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Radical Generation upon γ-Irradiation of Two Amorphous and Two Crystalline Forms of Water at 77 K

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The effects of γ-irradiation at 77 K on two crystalline forms of water, namely, cubic and hexagonal ice, and on two amorphous forms of water, made by hyperquenching of liquid water or deposition of water vapors, have been studied by electron spin resonance (ESR) spectroscopy. Mainly OH radicals are formed from cubic ice directly made from liquid water. In contrast, comparable amounts of OH and HO_2 radicals are formed on irradiation of cubic ice made by heating glassy water, and their relative yields depend strongly on the irradiation dose. Comparable yields of OH and HO_2 radicals were observed on γ-irradiation of the two amorphous solids, and their ratio did not depend on irradiation dose. The formation of HO_2 radicals is attributed to the presence of shallow proton traps, or Bjerrum-like L-defects, in the two amorphous solids and in disordered regions of cubic ice.

Introduction

Studies of the effects of γ-irradiation on the solid forms of water have been restricted until recently to hexagonal ice (Ih) and about 500 publications have appeared on this topic.[1−5] When ice Ih is irradiated and the electron spin resonance (ESR) spectrum is recorded at 77 K, the OH radical is the only primary irradiation product for irradiation doses up to several hundred kilograys. The weak ESR signal of the hydroperoxy (HO_2) radical starts to build up on top of the spectrum of OH radicals only at even higher doses. We have recently reported a first study of the effects of γ-irradiation on glassy water made by hyperquenching of micrometer-sized water droplets (i.e., hyperquenched glassy water, HGW).[6,7] Surprisingly similar amounts of OH and HO_2 radicals were formed at 77 K under conditions where in ice Ih only the OH radical is formed. We have attributed the formation of HO_2 as primary radiation product to an abundance of shallow proton traps, or Bjerrum-like L-defects, in HGW and postulated a $(H_2O)_2^+$ dimer with a weak three-electron oxygen−oxygen bond as intermediate.

Here we report a comparative study of the effects of γ-irradiation on two amorphous forms of water, namely, vapor-deposited amorphous solid water (ASW) and HGW, and two crystalline forms of water, cubic ice (Ic) and hexagonal ice (Ih). The results are important for our understanding of radical formation on γ-irradiation of the solid forms of water,[1−7] of short-lived radicals generated by high-energy irradiation of liquid water as one of the basic sources of radiation damage to biomolecules,[8,9] and of the effects of γ-irradiation on the solid forms of water in outer space.[10]

Experimental Section

Vapor-deposited amorphous water (ASW) was prepared by admitting water vapors from a water reservoir held at 298 K through a fine metering valve and a tube of 13 mm inner diameter into a high vacuum system, where the vapors condensed on a demountable Cu substrate (50 mm diameter) precooled to 77 K.[11−13] In control experiments of our ASW deposits by X-ray diffraction, no sharp peaks (indicating crystalline ice) were observed.[11] Because our X-ray technique is sensitive to a crystallinity of >2%, we infer that our ASW was at least 98% amorphous. It was then heated in a vacuum to ∼115 K for reduction of its surface area and closure of micropores, before its exposure to N_2. ASW treated this way is called “sintered”.[11−13]

Glassy water (HGW) was prepared by hyperquenching—that is, by acceleration of droplets of water (∼5 μm diameter) from an aerosol by supersonic flow and then by their deposition on a Cu plate held inside a high-vacuum cryostat at 77 K.[6,13−15] One hour of deposition produced a 2−3-mm-thick opaque layer of glassy solid water with a porcelainlike appearance and texture. According to X-ray diffractograms, it contained at most 5% crystalline, mainly cubic, ice.[14,15]

Cubic ice was made either by heating HGW to 160 K and holding it at 160 K for 5 min[16,17] or by hyperquenching water droplets in the same manner as described for HGW except that the cryoplate was held at 170 K.[18]

Samples and Cu plates were removed from the high-vacuum systems by breaking the vacuum with gaseous N_2 (99.999%) and stored in liquid N_2. All transfers of a sample from one container to the other were made when it was immersed in liquid N_2.

