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ARTICLE *in* RADIATION PHYSICS AND CHEMISTRY · AUGUST 2002

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Hydrogen peroxide yields in water radiolysis by high-energy ion beams at constant LET

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Received 15 July 2001; accepted 12 November 2001

Abstract

The radiolytic yields of hydrogen peroxide in aqueous solution irradiated with ion beams at constant linear energy transfer (LET) values ranging from 2.5 keV/μm (30 MeV protons) to 30 keV/μm (1140 MeV carbon ions) and with ¹³⁷Cs γ-rays, where the mean LET is 0.53 keV/μm, were determined. They are compared with those in the literature. The evolution of hydrogen peroxide yields is studied as a function of radical scavenger concentration. The radical-scavenging curves are discussed in terms of radical spatial distribution around the tracks. This distribution depends on both the type and the energy of radiation. This study also shows that the probing of the spatial structure for the proton track can be achieved by nitrate/methanol systems where the role of the nitrate is to protect hydrogen peroxide from the attack of hydrated electron. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Water radiolysis; LET effects; Hydrogen peroxide; Radiolytic yields

1. Introduction

Radiolysis of water at low linear energy transfer (LET) condition, such as γ-rays has been studied extensively in the last 50 years and the radiolytic yields are well known (Draganic and Draganic, 1971). The molecular products (H₂O₂, H₂) are formed by the combination of radicals (e_{aq}⁻, H[•], OH[•]) in the spurs. With increasing LET, the density of the radicals increases in the ionization tracks and the probability of a combination of these radicals is higher than their diffusion from the spurs in which they are formed (Allen, 1961). Consequently, with high LET radiations, the radical yields decrease whereas the molecular product yields increase due to radical–radical reactions. Only a few high LET experiments have been carried out to determine radiolytic product yields (Schwarz et al., 1959; Burns and Sims, 1981; LaVerne and Schuler, 1983,

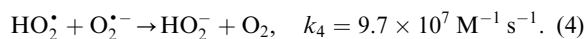
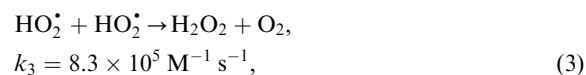
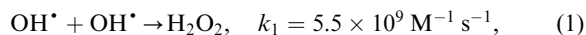
1987a, b; LaVerne, 1989a, b; Elliot et al., 1996). In many of these experiments, the energy of the particles is somewhat low and the particles stop in the sample. In this case, the LET varies along the track and the radiolytic product yield measured corresponds to an average LET and should not be correlated to a single LET value. Moreover, in the calculation codes currently used and based on Monte Carlo simulations, the sample thickness is very low (around 10 μm) in order to avoid a large quantity of created species and the LET is considered as constant (Frongillo et al., 1996, 1998; Cobut et al., 1998). The yields determined from the experiments performed with a constant LET are necessary in order to compare them with the results obtained by Monte Carlo simulations as obtained for irradiation at low LET with high-energy electron beams. This would allow the validation of the model and the parameters used in these simulations. These experiments require high-energy ion beams.

It is now not possible to have temporal information on the formation of hydrogen peroxide. One possibility is to follow the yield of hydrogen peroxide as a function

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of OH^\bullet scavenger concentration. It is well established that hydrogen peroxide is formed by the combination of two OH^\bullet radicals (Reaction 1) in the regions of high radical concentration along the radiation track. With high LET radiation, another source of hydrogen peroxide is the hydroperoxyl radical. Its dismutation (Reactions 3 and 4) leads to the formation of hydrogen peroxide. However, considering the low yield of hydroperoxyl radical (LaVerne and Schuler, 1987a,b; Baldacchino et al., 1998a,b; Wasselin-Trupin et al., 2000), the fraction of hydrogen peroxide formed by this route can be neglected:



The higher the concentration of any efficient radical scavenger S in reaction 2, the lower the primary yield of H_2O_2 . The effect of scavengers on the molecular product yields has been described in the case of γ -radiolysis (Sworski, 1954, 1955; Allen and Holroyd, 1955; Draganic and Draganic, 1969) but only a few studies have been performed with other particles and particularly with high LET (Schwarz et al., 1959; Burns and Sims, 1981; Pastina and LaVerne, 1999). When the LET increases, the spatial distribution of the OH^\bullet radicals in the tracks changes. One can probe the effects of the track structure by examining the influence of the scavenging capacity of the OH^\bullet radical on the primary yield of hydrogen peroxide for various LET values. Such experiments are described in this study with constant LET.

The concentration of the hydrogen peroxide generated has been measured using chemiluminescence after irradiation of aqueous solutions at neutral pH. Two OH^\bullet radical scavengers have been used: nitrite ion and methanol. The high-energy ion beam used and the thickness of the irradiation cell allow us to have a constant LET in the samples which is not the case in most of the high LET studies in the literature (Schwarz et al., 1959; Burns and Sims, 1981; Pastina and LaVerne, 1999). Experiments have been carried out with ^{137}Cs γ -rays, protons and carbon ion beam.

