Chemistry in Porous Materials

Radiolysis of Confined Water: Production and Reactivity of Hydroxyl Radicals**

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As technology progresses to the nanoscale, the question of how chemical reactions are perturbed by the size of the environment needs further consideration. Such supramolecular steric effects provide new strategies to orientate reactivity towards desired functionality.[1,2] Confinement and interfacial phenomena are expected to have dramatic effects on reaction rates and mechanisms.[3] However, studies on these effects are still very limited, as most kinetic methods are difficult in a nanometer-confined environment.[2,4] Radiolysis of liquids is an efficient tool which can be used to investigate chemical reactivity in complex environments. As ionizing radiation induces reactions throughout the entire sample, whatever its complexity, information on the chemical reactivity at the microscopic scale can be obtained from macroscopic analytical strategies. Such studies of radiation-induced chemical processes in nanostructured materials have mostly been concerned with the effects on the solid material itself[5] or the reactivity of molecules adsorbed at the solid surface.[6] The present study aims to establish how radiation affects the reactivity of radiolytically produced radicals within nanometric water-filled pores in comparison to that in homogeneous solutions.

Radiation chemists have thus typically sought a target that can trap radicals in order to generate a change in some easily measurable property, as in chemical dosimeters.[7] Such traps are useful since they can probe cavities of any size and shape. High sensitivity can be achieved by choosing a system in which radiolysis results in the formation of a fluorescent compound and thus can be detected by spectrofluorimetry.[8,9] One of these profluorescent compounds is coumarin, which has the advantage of only measuring the formation of the $HO^{\bullet}$ radical whilst disregarding other primary radiolysis species. In aqueous solution, nonfluorescent coumarin is converted on irradiation into fluorescent 7-hydroxycoumarin (7-OHC).[10–14] The fluorescence intensity is proportional to the number of 7-OHC molecules formed, and this in turn is proportional to the locally available $HO^{\bullet}$ concentration down to 10^{-8} mol dm^{-3}. Such a selectivity and sensitivity with respect to $HO^{\bullet}$ can not be achieved by measuring the bleaching of a dye under irradiation.

We have determined the concentration of 7-OHC produced in a variety of controlled pore glasses (CPGs) with pore sizes ranging from 8 to 300 nm[15,16] to ascertain the influence of pore size on radiolytic radical production and reaction in a confined space. Figure 1 shows the fluorescence of 7-OHC

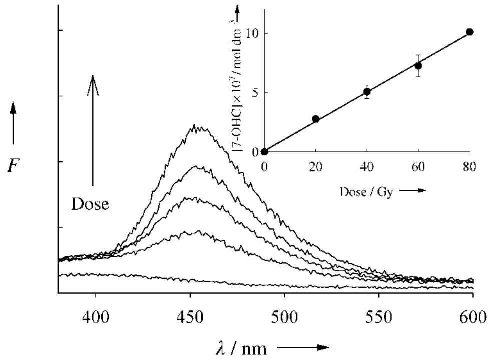

Figure 1. Fluorescence spectra of 7-OHC extracted from irradiated CPG of 200 nm pore size (excitation wavelength 332 nm, excitation and emission slits 0.5 mm, gamma irradiation with ^{137}Cs, 2 Gy min^{-1}). The inset shows the concentration of 7-OHC produced as a function of dose.

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[**] The authors thank the Direction de L'Energie Nucléaire (CEA/Saclay) for financial support and Hervé Coffigny of the Direction des Sciences du Vivant (CEA/Fontenay aux Roses) for use of the gamma irradiator.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/anie.200460284

produced when 1 mM coumarin was irradiated in a CPG with a pore size of 200 nm. To ensure that all the 7-OHC produced in the CPG was extracted, control experiments were performed in which aqueous solutions of coumarin containing varying concentrations of 7-OHC were mixed with the CPGs. The amount of 7-OHC that could be extracted from these glasses was measured by using a fluorescence calibration curve down to 2×10^{-8} mol dm^{-3}; 95 ± 5% of the 7-OHC introduced could be recovered, irrespective of the CPG used. The concentration of 7-OHC produced in the pore was determined from the extraction coefficient of 95% and the fluorescence calibration curve. The results for a CPG with a pore size of 200 nm are shown in the inset of Figure 1. The concentration of 7-OHC produced remains proportional to the dose, as in aerated homogeneous solutions. Similar results were obtained for all the CPGs. The concentration of 7-OHC produced was also measured for CPGs with pore sizes of 8, 50, and 300 nm filled with solutions flushed by N_2O. Under these conditions, the reducing hydrated electrons e^-_{aq} are converted into HO$^\bullet$ radicals. Thus, in homogeneous solution, N_2O induces a 40% increase in the production of 7-OHC.[11] After exposure of the porous material to N_2O, the concentration of 7-OHC is increased by a factor of 1.5 relative to that obtained under Ar, a value which is in good agreement with that obtained by Makrigiorgos et al.,[11] and which shows that HO$^\bullet$ radicals are responsible for the formation of 7-OHC. The similarities between the behavior of coumarin in homogeneous solutions and in porous glasses and the possibility to efficiently quantify the 7-OHC produced allowed us to apply the capture of HO$^\bullet$ radicals by coumarin to the case of confined water.