The ESR spectra were recorded with an X-band ER 200D-SRC spectrometer, on line with ESP 3220−200SH data acquisition and processing system (Bruker, Analyt. Messtechnik GmbH).[6,7] For irradiation and measurements at 77 K, liquid N_2 was used.

Results

In Figure 1 we compare ESR spectra of radicals generated by γ-irradiation of the amorphous and crystalline water forms.

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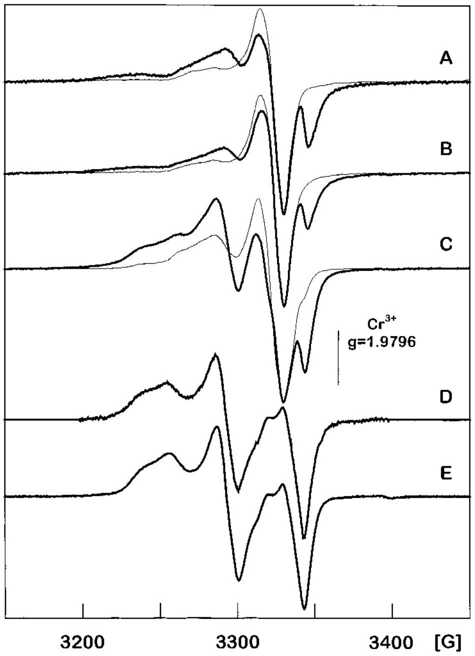

Figure 1. X-band ESR spectra recorded at 77 K after γ-irradiation (with dose rate 4.5 kGy/h for 1 h) at 77 K of sintered ASW (A) and HGW (B); of cubic ice made by heating HGW to 160 K for 10 min (C) and by hyperquenching liquid water onto a cryoplate held at 170 K (D); and of hexagonal ice made by heating HGW to 250 K for 10 min (E). In spectra A−C, thin lines indicate the contribution of HO_2 radicals to the spectra.

All samples were irradiated at 77 K with the same dose rate of 4.5 kGy/h for 1 h and the spectra were recorded at 77 K. Curves A and B are ESR spectra of irradiated sintered ASW and of HGW. Curves C and D are the spectra of γ-irradiated ice Ic made by heating HGW to 160 K for 10 min (C) and by hyperquenching liquid water on a cryoplate held at 170 K (D). Curve E is the spectrum of irradiated ice Ih prepared by heating HGW to 250 K for 10 min. Its spectral features are those of the OH radical, and they are identical with those of γ-irradiated ice Ih made by slow-cooling of liquid water. Curves A−C contain varying contributions of the HO_2 radical (indicated by thin lines) and curve D as well as curve E is mainly the spectrum of the OH radical. We have recently shown that the spectrum of γ-irradiated HGW consists of comparable amounts of OH and HO_2 radicals (see Figure 3 in ref 6) and, by comparison of B with A, the same is true for the spectrum of γ-irradiated sintered ASW.