2. Experimental section

2.1. Aqueous solutions

Deaerated solutions of various concentrations of sodium nitrite or methanol were irradiated. A known

concentration of sodium nitrate was added to the solutions in order to protect hydrogen peroxide from the attack of e_{aq}^- . In the case of sodium nitrite solutions, the concentration of sodium nitrate was $5 \times 10^{-4} \text{ M}$ whereas for the methanol solutions, it was 2.5×10^{-3} or $2.5 \times 10^{-2} \text{ M}$. All samples were prepared using ultra-pure water (Millipore Alpha-Q with a conductivity of $18.2 \text{ M}\Omega$ and a very low total organic carbon, TOC $< 10 \text{ ppb}$).

2.2. Hydrogen peroxide assay

Hydrogen peroxide concentrations were measured by chemiluminescence using a luminometer (TD20/20, Turner Design). The chemiluminescence method is used due to its high sensitivity which is thus able to detect very low concentrations of hydrogen peroxide (as low as 10^{-8} M). The chemiluminescence reagent is a mixture of 6-amino-2,3-dihydro-1,4-phtalazinedione (isoluminol, Sigma), microperoxidase (MP 11, Sigma), sodium hydroxide (Aldrich, 99.99%) and methanol (UVASOL, Merck) (Olsson, 1982; Thérond et al., 1993). The chemiluminescence method gives only relative values which are related to determined known concentrations of hydrogen peroxide by a calibration curve. An example of the calibration curve is given in Fig. 1, showing both good linearity and an excellent signal-to-noise ratio in the range of H_2O_2 concentration 3×10^{-7} to $3 \times 10^{-6} \text{ M}$. The concentration of hydrogen peroxide in these solutions has been determined with absorption spectroscopy and the Ghormley method (Hochanadel, 1952). This method consists of the oxidation of the iodide ion by hydrogen peroxide. The absorption of the triiodide complex is then measured at 350 nm with a molar extinction coefficient of $25800 \text{ l mol}^{-1} \text{ cm}^{-1}$.

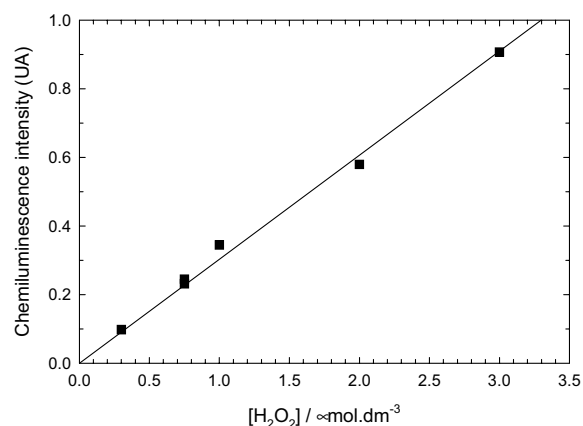


Fig. 1. Chemiluminescence calibration curve: chemiluminescence intensity as a function of the concentration of hydrogen peroxide.

(Hochanadel, 1952). The absorption measurements were performed with a Cary 500 spectrophotometer.

2.3. Irradiations

In the γ -radiolysis experiments, irradiations were carried out with a ^{137}Cs γ -source. A Fricke dosimeter was used to determine the dose rate, taking $G(\text{Fe}^{3+}) = 1.59 \times 10^{-6} \text{ mol J}^{-1}$ (Spinks and Woods, 1990). The dose rate was then 0.019 Gy/s.

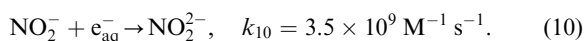
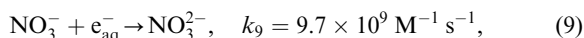
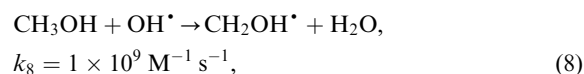
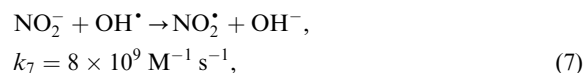
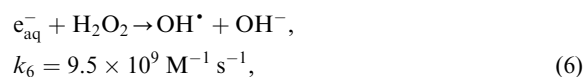
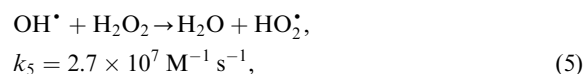
In the case of ion beam experiments, the irradiation cell, made of suprasil quartz, was a 3 mm thick flow cell. The flow rate was around 1 ml/s. The input window was 1 mm thick allowing an almost constant LET in the cell. The calculations of the energy of the particles after passing through all the windows was performed by the TRIM compilation (Ziegler et al., 1985). The dose delivered to the sample is then calculated by the energy loss of the ion in the water and the intensity of the beam. The proton experiments were performed at the “Centre d’Etudes et de Recherches par Irradiation” at Orléans. The beam was produced by a cyclotron. The initial energy of the protons was 30 MeV. The proton beam has an LET of $2.5 \pm 0.36 \text{ keV}/\mu\text{m}$ in water. Its intensity has been measured with a Faraday cup before and after irradiation of the sample. To change the dose values, it was necessary to perform experiments with three values of intensity: 10, 20 and 30 nA and the dose delivered to the samples did not exceed 500 Gy in the range of dose rate 10–100 Gy/s.