Figure 2 shows how the concentration of 7-OHC in CPGs varies as a function of the pore size of the glass. The amount of solution added was equal to the available pore volume. The concentration of 7-OHC produced per Gy absorbed by water (the radiolytic yield) increases with increasing pore size of the CPGs. When the pore diameter decreases from 100 to 8 nm, the radiolytic yield of 7-OHC is divided by three, and thus we can assume that the radiolytic yield of HO$^\bullet$ radicals decreases by the same amount. Above a pore diameter of 150 nm, the behavior of confined coumarin solutions is similar to that of homogenous solutions.[10,17]

Such results can be attributed either to a cagelike effect which favors radical recombination in the pores[2] or to an enhanced surface reaction of HO$^\bullet$ at the water/silica interface.[18] To identify a possible role of this interface, CPGs with pore sizes of 8, 50, and 300 nm were filled with various amounts of 1 mM coumarin solution and irradiated as described above. In hydrophilic porous materials such as CPGs and Vycor glasses, when the amount of solution decreases, first the center of the pore empties leaving a layer of water on the silica surface, after which the thickness of this layer gradually diminishes.[19] The concentration of 7-OHC produced per Gy absorbed by water was determined as described above. The radiolytic yield of 7-OHC was found to increase when the amount of solution in the pores was decreased but the coumarin concentration was kept constant, that is, the thickness of the water layer on the silica decreased and the relative amount of silica surface available for a possible capture reaction of the HO$^\bullet$ radical on the surface increased (Figure 3a). The increase in the 7-OHC radiolytic yield shows that the capture of HO$^\bullet$ radicals at the surface is not efficient. At constant coumarin concentration, the only explanation for this increase is thus enhancement of radiolytic production of HO$^\bullet$ radicals.

Figure 3b shows the 7-OHC production per gram of glass and per Gray when the degree of pore saturation is increased. This value increases linearly with respect to the amount of water confined in the pores, but has a positive intercept. The linear increase with respect to the filling of the pore is due to

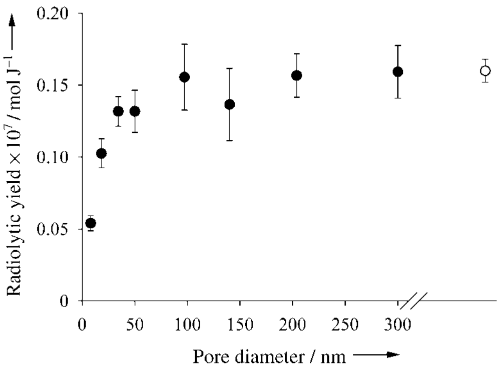

Figure 2. Effect of pore size on the yield of 7-OHC in CPGs. The empty circle refers to the yield in solution taken from Louit et al.[10]

