GEOCHEMISTRY AND COSMOCHEMISTRY OF FULLERENES III : REACTION OF C_{60} AND C_{70} 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.

C_{60} and C_{70} dissolved in toluene were treated with O_2 gas containing 2.6 volume% ozone and with O_3-free oxygen. No reaction products were detected for 0.1 mole of O_2 passed through the solution, but destruction of C_{60} was clearly detectable for a dose of 10^{-6} moles of O_3. C_{70} was destroyed more slowly than C_{60}. Among the substances remaining in solution, we identified $C_{60}O$, $C_{70}O$, $C_{60}O_2$, $C_{60}O_3$, and $C_{60}O_4$. C_{60} crystals exposed to O_3 at room temperature became less soluble in toluene in a matter of days, but oxides were apparently not formed.

The discovery of C_{60} and C_{70} 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 O_3 rather than O_2 might be the dangerous chemical in air, we exposed C_{60} and C_{70} in solution to O_2 gas containing 2.6 volume % O_3. The gas mixture was bubbled through the solutions. Figure 1 shows the decrease of C_{60} concentration as a function of ozone dose. Within about 3 minutes, C_{60} is essentially destroyed and a buff colored precipitate has formed. Treatment with ozone-free O_2 (a total of 0.1 mole) showed no decomposition of the C_{60}. 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 C_{70} to $C_{70}O$ is about 0.7 that of C_{60} to $C_{60}O$. Figure 3 is an HPLC chromatogram of the solution in which 0.66% and 2.10% of the original C_{60} and C_{70} had remained. The substance labels are certain except for $C_{60}O_4$ and $C_{70}O_2$. The oxides are well-soluble in toluene. Figure 4 shows the areas of the $C_{60}O$ and $C_{60}O_2$ 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 C_{60} to $C_{60}O$ to $C_{60}O_2$ to $C_{60}O_3$, etc to insoluble matter. We cannot deduce for which value of n in $C_{60}O_n$ 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 C_{60} 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 C_{60} 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 obviosly 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

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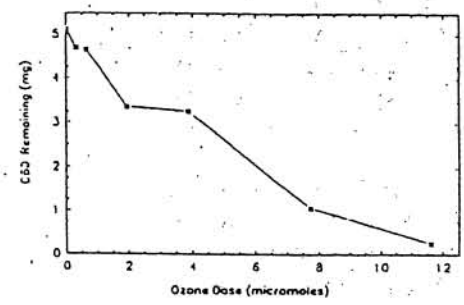
to oxygen by the matrix (coal, graphite).

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.



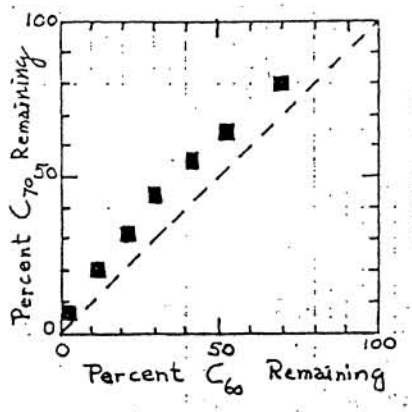


Figure 2

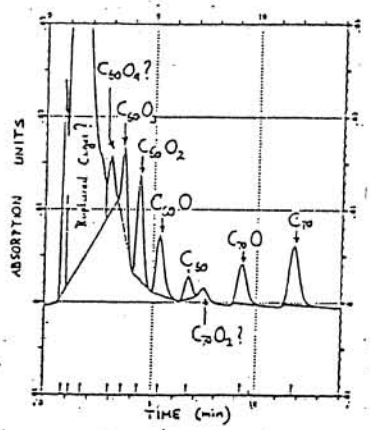


Figure 3

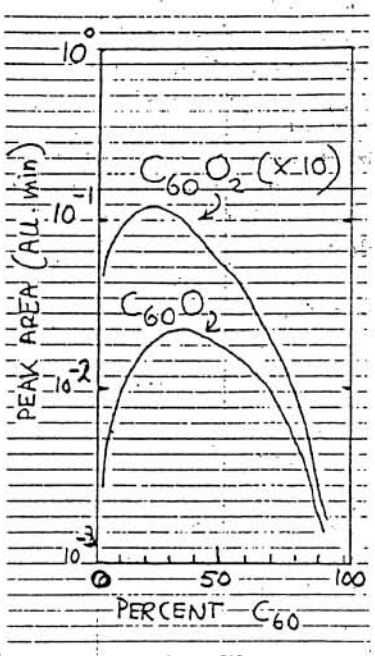


Figure 4

SOME CHEMISTRY. It is generally believed that the O-atoms bridge C-C bonds between two adjacent 6-membered C-rings. For C_{70} it has been postulated that the O occurs in a bridged annulene-like structure. For C_{60}, an epoxide structure has been proposed. In principle, $C_{60}O$ can have two isomers and $C_{70}O$ can have eight; in each case equal to the number of different C-C bonds. $C_{60}O_2$ 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 C_{60} oxides decompose on dry neutral alumina, which can, therefore, not be used as a substrate for their separation by liquid chromatography.

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