Similar experiments have been carried out with carbon ions at the “Grand Accélérateur National d’Ions Lourds” at Caen. The initial energy of the carbon ions was 1140 MeV and the LET in the sample was $30 \pm 1 \text{ keV}/\mu\text{m}$. The section geometry of the ion beam is defined by a horizontal slit in front of the cell. The beam intensity is measured with a secondary electron detector located in the beam. It consists of a thin titanium foil placed between two thin aluminum foils. A potential of 48 V is applied to these aluminum foils and between these polarized foils, a current corresponding to the intensity of the ion beam can be easily measured. This intensity is calibrated before the actual irradiation with a current provided from a Faraday cup. The same device has been used in previous experiments (Baldacchino et al., 1998a, b, 1999; Wasselin-Trupin et al., 2000).

3. Results

Radical scavengers at low concentration are added in the solutions in order to protect the hydrogen peroxide from the attack of the radical (Reactions 3 and 4). Nitrite ions and methanol react with OH^\bullet radical (Reactions 7 and 8; Buxton, 1969; Elliot and McCrack-

en, 1989) whereas nitrate and nitrite ions react with e_{aq}^- (Reactions 9 and 10; Elliot et al., 1990). All rate constants are from the compilation of Buxton et al., (1988) unless otherwise stated specifically in the text. Wherever possible, the recommended values of this compilation have been used. The pH and temperature conditions and the chemical systems used in their determination were helpful in choosing the rate constant corresponding to the closest conditions of this study if an exact match was not possible:



For each concentration of OH^\bullet scavenger, the measured concentration of hydrogen peroxide is plotted as a function of dose. The slope of the linear regression gives the yield of hydrogen peroxide (Fig. 2a). The test

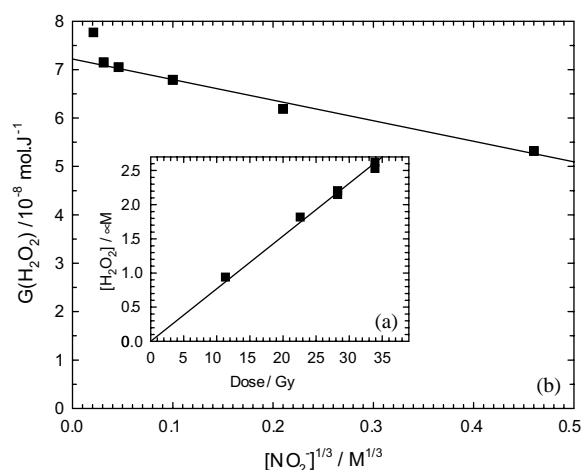


Fig. 2. (a) Hydrogen peroxide concentration formed in aqueous solutions of NO_3^- ($5 \times 10^{-4} \text{ M}$) and NO_2^- (this example: 10^{-5} M) as a function of the dose delivered by γ -rays. (b) Hydrogen peroxide yield formed in aqueous solutions of various NO_2^- concentrations and constant NO_3^- concentration irradiated by γ -rays as a function of the cube root of the concentration of NO_2^- .

of the linear relationship between the concentration and the dose permits us to avoid a dose rate effect in which hydrogen peroxide is destroyed by radiolytic products. For that, low doses have been used to avoid the reactions of the radicals with hydrogen peroxide in the bulk of the solution. Experimental results obtained in the case of ^{137}Cs γ -rays have been collected and an example is presented in Fig. 2a.

The OH^\bullet -scavenging effect of the solute on $G(\text{H}_2\text{O}_2)$ can be described by empirical relationships. Some authors give elaborate expressions to simulate the time-dependence of the kinetics of high LET tracks (for a large LET range between 1 and 10^5 eV/nm) (Pimblott and LaVerne, 1994) or to describe the observed concentration dependence with solute concentration (Warman et al., 1969).

Sworski has shown, in a first approximation, that a linear relationship exists between the yield of hydrogen peroxide and the cube root of the concentration of solute. He used Br^- ion as a scavenger (Sworski, 1954). This relationship implies that the rate of reaction of bromide ion with the OH^\bullet radical in regions of high ionization density is to be related to the average distance separating the bromide ion from the regions of high ionization density.