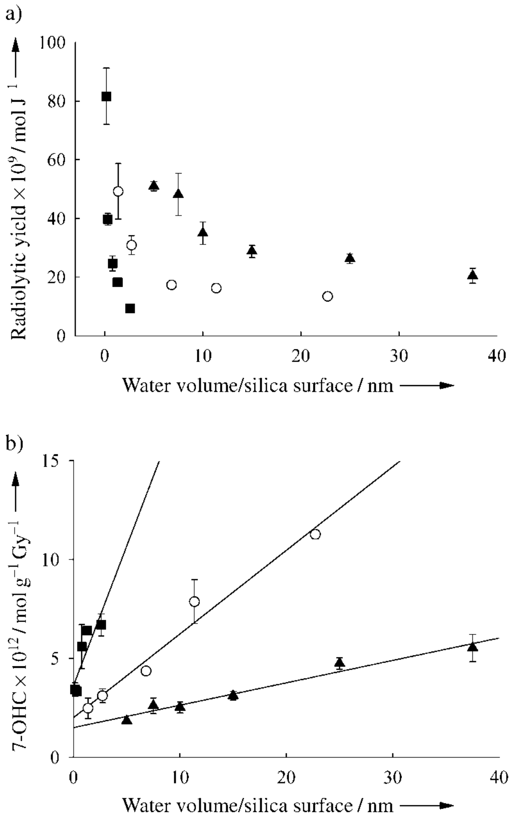

Figure 3. a) Yield of 7-OHC as a function of the ratio of introduced coumarin solution volume with respect to the wetted silica surface area for CPGs with pore sizes of 8 (■), 50 (○), and 300 nm (▲). b) Total amount of 7-OHC produced per gram of CPG and per Gray directly received by the glasses as a function of this ratio.

the direct radiation–water interaction, that is, to the direct production of hydroxyl radicals in water. On the other hand, the intercept is linked to an overproduction of oxidative species at the water/silica interface. Such an overproduction can be associated with energy transfer from the oxide to the adsorbed water.[20] As expected, this energy transfer is more efficient for materials with a large specific surface area, that is, for smaller pores. Therefore, the contribution of water to the production of HO$^\bullet$ radicals can be separated from the surface contribution. A more accurate determination of the effects of confinement on 7-OHC production inside the pores can be obtained by subtracting the surface contribution. When this is done for the data in Figures 2 and 3b, the amount of HO$^\bullet$ available for reaction with coumarin is decreases by a factor of almost 6 for 8 nm pores and by a factor of 1.5 for 50 nm pores with respect to the amount for 300 nm pores.

To explain this effect, we must take into account that the quantity of 7-OHC produced is the result of competition between recombination of radiolytic radicals and their capture by coumarin. In the 8 nm pores the hydroxyl radicals cannot migrate as far apart as in bulk water, and thus they recombine faster with radicals produced in the same radiolytic track than they can react with a solute such as coumarin.[21] This recombination is reminiscent of the recombinations of both the primary and secondary geminate radical pairs resulting from photolysis of ketones in the "void space" of MFI zeolites, although the diameters of the cylindrical channels and their spherical intersections are smaller (5.5 and 9 Å, respectively).[2] This acceleration of the reaction induced by confinement has been theoretically described by Tachiya in micelles.[22] From this model, such cage effects are not expected to be effective for pore sizes as large as 50 nm. A complementary explanation for the observed results can be provided by the model of Barzykin and Tachiya which was developed for gels.[23] In porous media, reactions on long timescales are expected to be slowed down by local depletion and impaired diffusion, especially for low concentrations of reactants. We assume that this slowing down of the capture of HO$^\bullet$ radicals by coumarin can explain part of the decrease in radiolytic yield of 7-OHC in porous glasses.

These results show that the effects of confinement, clearly identified at the nanopore scale, are important even at the mesopore scale, and this suggests the need to completely reevaluate our knowledge of reactivity in this type of environment. Experiments are underway to better understand the effects of confinement on the rates of radical reactions.

Received: April 9, 2004
Revised: September 6, 2004

Keywords: confinement effects · fluorescence spectroscopy · mesoporous materials · radical reactions · radiolysis

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[21] A simple way to understand the confinement effect of 8 nm pores is to evaluate whether HO$^\bullet$ reacts with coumarin before reaching the pore wall. Taking $D = 2.3\times10^{-9}\,\mathrm{m^2\,s^{-1}}$ for the diffusion constant of HO$^\bullet$ (G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513) one can estimate the average time needed for a hydroxyl radical to reach the pore wall as 5 ns. If the reaction constant between hydroxyl radical and coumarin is taken as $k = 8.2\times10^{9}\,\mathrm{mol^{-1}\,dm^3\,s^{-1}}$ (K. Gopakumar, U. R. Kini, S. C. Ashawa, N. S. Bhandari, G. U. Krishnan, D. Krishnan, *Radiat. Eff.* **1977**, *32*, 199) the half-life of HO$^\bullet$ in $10^{-3}\,\mathrm{mol\,dm^3}$ coumarin solution is about 85 ns. According to this analysis, confinement in 8 nm pores can effectively prevent diffusion of HO$^\bullet$ out of their production site and increase their recombination with their parent radicals prior to reaction with coumarin.

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