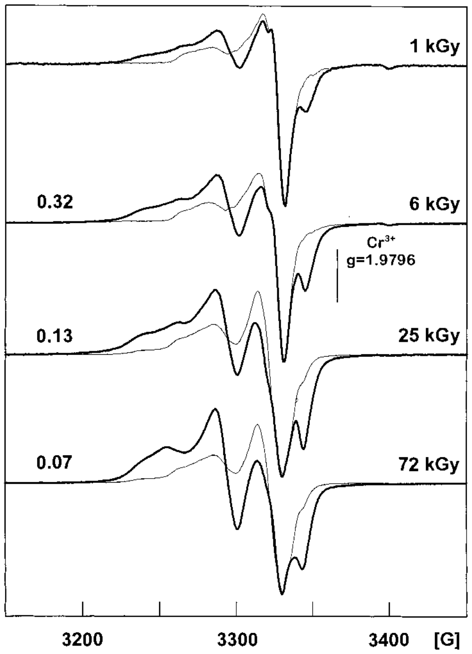

Figure 2. Effect of radiation dose on the X-band ESR spectrum of irradiated cubic ice made by heating HGW up to 160 K and keeping it at 160 K for 10 min. The same sample was irradiated at 77 K with increasing doses of 1, 6, 25, and 72 kGy, and the spectra were recorded thereafter at 77 K. The thin lines indicate the contribution of HO_2 radicals, which amounts to 60% for for irradiation dose of 1 kGy, and decreases to 51%, 27%, and 23% for irradiation doses of 6, 25, and 72 kGy, respectively. The numbers on the left-hand side of the spectra are the gain reducing factors used to present the spectra on the same scale.

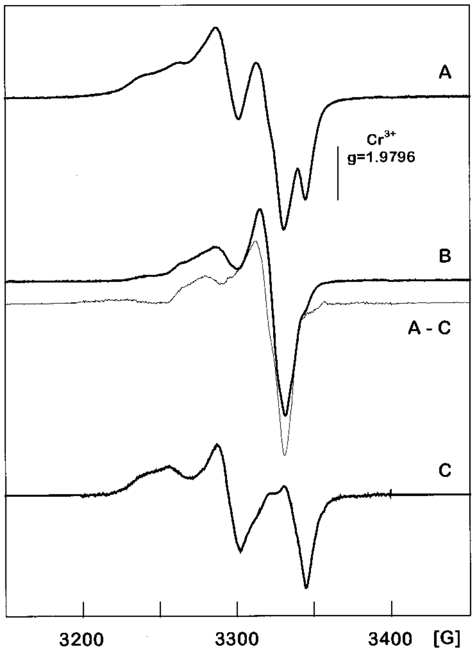

Figure 3. Analysis of the X-band ESR spectrum of cubic ice made by heating HGW to 160 K and irradiated at 77 K (25 kGy): (A) spectrum recorded at 77 K immediately after irradiation; (B) spectrum obtained after heating the sample to 140 K, annealing it at 140 K for 5 min, cooling to 77 K and recording the spectrum; (C) spectrum of OH radicals trapped in ice Ic prepared by hyperquenching of liquid water at 170 K. The subtraction of spectrum C from spectrum A, depicted with the thin line, matches spectrum B, which is assigned to HO_2 radicals.

The effect of radiation dose on the relative radical yields is, for the dose range up to about 70 kGy, negligible for ice Ih, sintered ASW, and HGW and minor for ice Ic made by hyperquenching liquid water on a cryoplate held at 170 K. In contrast to that, pronounced spectral changes were observed for ice Ic made from HGW on increasing the radiation dose from 1 to 72 kGy (see Figure 2). These ESR spectra can be assigned to varying contributions from OH and HO_2 radicals as shown in Figure 3. Curve A shows the ESR spectrum of irradiated ice Ic (25 kGy) made from HGW and recorded at 77 K immediately after irradiation. Curve B is the ESR spectrum obtained after heating this sample to 140 K, annealing it at 140 K for 5 min, cooling it to 77 K, and recording the spectrum. Curve C is the spectrum of OH radicals trapped in ice Ic prepared by hyperquenching of water at 170 K at 77 K. The subtraction of spectrum C from spectrum A, depicted with the thin line, matches spectrum B, which was assigned to the HO_2 radical, and its stability at 140 K is consistent with the behavior observed before for HGW (see Figure 1 in ref 6). The relative yields are 40% for HO_2 radicals and 60% for OH radicals (curves B and C). These relative yields depend on the radiation dose as shown by Figure 2: at low dose the spectrum is dominated by HO_2 radicals (top, 1 kGy), and with increasing radiation doses, the OH radicals start to dominate (25 and 72 kGy).