The relationship obtained is the following (A):

$$(A) \quad G(\text{H}_2\text{O}_2) = G^0(\text{H}_2\text{O}_2) - p \times \sqrt[3]{[S]},$$

where $G^0(\text{H}_2\text{O}_2)$ is the yield of hydrogen peroxide extrapolated for a concentration of OH^\bullet scavenger equal to zero, p is a factor dependent on the type of radiation and of the rate constant k of the reaction between OH^\bullet and the scavenger S . This is the reason why the p factor can be interpreted as an efficiency of the scavenging of the radical by the solute meaning that the efficiency, also called scavenging capacity,¹ is usually calculated by the product between the rate constant and the scavenger concentration: $k[S]$. This efficiency is the reverse of the scavenging reaction time scale, thus the p factor can be related to this time scale as well. The larger this p factor is, the more the OH^\bullet radical is scavenged and cannot recombine to form H_2O_2 . This relationship is only observed for scavenger concentrations lower than 10^{-2} M in the case of Br^- . Schwarz used such a relationship for $\text{NO}_2^{\bullet-}$ solute (OH^\bullet scavenger) to interpolate the experimental determination of $G(\text{H}_2\text{O}_2)$. He showed that the relationship well describes $G(\text{H}_2\text{O}_2)$ for a concentration of $\text{NO}_2^{\bullet-}$ lower than 0.1 M (Sworski, 1954). Since our irradiation conditions are very similar (relatively low LET, low concentration of solute), we have decided to use this relationship to compare our results. Nevertheless, one must be aware

¹ It can be reminded that the scavenging capacity is given by $k_{\text{OH}+\text{S}} \times [S]$ where $k_{\text{OH}+\text{S}}$ is the rate constant of the reaction $\text{OH}^\bullet + \text{S}$ and $[S]$ is the concentration of the OH^\bullet scavenger.

that this relationship is limited and, in particular, cannot explain itself the intra-track processes.

The experimental yield, $G(\text{H}_2\text{O}_2)$, measured in γ -ray experiments, decreases linearly as a function of the cube root of the concentration of OH^\bullet scavenger (nitrite ions) (Fig. 2b).

The experimental results obtained with γ -rays and those described by other authors are shown in Fig. 3. Our values are higher than those related in the literature for the same scavenger capacity. Two reasons can explain this. First, the OH^\bullet scavenger used NO_2^- also reacts with e_{aq}^- , and especially for the point in Fig. 3 corresponding to the highest concentration of nitrite ions where it clearly corresponds to a high scavenging capacity of NO_2^- considering the scavenging of OH^\bullet radicals and to an early time scale too. The concentration of OH^\bullet is high at this early time in the spurs and the reaction giving H_2O_2 is very efficient. At the same moment, the hydrated electrons can destroy H_2O_2 by reacting with it. If the hydrated electrons are efficiently scavenged by NO_2^- , this reaction does not occur and H_2O_2 survives thus increasing the measured yield. NO_2^- has a protector role in the formation of H_2O_2 , thus for the same OH^\bullet -scavenging capacity, in our case e_{aq}^- reacts with NO_2^- and cannot react with OH^\bullet or H_2O_2 in the spurs. Consequently, the yield of H_2O_2 is higher than that for a lower e_{aq}^- scavenger concentration in the case of the highest concentration of NO_2^- . The second reason is that ^{137}Cs γ -rays were used whereas in most of the results reported in the literature, ^{60}Co γ -rays were used and these have higher γ -energy and lower LET than Cs. The difference in LET between them is about a factor of

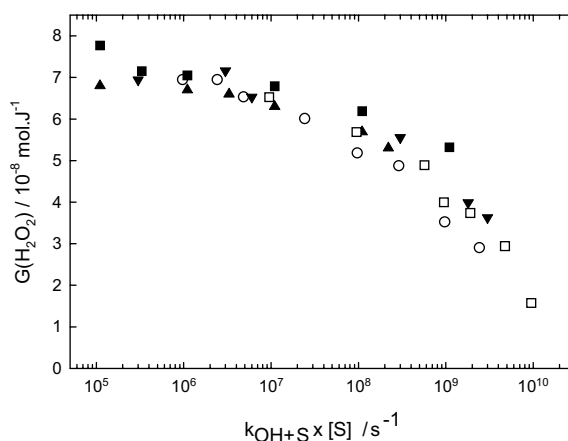


Fig. 3. Hydrogen peroxide yield as a function of scavenging capacity of OH^\bullet radical for different solutes in the case of γ -rays irradiation (^{60}Co): (■) $\text{NaNO}_2 + \text{NaNO}_3$ (^{137}Cs γ -rays) (this work); (▲) KBr (Allen and Holroyd, 1955); (○) $\text{C}_2\text{H}_5\text{OH} + \text{NaNO}_3$ (Draganic and Draganic, 1969); (□) $\text{C}_2\text{H}_5\text{OH} + \text{C}_3\text{H}_6\text{O}$ (Draganic and Draganic, 1969); (▼) acrylamide (Armstrong et al., 1959).

two (Spinks and Woods, 1990) and the molecular yields increase with the LET due to the recombination of radicals. This effect cannot be exclusively explained by the small change of LET. The difference of energy between γ -rays from ^{137}Cs (600 keV) and γ -rays from ^{60}Co (1.2 MeV) must also be taken into account. So in this study, the Compton electrons ejected from water have lower energies and, therefore, a smaller range than the Compton electrons produced from Co γ -rays. In the case of Cs γ -rays, the size of the spurs is smaller and the recombinations leading to higher molecular yields become more efficient. These two characteristics, in the LET and in the energy of the γ -rays, have the same effect, although it also seems that the accuracy of the yield determination is not good enough to discuss these great differences in H_2O_2 yields.

