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GEOCHEMISTRY AND COSMOCHEMISTRY OF FULLERENES III : REACTION OF C₆₀ AND C₇₀ WITH OZONE. D. Heymann and L.P.F. Chibante. Department of Geology and Geophysics and of Chemistry. Rice University, Houston 77251, USA. (713) 527 4890.

C₆₀ and C₇₀ dissolved in toluene were treated with O₂ gas containing 2.6 volume% ozone and with O₃-free oxygen. No reaction products were detected for 0.1 mole of O₂ passed through the solution, but destruction of C₆₀ was clearly detectable for a dose of 10⁻⁶ moles of O₃. C₇₀ was destroyed more slowly than C₆₀. Among the substances remaining in solution, we identified C₆₀O, C₇₀O, C₆₀O₂, C₆₀O₃, and C₆₀O₄. C₆₀ crystals exposed to O₃ at room temperature became less soluble in toluene in a matter of days, but oxides were apparently not formed.

The discovery of C₆₀ and C₇₀ on the Earth (1) has stimulated interest in the geochemistry of these compounds. We found earlier that these substances decomposed so swiftly when heated in ambient air (2,3) that their survival in a Precambrian rock (1) seemed puzzling. Acting, as we did, on a hunch that O₃ rather than O₂ might be the dangerous chemical in air, we exposed C₆₀ and C₇₀ in solution to O₂ gas containing 2.6 volume % O₃. The gas mixture was bubbled through the solutions. Figure 1 shows the decrease of C₆₀ concentration as a function of ozone dose. Within about 3 minutes, C₆₀ is essentially destroyed and a buff colored precipitate has formed. Treatment with ozone-free O₂ (a total of 0.1 mole) showed no decomposition of the C₆₀. The reaction with ozone is at least five orders of magnitude faster than with oxygen.

Figure 2 shows the results of the ozonation of both fullerenes in toluene solution. The deduced rate of C₇₀ to C₇₀O is about 0.7 that of C₆₀ to C₆₀O. Figure 3 is an HPLC chromatogram of the solution in which 0.66% and 2.10% of the original C₆₀ and C₇₀ had remained. The substance labels are certain except for C₆₀O₄ and C₇₀O₂. The oxides are well-soluble in toluene. Figure 4 shows the areas of the C₆₀O and C₆₀O₂ peaks determined spectroscopically at 290 nm, during the ozonation. Since we have not yet determined the molar extinction coefficients at any wavelength, the area ratios are only closely equal to the molar ratios. However, these results are consistent with the hypothesis that the transformation of the fullerenes to (toluene) insoluble matter proceeds along chains such as C₆₀ to C₆₀O to C₆₀O₂ to C₆₀O₃, etc to insoluble matter. We cannot deduce for which value of n in C₆₀O_n the cage ruptures. Our results are not in conflict with a report (4) that n = 5 when oxygen is adducted electrochemically.

A crystalline sample of C₆₀ was exposed to oxygen/ozone at room temperature. After 24 hours, about 95% of the original mass was still soluble in toluene. After seven days, only about 20% went into solution. However, no oxides were detected in the solutions.

A sample of C₆₀ in toluene was completely transformed to insoluble matter with ozone. The weight of the recovered precipitate was 2.2 times that of the untreated sample. The precipitates are obviously highly polar substances such as ketones, aldehydes, and/or carboxylic acids with an over-all C : O ratio close to unity!

A major requirement for fullerene survival in nature is that the environment must be essentially free of ozone. The survival of fullerenes in coal or graphite might be aided by the catalytic conversion of ozone

to oxygen by the matrix (coal, graphite).

References. (1) Buseck, P.R., Tsipurski, S.J. and Hettich R. (1992) *Science* 257, 215-217. (2) Heymann, D. in *Lunar and Planetary Science XXIII* (1992), pp. 531-532. (3) Chibante, L.P.F. and Heymann, D. (1992/93) *Carbon* (in print). (4) Kalsbeck, W.A. and Thorp, H.H. (1991) *J. Electroanal. Chem.* 314, 363-370.

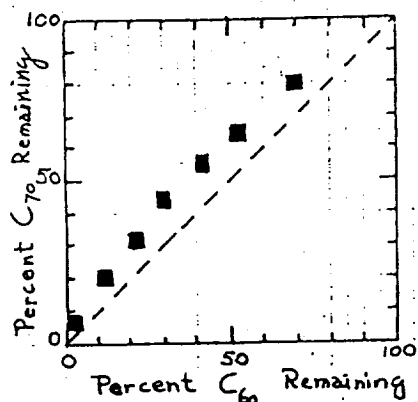
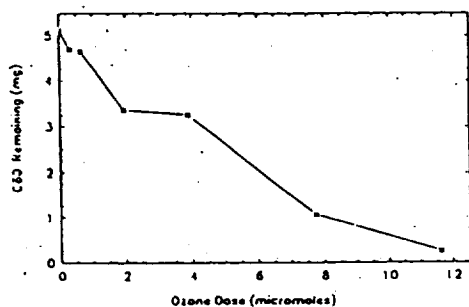


Figure 2

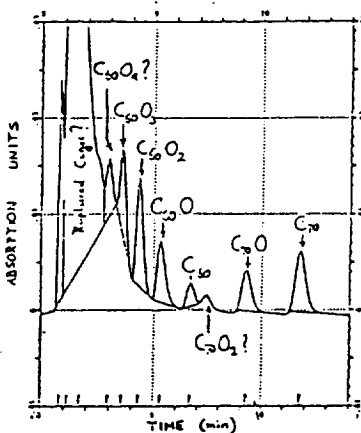


Figure 3

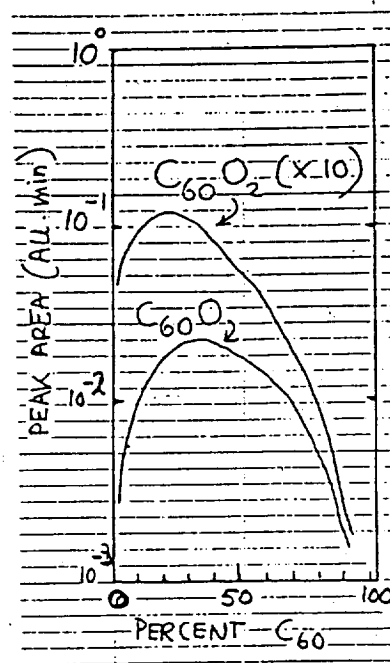


Figure 4

SOME CHEMISTRY. It is generally believed that the O-atoms bridge C-C bonds between two adjacent 6-membered C-rings. For C₇₀ it has been postulated that the O occurs in a bridged annulene-like structure. For C₆₀, an epoxide structure has been proposed. In principle, C₆₀O can have two isomers and C₇₀O can have eight; in each case equal to the number of different C-C bonds. C₆₀O₂ will have nine structural isomers if O bridges are (6-6) types. The number of isomers of the higher oxides is even larger. There are indications that the oxides are less thermally stable than their respective parent molecules. The C₆₀ oxides decompose on dry neutral alumina, which can, therefore, not be used as a substrate for their separation by liquid chromatography.