beam transport parameters at the NSCL facility for major changes in particle energy dictated that absorbers be used for attenuation of the incident ion energy. However, large attenuations of the beam energy can induce straggling and

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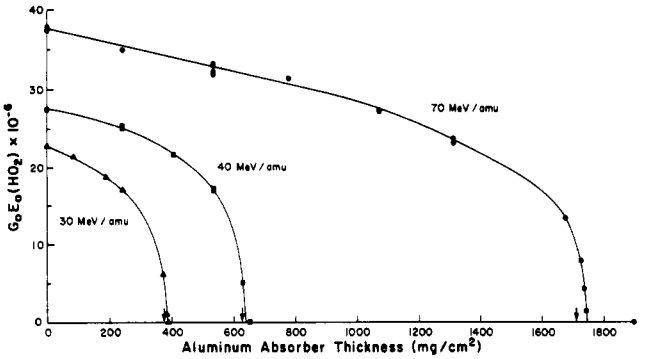

Figure 1. Production of $HO_2^{\bullet}$ ($G_0E_0(HO_2^{\bullet})$ in molecules/100 particles) as a function of aluminum absorber thickness for nominal 30 (▲), 40 (■), and 70 (●) MeV/nucleon carbon ion beams. The arrows show the predicted end points using the stopping power compilation TRIM91 (ref 9).

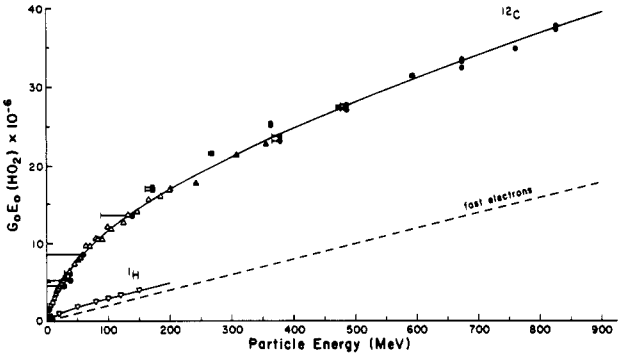

Figure 2. Production of $HO_2^{\bullet}$ ($G_0E_0(HO_2^{\bullet})$ in molecules/100 particles) as a function of incident ion energy (E_0) for ^{12}C, this work at NSCL (same symbols as in Figure 1): (△) ^{12}C, from Argonne ATLAS, refs 5 and 7; (□) ^{12}C, from Notre Dame, ref 6; (▽) ^1H, ref 6. The dashed line shows the limiting value for fast electrons (G_0 = 0.02 molecules/100 eV, refs 10 and 11). The solid lines through the data were obtained by the integration of the appropriate curves in Figure 4. The error bars show the particle energy as determined using the uncorrected stopping power compilation; see text.

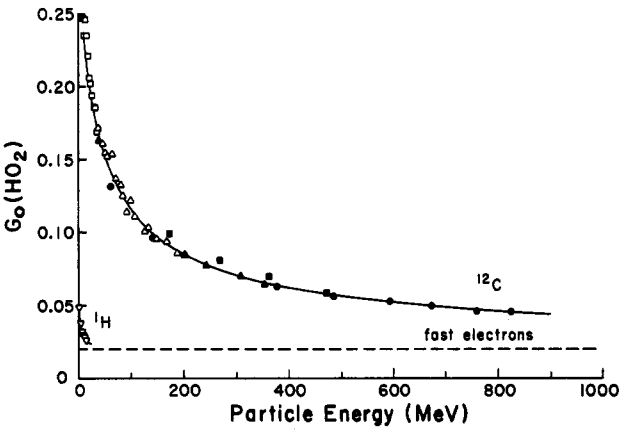

Figure 3. Radiation chemical yields of $HO_2^{\bullet}$ (molecules/100 eV) as a function of particle energy for ^{12}C, this work (same symbols as in Figure 1): (△) ^{12}C, from Argonne ATLAS, refs 5 and 7; (□) ^{12}C, from Notre Dame, ref 6; (▽) ^1H, ref 6. The dashed line shows the limiting value for fast electrons.

fragmentation at high particle energies. In addition, while the newer stopping power compilations are accurate to a few percent, errors accumulate and can have a significant consequence on the determination of E_0 near the end of the particle range. One of the experimental objectives of these studies was to test the use of absorbers to reduce the beam energy.