Similar experiments have been performed with protons and carbon ion beams (Fig. 4). Comparable results have been obtained: decreasing of the hydrogen peroxide yield with increasing concentrations of OH^\bullet scavenger and a relationship between the hydrogen peroxide yield and the cube root of OH^\bullet scavenger concentration. The nitrite–nitrate chemical system has been used for these two beams. In the case of the proton beam, another system methanol–nitrate has been used

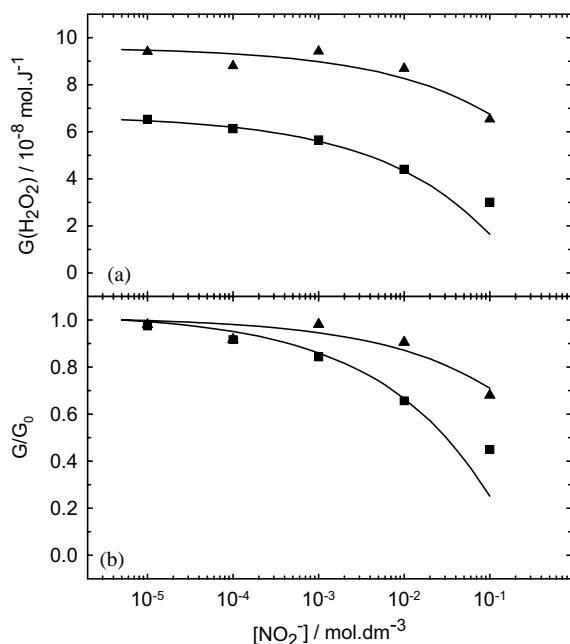


Fig. 4. (a) Hydrogen peroxide yield formed in aqueous solutions of NO_3^- ($5 \times 10^{-4} \text{ M}$) and various NO_2^- concentrations as a function of NO_2^- concentration: (■) protons beam; (▲) carbon ions beam; (—) calculated curve with the equation A: $G(\text{H}_2\text{O}_2) = G^0(\text{H}_2\text{O}_2) - p \times \sqrt[3]{[\text{S}]}$ (coefficients are given in Table 1). (b) Evolution of the ratio $G(\text{H}_2\text{O}_2)/G_0(\text{H}_2\text{O}_2)$ deduced from the curves in (a).

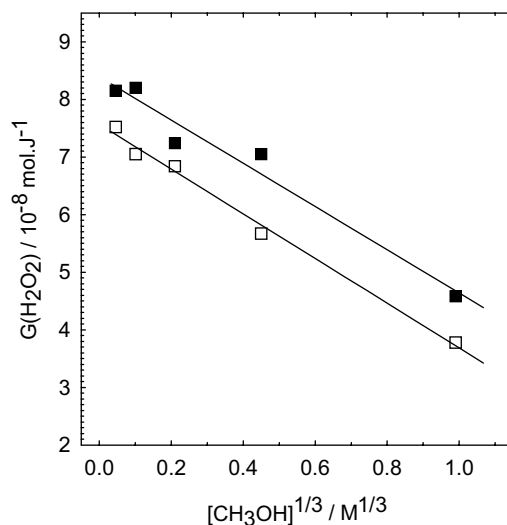


Fig. 5. Hydrogen peroxide yield formed in aqueous solutions of various methanol concentrations and constant NO_3^- concentration irradiated by proton beam as a function of the cube root of the concentration of methanol: (■) $[\text{NO}_3^-] = 2.5 \times 10^{-2} \text{ M}$; (□) $[\text{NO}_3^-] = 2.5 \times 10^{-3} \text{ M}$.

where methanol is an efficient OH^\bullet scavenger. Two nitrate concentrations were studied: 2.5×10^{-3} and $2.5 \times 10^{-2} \text{ M}$. Nitrate ions react only with e_{aq}^- . Fig. 5 shows that the yield of hydrogen peroxide decreases proportionally with the cube root of methanol. The results obtained by fitting equation A to the different experiments are summarized in Table 1. It is noted in the case of the nitrite/nitrate chemical system that the hydrogen peroxide yield increases with LET from the value 2.5 (proton beam) to $30 \text{ keV}/\mu\text{m}$ (carbon ion beam). The factor p decreases when the LET increases between 2.5 and $30 \text{ keV}/\mu\text{m}$. This means that for the same concentration of scavenger, the yield of H_2O_2 created in proton tracks is smaller than in carbon ion tracks. This effect is probably due to the track structure which is different for two types of particles. Concerning the methanol system, $G^0(\text{H}_2\text{O}_2)$ increases with the nitrate concentration (Table 1), although the factor p remains roughly the same for the two concentrations of nitrate.

