

SURVIVABILITY OF FULLERENES UNDER γ -IRRADIATION IN THE INTERSTELLAR MEDIUM.

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Introduction: Although the presence of fullerenes in the interstellar medium remains a subject for considerable discussion and waits for an unambiguous experimental confirmation, it is generally assumed that the large spherical carbon clusters can be generated within circumstellar envelopes of mass-losing carbon-rich stars [1-14]. The detection of fullerenes in carbonaceous chondrites, in the geological strata of the Cretaceous-Tertiary and the Permian-Triassic boundary layers, associated with bolide impacts, can be considered as an indirect evidence of their formation in circumstellar envelopes [15-19]. Besides that, the presence of fullerene species in the extraterrestrial samples found on Earth implies that these compounds are able to survive very long passages through diverse space environments. Some of them (especially those in close proximity to the stars where the fullerenes can be produced) are characterized by strong ionizing radiation. One can expect that any kind of radiation (UV, proton, γ -irradiation, etc.) decomposes the newly formed fullerene (as any other carbon-containing) molecules, thus rising a question on the fate of fullerenes in harsh radiation environments. In other words, the existence of the large spherical carbon clusters must finally depend on competition between the rates of their formation and radiation decomposition. Despite fullerene chemistry as a whole remains a subject for numerous studies, there is an obvious lack of experimental data in this area. We tried to roughly estimate the capability of C₆₀, the most common member of fullerene family, to withstand prolonged γ -irradiation. We exposed C₆₀ to very high irradiation doses exceeding 6 MGy, and analyzed the irradiated samples by high-performance liquid chromatography (HPLC) and infrared (IR) spectroscopy.

Experimental: Crystalline fullerene C₆₀ (from MER Corporation, 99.5%+ purity), toluene (Aldrich, 99.8%, HPLC grade) and methanol (EM Science, HPLC grade) were used as received. C₆₀ was finely ground, and two sample series were prepared: (1) dry samples, 50 mg C₆₀ each (in vials open to air); and (2) 50 mg C₆₀ mixed under ultrasonication with 0.5 ml of distilled deionized water, sealed in glass vials. The irradiation experiments were performed in a Cobalt-60 source facility at ICN UNAM at room temperature. The samples were placed as close as possible to the radiation source, at dose rate of 9.7 kGy per hour. Irradiation periods were 255, 534 and 640 h, correspond-

ing to a doses of 2.47, 5.18 and 6.21 MGy, respectively. One dry and one wet sample were removed after a given period of irradiation for further analyses. The wet samples were dried in vacuum under room temperature. For HPLC analyses, 10 mg of each sample were dissolved in 10 ml of toluene. The resulting solutions were chromatographed on an Agilent 1100 Series instrument, equipped with an Alltima (Alltech) reversed-phase C-18 column, particle size of 3 μ m, and dimensions 50 \times 4.6 mm I.D. UV detection was performed at 330-nm wavelength. As a mobile phase, we used a 1:1 mixture (by volume) of toluene and methanol, at 0.5 ml min⁻¹. IR spectra were recorded in KBr pellets on a Nicolet 5SX FTIR spectrometer, or in dry films (attenuated total reflection mode, ATR) on a Perkin Elmer Spectrum One FTIR instrument.

Results and Discussion: C₆₀ was subjected to very high doses exceeding 6 MGy, under room temperature. Although irradiation of frozen samples would be more adequate to simulate the cold interstellar conditions and interstellar ices, this was impractical due to very long exposures (up to almost one month) and slight heating effects produced by the irradiation. We irradiated two series of C₆₀ samples. In one of them, C₆₀ remained dry under ambient atmospheric conditions; in the second series, we added water. Although there are significant differences between the crystalline solid phase and aqueous suspensions in terms of radical and ion mobilities, and thus in the yields of radiolytic products, adding water allows to roughly account for the presence of ice in comets and interstellar dust particles. Another big difference from the real space bodies (meteorites, comets and dust particles), as well as from the interstellar medium, is that the fullerenes are most likely present there as separated molecules: this requirement is impossible to fulfill under room temperature in the laboratory due to zero C₆₀ volatility and solubility in aqueous media.