The use of absorbers is illustrated in Figure 1 where the amount of oxygen produced per 100 incident particles (i.e., in units of G_0E_0) is given as a function of added aluminum absorber. It is seen that, as expected from the increasing stopping power, G_0E_0 decreases very rapidly near the particle range. The ranges in aluminum indicated by these chemical measurements are respectively 383, 638, and 1748 mg/cm² for 356, 473, and 826 MeV carbon ions. These ranges have been corrected for the fact that the stopping power of air and mica are slightly different than for aluminum. (The ordering of the absorbers is critical and must be properly taken into account in determining the energy loss, particularly near the end of the range.) The corresponding ranges given by the TRIM91 tables (377, 628, and 1710 mg/cm²) are indicated by the arrows along the abscissa. The particle energies obtained from these measured ranges and TRIM91 are respectively 0.9, 0.9, and 1.3% higher than the measured energies.[13]

There is a considerable uncertainty in the magnitude of the effects due to particle fragmentation and range straggling in radiation chemistry studies with high-energy particles. Nuclear processes reduce the heavy particle to two or more lighter particles of equal velocities and therefore with lower LETs. The tracks and subsequent chemistry produced by the fragment particles are different than that produced by the incident particle. In addition, they also have a considerably greater range so that the total energy deposited in a thin sample is less than would be obtained with the incident heavy ion. Both range straggling and fragmentation should lead to characteristic tails toward higher absorber thicknesses as the values of G_0E_0 in Figure 1 approach zero. One can clearly see from Figure 1 that the particles used here have well-defined ranges with little or no observable straggling or fragmentation.

Figure 2 gives a plot of G_0E_0 as a function of energy with the three sets of data determined in the present study given by the solid points. Data with initial particle energies of less than 35 MeV previously obtained at the Notre Dame Nuclear Structure Laboratory[6] and for energies up to 200 MeV obtained at the ATLAS Facility at Argonne National Laboratory[7] are given by the open points. These latter data were determined with particles of much lower energy and little or no added absorbers so that they do not have the energy uncertainty associated with absorber attenuation. As a result, they can be used to pinpoint the end point of the data of Figure 1. The energy scale in Figure 2 was obtained by assuming that the initial ion energy is accurately known and that the stopping power for carbon ions above 10 MeV is 2.1% higher than given in TRIM91.[14] The lefthand limits of the error bars in Figure 2 correspond to the energies obtained solely on the basis of the TRIM91 tabulations. It is seen that, based on the latter, the energy appears to be much too low for the experiments where absorbers were used to attenuate the particle energy to less than one-third of its initial value. For attenuations less than 50% the resultant values are well within the other uncertainties.

In considering the data of Figure 2, one should recognize that the experiment determines the amount of product produced per irradiating particle and that the principal uncertainty is in the particle energy. It is seen in Figure 2 that the data obtained with 356-MeV carbon ions from the K500 facility at the NSCL attenuated with absorbers to 200 MeV overlap quite well with those obtained with carbon ions initially at 200 MeV from the Argonne ATLAS facility and similarly that data from the two energies used at the K1200 facility overlap nicely at 450 MeV. Considering that the data were collected over a number of years at four different accelerators under rather different experimental conditions, the consistency among the data is, in fact, remarkable. The data show a monatonically decreasing radiation chemical yield (Figure 3). In the 200–800-MeV region the slope of the data in Figure 2, which represents G_i, is still well above the value for fast electrons, given by the dashed line in Figure 2, or for protons in the 5–10-MeV region.