4. Discussion

4.1. Hydrogen peroxide yield

The experimental values are presented as a function of LET in Fig. 6, which also includes those values obtained in the literature with ^{60}Co γ -rays (Schwarz et al., 1959; Burns and Sims, 1981); 26 MeV deuterons (Elliot et al.,

Table 1

Characteristics of the particles used in this work. Coefficients obtained for the equation $A:G(\text{H}_2\text{O}_2) = G^0(\text{H}_2\text{O}_2) - p \times \sqrt[3]{[S]}$ for the different experiments (ion beams and chemical system)

Particles	TEL keV/ μm	Chemical system	$G^0_{[\text{H}_2\text{O}_2]}$ (mol J ⁻¹)	p
¹³⁷ Cs γ -rays	0.53	$[\text{NO}_2^-]/[\text{NO}_3^-]$	7.2×10^{-8}	4.2×10^{-8}
Protons (30 MeV)	2.5	$[\text{NO}_2^-]/[\text{NO}_3^-]$	6.7×10^{-8}	1.1×10^{-7}
Carbon ions (1140 MeV)	30	$[\text{NO}_2^-]/[\text{NO}_3^-]$	9.6×10^{-8}	6.2×10^{-8}
Protons (30 MeV)	2.5	$\text{CH}_3\text{OH}/[\text{NO}_3^-] = 2.5 \times 10^{-3} \text{ M}$	7.6×10^{-8}	3.9×10^{-8}
Protons (30 MeV)	2.5	$\text{CH}_3\text{OH}/[\text{NO}_3^-] = 2.5 \times 10^{-2} \text{ M}$	8.4×10^{-8}	3.8×10^{-8}

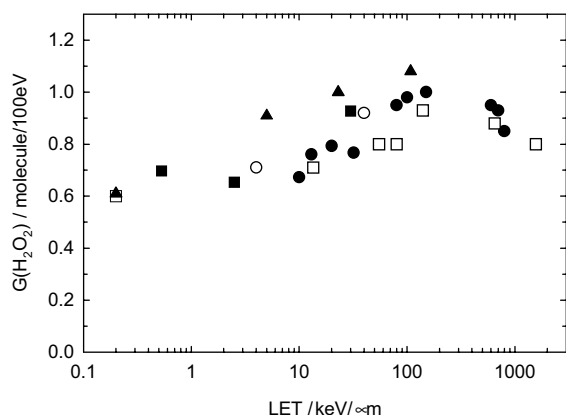


Fig. 6. Hydrogen peroxide yield as a function of LET: (■) ¹³⁷Cs γ -rays, 30 MeV protons, 1140 MeV carbon ions (this work); (□) ⁶⁰Co γ -rays; 10 MeV protons; 35, 18.5, 6.4 MeV helium ions; 46 MeV nitrogen ions; 30 MeV neon ions (Burns and Sims, 1981); (▲) ⁶⁰Co γ -rays; 18 MeV deuterons; 32, 18 MeV helium ions (Schwarz et al., 1959); (●) 15, 10, 5, 2 MeV proton; 15, 10, 5 MeV helium ions; 30, 20, 10 MeV carbon ions (Pastina and LaVerne, 1999); (○) rapid neutron; 26 MeV deuterons (Elliot et al., 1996).

1996); 18 MeV deuterons (Schwarz et al., 1959); 15, 10, 5, 2 MeV proton (Pastina and LaVerne, 1999); 32, 18 MeV helium ions (Schwarz et al., 1959), fast neutrons (Elliot et al., 1996), 35, 18.5, 6.4 MeV helium ions (Burns and Sims, 1981), 15, 10, 5 MeV helium ions (Pastina and LaVerne, 1999); 30, 20, 10 MeV carbon ions (Pastina and LaVerne, 1999); 46 MeV nitrogen ions (Burns and Sims, 1981); and 30 MeV neon ions (Burns and Sims, 1981). These yields have been determined at low scavenger concentrations and are comparable to the concentrations used in this work. A large dispersion of the values is observed. The values obtained for the same LET but different types of radiation vary widely.

In the case of γ -photons from ⁶⁰Co (0.2 keV/ μm), it is difficult to explain clearly the differences obtained in the hydrogen peroxide yields. Actually, different chemical systems have been used by many authors and the measurement of the yield performed using different methods. In some cases, hydrogen peroxide yield was

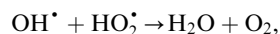
not measured directly but calculated from the mass balance (Haïssinsky, 1967). Normally, if extrapolation to zero scavenger concentration is performed, it allows a comparison between the chemical systems used. So as stated in the results section and the discussion about Fig. 3, a possible explanation concerns the LET values and the energies of the γ -rays used. In fact, when the LET rises from 0.2 to 0.52 keV/ μm between ⁶⁰Co γ -rays and ¹³⁷Cs γ -rays, a small difference appears in the yields. This difference cannot be only attributed to the discrepancy of the measurements and can to a certain extent be explained by the increase of molecular product yield when the LET increases. The same effect has already been observed in the Fricke dosimeter yield between ⁶⁰Co and ¹³⁷Cs γ -rays (Spinks and Woods, 1990). Moreover, the effect of the energies of the two types of γ -rays goes in the same way as stated before.