We emphasize that upon γ-irradiation at 77 K, no evidence for trapped hydrogen atoms or trapped electrons was found in any of the ESR spectra of the cubic ices, of sintered ASW, or of HGW.

Discussion

The OH radical is the only radical formed at 77 K upon γ-irradiation of ice Ih for irradiation doses up to several hundred kilograys.[1−5,19−21] Most probably the OH radicals are trapped in the original sites, and the accepted mechanism involves ionization of a tetrahedrally connected water molecule in a local configuration of C_{2v} symmetry (see Scheme 1 in ref 6).[3] OH radicals are also formed to varying degrees on γ-irradiation of the two types of ice Ic samples and of sintered ASW and HGW (see Figures 1−3). Their formation could occur via the same mechanism accepted for ice Ih because the same short-range order seems to exist for the two crystalline and the two amorphous forms of water. X-ray and neutron diffraction studies of ASW and HGW have shown that their structure can be modeled by a fully hydrogen-bonded continuous random network of water molecules.[22−24] In this network, the basic tetrahedral structure is the same hydrogen-bonded five-molecule cluster as in ices Ic and Ih (see Figure 4 in ref 23). The disorder in ASW and HGW arises on adding further water molecules to the five-molecule cluster because the disordered network contains disordered rings of 5, 6, 7, etc. water molecules, whereas in the regular lattice structure of ices Ic and Ih symmetric six-membered rings in the boat or chair conformation occur.

The formation of about equal amounts of OH and HO_2 radicals upon γ-irradiation of HGW at 77 K has been reported before and attributed to an abundance of shallow proton traps, or so-called Bjerrum-like L-defects, in comparison to hexagonal ice (see Scheme 1 in ref 6). These defects were postulated by Devlin for ASW[25] in order to rationalize isotopic exchange data of isolated D_2O in vapor-deposited amorphous solid H_2O water. It has been pointed out that the concept of L- (and D-) defects is strictly applicable only to crystalline ices and not to a topologically disordered network structure such as HGW and ASW.[26] In the micrometer-sized droplets of HGW and in vapor-deposited ASW, these defects could be not fully hydrogen-bonded (e.g., three-coordinated) oxygen atoms. In hexagonal ice about one site in five million is occupied by a Bjerrum L- (and D-) defect.[27] Much larger numbers of not fully hydrogen-bonded oxygen atoms are possible in ASW and HGW because X-ray and neutron diffraction studies of their structures modeled by a tetrahedral fully hydrogen-bonded continuous random network are accurate only with an error of at least ∼5%.[28] Stabilization of the HO_2 radical by hydrogen bonding is consistent with recent high-level ab initio calculations that predict for the $(HO_2{\cdot}H_2O)$ radical complex a binding energy of 6.9 kcal mol^{-1}.[29] We note that our postulated mechanism for HO_2 formation was discussed in two workshops (SORIS '96 and SORIS '98) attended by experts in chemistry of irradiated ices.

Figure 1 demonstrates that γ-irradiation of sintered ASW at 77 K produces a mixture of OH and HO_2 radicals in about the same proportion as in HGW. For irradiation doses up to about 70 kGy, the relative contributions of OH and HO_2 radicals to the total amount of paramagnetic oxygen-based radicals remain nearly constant for both amorphous solids.

The ESR spectrum obtained from ice Ih γ-irradiated and recorded at 77 K is that of the OH radical reported in the literature (Figure 1).[1−5,19−21] Ice Ih made either by slow cooling of liquid water or by hyperquenching liquid water into the glassy state and subsequent warming up to 250 K gave upon γ-irradiation the same ESR spectrum. This is an important point because it shows that possible impurities in HGW such as enclosed N_2 have no influence on the type of radical formed.