The solid curve in Figure 2 was constructed by an iterative procedure in which the slopes of the dependence of G_0E_0 on energy determined from a polynominal fit were integrated and subsequently adjusted to optimize agreement with the experimental results. The slopes (G_i) so obtained are plotted in Figure 4 as a function of LET. It should be noted that the curves in Figure 4 are slightly different than those presented in ref 6 because of

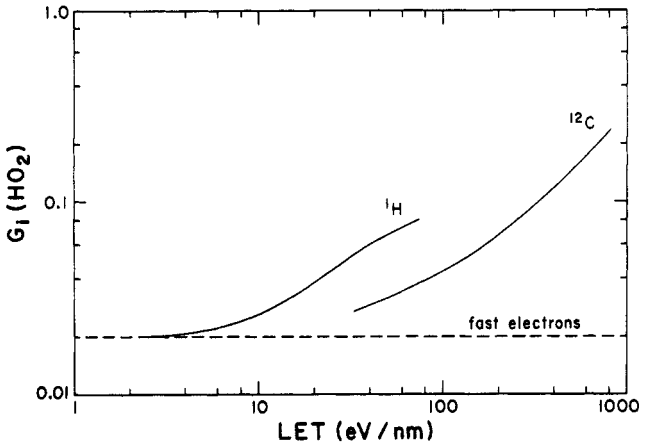

Figure 4. Differential yields of $HO_2^\bullet$ (molecules/100 eV) as a function of particle LET in water for carbon ions and protons. The dashed line shows the limiting value for fast electrons.

the use of different stopping power tables. The LETs at the highest carbon ion energies (85–36 eV/nm, corresponding to 280–800 MeV) overlap those of low-energy protons. It is seen in Figure 4 that, at a given LET, G_i for the carbon ions is appreciably less than for protons and that the LETs required to produce similar yields are about 3-fold greater. These differences are the manifestation of the greater velocity of carbon ions so that the diameter of the track core is considerably greater or, as indicated in ref 6, more energy is used in the production of δ-rays which give a negligible contribution to the formation of HO_2.

Kinetic–diffusion calculations with an initial Gaussian distribution of reactants in 100 eV/nm particle tracks suggest that a doubling of the track radius leads to halving of the $HO_2^\bullet$ yield.[15] For completely stripped particles the LET in a given medium is approximately proportional to the ratio of the squares of the particle charge to the velocity. Actual comparison of the data in the overlapping region of Figure 4 shows that the ratio of velocities is approximately 10 for equivalent LET protons and carbon ions. The calculations further show that the dependence of the $HO_2^\bullet$ yields on the track radius decreases with increasing LET. Obviously, the dependence of $HO_2^\bullet$ yield on particle velocity and charge is complicated.

Burns and co-workers have suggested that $HO_2^\bullet$ is not formed directly from excited or ionized water molecules, but it likely involves a series of reactions with molecular oxygen as the precursor.[3] Recent calculations indicate that the reaction of O atoms with OH within the track is a more likely source of $HO_2^\bullet$.[15] The exact mechanism of its formation is still uncertain and further comments will be made in a later study,[15] but it appears that the yields of $HO_2^\bullet$ reported in the cupric/ferric sulfate systems can contain a significant component of O_2 depending on the particle LET. The calculations indicate that at 100 MeV/nm approximately 20% of the reported yields of $HO_2^\bullet$ could be due to O_2 and that the proportion of O_2 increases with LET. Clearly, further experimental and theoretical studies are necessary as oxygen production in the track of high LET particles can have great chemical and biological consequences.

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References and Notes

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(13) Ranges in aluminum for high-energy carbon ions obtained from data in the various range-energy tables differ appreciably. For example, the range in aluminum for 826-MeV carbon ions by TRIM91 is 1722 mg/cm^2 where as TRIM85 gives a value of 1804 mg/cm^2. The present measurement (1748 mg/cm^2) falls in between. For the lower-energy particles the tabulated data agree much better, both internally and with the present results.
(14) This approach is purely pragmatic since it is not completely clear whether the difference of 38 mg/cm^2 between the value required by the present study and that given by TRIM91 is due to errors in the initial energy or in the stopping power tabulations. If we assume the error to be in the initial energy, the plot of Figure 2 would be very similar.
(15) LaVerne, J. A. Manuscript in preparation.