Fig. 6 is a literature overview of experimental data including the results of this work. Similar figures have been published elsewhere (Pastina and LaVerne, 1999). Fig. 6 shows both an increase and a decrease of the molecular products when the LET increases. In our study, a rise of the hydrogen peroxide yield is observed when the LET increases from 2.5 (proton beam) to 30 keV/ μm (carbon ion beam). When the LET rises, the structure of the irradiation track changes and the increase of the hydrogen peroxide yield can be explained by the “tracks theory” (Magee and Chatterjee, 1987). The structure of the tracks formed in the irradiation with these two ion beams is different. Magee has shown that the spurs overlap in the case of carbon ions of 1140 MeV and not for protons of 30 MeV (Magee and Chatterjee, 1987). This implies a higher probability of the combination of radicals OH^\bullet to form hydrogen peroxide in the carbon ions experiment, although it seems that for very high LET region (for carbon, nitrogen and neon ions), a decrease in the yield of H_2O_2 begins. This decrease could be explained by the reactions in the tracks of H_2O_2 with OH^\bullet radicals and hydrated electrons. Thus, a smaller concentration of H_2O_2 can escape from the tracks because of these reactions. This discussion is developed later in the text.

However, it is rather difficult to compare our results with some of those in the literature (Fig. 6) because in

our experiments, the LET is constant in the thickness of the cell. In the literature, the LET varies along the tracks and the measured yield is then a mean of the yields produced along these tracks for a continuously variable LET. It can be noted in Fig. 6 that 2 MeV protons have a mean LET close to the constant LET of the 1140 MeV carbon ions used in this work. Nevertheless, the hydrogen peroxide yield is different for those two particles. This difference could be explained by physical parameters of the tracks. An ionization track for high LET particles is depicted like a cylinder divided into two parts: the core of the track with the primary ionizations and the penumbra with the ionizations due to ejected secondary electrons. In the case of carbon ions, the maximum energy of the secondary electrons is higher than those of 2 MeV protons (Magee and Chatterjee, 1987). The range of the electrons varies with their energy. The range of the higher energy electrons is greater than those of lower energy electrons. Then in the case of the carbon ion tracks, a large part of the energy is taken away from the core of the track. Considering that the particles have the same LET, they deposit the same energy along the track but the irradiated volumes are different. The volume in the case of carbon ions is about 30,000 times higher than that with 2 MeV protons. With the 2 MeV proton beam, the ionization events produced from the secondary electrons are closely spaced from one another by comparison with those produced using the carbon ion beam. So in the case of 2 MeV protons, the concentration of radicals is locally high and, therefore, increases the probability of the combining of radicals to form molecular products.

It is theoretically expected that the yield of H_2O_2 obtained with carbon ions is lower than that obtained with protons, which is definitely not observed. Two explanations have previously been given. In high ionization density zones, like with 2 MeV protons, high concentrations of radicals OH^\bullet , e_{aq}^- and HO_2^\bullet are formed locally. Burns suggested that the concentration of hydrogen peroxide is enormous at high LET and may react (Reactions 5 and 6; Greenstock and Wiebe, 1981) with other primary species in the ionization track before diffusing into the bulk medium, so its radiolytic yield is reduced (Burns and Sims, 1981). At high LET, hydrogen peroxide reacts like a radical scavenger in the ionization track. This phenomenon could also explain the decrease observed at LET greater than 110 keV/ μm in Fig. 6. A second possible explanation is that the hydroperoxyl radical is generated with a high yield at high LET and could also deplete OH^\bullet radicals in the track before it recombines to form hydrogen peroxide (Reaction 11; Elliot and Buxton, 1992) (Pastina and LaVerne, 1999)



$$k_{11} = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}. \quad (11)$$

In these arguments, Reactions 5 and 11 compete with Reaction 1 for the formation of hydrogen peroxide. Some articles mention a decrease in hydrogen peroxide after an average LET of 100 keV/ μm (Burns and Sims, 1981; Pastina and LaVerne, 1999) due to intra-track reactions occurring at high LET.

Considering the dispersion of the hydrogen peroxide yield for the same LET value, it can be discussed that the LET parameter alone is not sufficient to characterize spatial distribution of the radicals in the tracks in agreement with other authors (LaVerne and Schuler, 1992). It seems that it is necessary to consider the nature and the energy of the particles to characterize the energy deposition in the solution.