In the dry series, no visible changes of the samples were observed after γ -irradiation. In the wet series, we noticed the appearance of fine light-colored precipitate, especially under higher doses. This observation implies the formation of molecular species with a lower number of conjugated π -bonds as compared to C₆₀, exhibiting a lower absorption in the visible spectrum. After dissolving in toluene, minute amounts of a

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very fine insoluble substance (possibly polymerization products) were found in all the samples.

The results of HPLC quantification of C_{60} in the irradiated samples showed that even after almost one-month irradiation, with the doses over 6 MGy, the degree of decomposition did not exceed 5% in both series. A general trend was that in the wet samples C_{60} decomposed more rapidly than in the dry samples. It can be explained by high efficiency of the formation of OH radicals (and possibly other radical and ion species) and by their high reactivity towards the conjugated π -bond system. Apparently, this effect cannot be expected under the cold space conditions, since in the latter case the radical/ion mobility drops by several orders of magnitude.

We were not able to distinguish any major decomposition product by HPLC: no evident new peaks evolved in the chromatograms. At the same time, the whole UV-absorption background after the C_{60} peak slightly increased, indicating the formation of numerous oligomeric products. Direct IR spectroscopic measurements of the irradiated samples did not reveal drastic changes either. The band intensities corresponding to characteristic vibrational modes of C_{60} at 526, 575, 1182 and 1427 cm^{-1} [20,21] did not exhibit reliably detectable changes. In the samples of the wet series we have found two broad absorption bands at about 1100 and 1645 cm^{-1} . The latter is indicative of OH-containing compounds (including water), due to ν_{OH} vibrations, and the former is typical just for alcohols, due to $\nu_{\text{C-O}}$ vibrations.

Nevertheless, as we already noticed, we found that the irradiation produces minute amounts of polymeric products, insoluble in toluene (unlike C_{60}). We were able to separate them and characterize by ATR-IR spectroscopy. There are striking differences between the products generated in the dry and in the wet experiments. For the samples irradiated in the absence of liquid water, only three evident IR absorption bands were detected, at 678, 1085, and 1720 cm^{-1} , which were assigned to bending C=C vibrations in *cis*-substituted alkenes, $\nu_{\text{C-O}}$ in alcohols, and a carbonyl band $\nu_{\text{C=O}}$ in carboxylic groups, respectively. The O and H atoms, introduced into the products, apparently originate from atmospheric moisture and molecular oxygen. The same three bands were detected for the wet-condition products, and in addition to that, IR absorption at 968, 1377, 1460, and 2800-3000 cm^{-1} . All of these bands are associated with breaking the fullerene cage along with hydrogenation of its carbon atoms. In particular, the band at 968 cm^{-1} can be due to bending C=C vibrations in *trans*-substituted alkenes; those at 1377 and 1460 cm^{-1} correspond to symmetric bending modes of methyl groups ($\delta^{\text{s}}_{\text{CH}_3}$) and

asymmetric $\delta^{\text{as}}_{\text{CH}}$ in CH_2 and CH_3 (possibly mixed with $\nu_{\text{C=C}}$ stretches in alkenes), respectively. Finally, the group of bands around 2800-3000 cm^{-1} ($\nu^{\text{s}}_{\text{CH}}$ and $\nu^{\text{as}}_{\text{CH}}$) are also indicative of a high degree of hydrogenation in the insoluble products of C_{60} γ -irradiation.

Thus, the HPLC results along with the IR bands observed suggest general pathways of C_{60} radiolysis in the aqueous phase to be polymerization (most likely cross-linking), breaking the carbon backbone, C—H group formation, and incorporation of oxygen atoms as carbonyl and OH groups. In the absence of liquid water, attachment of other radicals generated in the environment is possible, along with the polymerization. As a whole, crystalline C_{60} fullerene exhibited an extremely high stability against prolonged γ -irradiation (the doses exceeding 6 MGy). To some extent, this conclusion can be extrapolated to different space environments, where the large carbon clusters are formed, incorporated into interstellar dust particles and subsequently into comets, and travel through the Universe.

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