For ice Ic, the type of radical formed on γ-irradiation at 77 K and the dependence on irradiation dose depend strongly on the mode of preparation. Ice Ic prepared by hyperquenching liquid water droplets on a cryoplate held at 170 K gives upon γ-irradiation an ESR spectrum that consists of OH radicals and its spectral pattern changes very little for irradiation doses up to about 70 kGy. However, ice Ic made by heating HGW up to 160 K behaves very differently: first, its ESR spectrum recorded at 77 K contains significant amounts of HO_2 radicals, in addition to OH radicals, and second, the ratio of OH to HO_2 radical yield depends strongly on the irradiation dose (see Figure 2). These remarkable differences between the two types of ice Ic require discussion of its properties and are interpreted as follows.

Ice Ic appears to be always metastable relative to ice Ih.[30] It can be made in the laboratory by warming high-pressure forms of ice,[31] by warming ASW[32,33] and HGW[16,17] and pressure-amorphized amorphous solid water,[34] by hyperquenching liquid water droplets on a cryoplate held between 170 and 200 K,[18] and by slow cooling of water in confined geometries of less than ∼100 Å diameter.[35] Ice Ic apparently can be formed in Earth's upper atmosphere from micrometer-sized supercooled water droplets in cirrus clouds.[36] In X-ray and neutron powder diffractograms of all these cubic ices, particle size effects are important, the sharp cubic Bragg peaks are superimposed on broad features, and one noncubic Bragg peak can be indexed as 100 in the lattice of hexagonal ice.[18,37−39] The broad features cannot be removed by annealing at various temperatures and they only disappear on phase transition to hexagonal ice. Kuhs et al.[38] concluded in their high-resolution neutron powder diffraction study of ice Ic that the small particle size, the broad features, and the presence of some hexagonal component are inherent features of this material. These features have been attributed either to the existence of deformation faults in the stacking sequence or to the presence of some amorphous/disordered water.[18,37−39] Recently Jenniskens et al.[40] proposed that viscous *liquid* water coexists with cubic ice down to 140 K, and Johari[41] analyzed the coexistence of cubic and hexagonal ice and their broad transformation range with respect to bulk and interfacial energy changes on growth of ice Ih crystals in the bulk of ice Ic. These various samples of ice Ic can differ with respect to the amount of amorphous/disordered water or deformation faults in the stacking sequence. For example, heating thermograms of ice Ic samples that were prepared by rapid quenching of liquid water on a cryoplate held at 190 and at 170 K differed in that the ice Ic sample quenched at 170 K produced a second exotherm centered at ∼200 K, in addition to the one centered at ∼223 K from the cubic to hexagonal ice phase transition (see Figure 2 in ref 18).

The relative yields of OH and HO_2 radicals on γ-irradiation of the cubic ices can be rationalized by assuming that ice Ic made by heating HGW to 160 K contains in disordered regions a much larger number of shallow proton traps, or Bjerrum-like L-defects, than ice Ic made by hyperquenching liquid water at

170 K. In the same manner, the dependence of OH to HO_2 radical yield ratio on irradiation dose for ice Ic from HGW can be attributed to changes in the number of shallow proton traps: at low doses the HO_2 radical is the major species (see Figure 2, 1 kGy) because sufficient defects are present for its formation; at high irradiation doses the OH radical begins to dominate the ESR spectrum (Figure 2, 25 and 72 kGy) because the defects required for formation of HO_2 have been depleted.

In ice Ih γ-irradiated at 77 K, HO_2 radicals might be formed as primary radiation products only with irradiation doses of several hundred kilograys. Their formation could occur in the same manner discussed above for ice Ic. Ice Ih can be amorphized by an electron beam,[42] by UV irradiation,[43] and by an ion beam.[44] This amorphization becomes observable only when the temperature is below 77 K, whereas at 77 K the ice lattice is sufficiently dynamic to "heal" the defects. It is conceivable that high doses of γ-irradiation generate in the ice Ih lattice even at 77 K sufficient short-lived disordered regions with Bjerrum-like L-defects that can form and stabilize the HO_2 radical.

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