It can be noted from Table 1 that the hydrogen peroxide yield measured with the methanol/nitrate chemical system increases with increasing concentration of the nitrate ion. In this system, methanol is chosen to react specifically with OH^\bullet radicals whereas nitrite reacts with OH^\bullet and hydrated electrons. The discrimination between the OH^\bullet effect and the hydrated electrons on yield of hydrogen peroxide can clearly be performed here. The role of the nitrate ions is to react with the hydrated electrons (Reaction 7) and to prevent them from reacting with the hydroxyl radical. Thus, the fraction of hydroxyl radicals that recombine to form hydrogen peroxide can increase (Reaction 1). Moreover, when the hydrated electron is scavenged earlier, it can no longer attack the hydrogen peroxide. Finally, an increase of the hydrated electron scavenger leads to an increase in the yield of hydrogen peroxide, which is clearly shown by the G^0 values in Table 1 for the two methanol/nitrate systems.

4.2. Influence of scavenger concentrations on measured hydrogen peroxide yields

The scavenging curves show the evolution of the yield of hydrogen peroxide as a time-dependent function of the radical scavenger concentration (Fig. 4a). To compare the different results obtained with different particles beams, the parameter G/G_0 has been used (Fig. 4b), which is the ratio between the yield of hydrogen peroxide G corresponding to a OH^\bullet scavenger concentration and the yield of hydrogen peroxide extrapolated to a scavenger concentration equal to zero, G_0 . This ratio is plotted as a function of the concentration of nitrite ion for the two beams: 30 MeV protons and 1140 MeV carbon ions (Fig. 4b).

The evolution of the ratio G/G_0 depends on the particles beam used. Actually, the ratio G/G_0 diminishes rapidly when radicals are scavenged earlier and cannot react together to form hydrogen peroxide. The factor p also follows this evolution. Nevertheless, this factor is lower for a carbon ion irradiation than for a proton irradiation (Table 1). This is a consequence of a better

OH[•] radical scavenging in the case of protons than in the case of carbon ions.

For the same scavenger concentration, the ratio G/G_0 is higher for carbon ions than for protons. In the case of the carbon ion beam with a constant LET value of 30 keV/μm, the ionization density in the core is higher than that of a proton beam, with a constant LET value of 2.5 keV/μm, and leads to a dense spatial distribution of the radicals around the track. With this proton beam, the limit of the spur overlapping is not reached whereas under carbon ion irradiation, the spurs coalesce to form a cylindrical track. In this last configuration, the probability of radical–radical combination increases with the local radical concentration and cannot react with their specific scavenger. In the proton ionization track, the radical spatial distribution is large and the scavenging of hydroxyl radicals becomes easier before they could react together to form hydrogen peroxide. This could be the reason why the ratio G/G_0 rapidly decreases. These radical-scavenging curves should characterize a radical spatial distribution and are representative of the effect of a particle with a given energy.

In the methanol/nitrate chemical system used in the proton experiments, the factor p obtained for the two nitrate concentrations is equal. When the concentration of nitrate ions is increased, the hydrated electrons are scavenged earlier. Actually, it can be seen from Fig. 4 that an increase of nitrate concentration increases the yield of hydrogen peroxide and does not affect the efficiency p factor (or the time scale) of the OH-scavenging reaction by methanol. It means that the hydrated electrons do not influence the reaction of OH with methanol because the scavenging reaction is performed in the same way and then the role of the nitrate ions is only a protection role from the attack of hydrated electrons on the hydrogen peroxides. In terms of radical spatial distribution for proton beam irradiation, it could mean that the fraction of OH radicals and hydrated electrons are not localized in the same region around the track in the time scale considered by these nitrate-scavenging reactions i.e., from 4 to 40 ns.

5. Conclusion

The primary yields of hydrogen peroxide at constant LET values, 2.5 and 30 keV/μm, increase with LET as expected. Nevertheless, the comparison of our results with those in the literature has shown that the LET parameter is not sufficient to correctly characterize the energy deposition structure in the matter because the yields of hydrogen peroxide obtained for the same LET value but with different types of radiation are very different. The hydroxyl radical-scavenging curve obtained for a particle beam of different LET is in good agreement with the physical parameters of the tracks

depending on the energy of the ionizing particles. Based on the scavenger curves and the diffusion theory, it is possible to describe the radical distribution around the track. Consequently, one can probe the radical topology in the track by determining these radical-scavenging curves. It has been shown that the hydrated electron has no influence on the evolution of the OH[•] radical-scavenging curve meaning that hydrated electrons are not localized in the same place in the structure of the track. Moreover, the existence of hydrogen peroxide in the tracks is dependent on the attack of hydrated electrons since a protection with the nitrate ion can increase the yield of hydrogen peroxide.

Acknowledgements

The authors thank the personnel of CIRIL (Centre Interdisciplinaire de Recherche Ions Lasers) and GANIL (Grand Accélérateur National d'Ions Lourds) in Caen and CERI (Centre d'Etudes et de Recherche par Irradiation) in Orléans for technical assistance. They also thank Dr. A. Averbeck for making the facilities at the Institut Curie in Paris.

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