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GEOCHEMISTRY AND COSMOCHEMISTRY OF FULLERENES III : REACTION OF C<sub>60</sub> AND C<sub>70</sub> 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<sub>60</sub> and C<sub>70</sub> dissolved in toluene were treated with O<sub>2</sub> gas containing 2.6 volume% ozone and with O<sub>3</sub>-free oxygen. No reaction products were detected for 0.1 mole of O<sub>2</sub> passed through the solution, but destruction of C<sub>60</sub> was clearly detectable for a dose of 10<sup>-6</sup> moles of O<sub>3</sub>. C<sub>70</sub> was destroyed more slowly than C<sub>60</sub>. Among the substances remaining in solution, we identified C<sub>60</sub>O, C<sub>70</sub>O, C<sub>60</sub>O<sub>2</sub>, C<sub>60</sub>O<sub>3</sub>, and C<sub>60</sub>O<sub>4</sub>. C<sub>60</sub> crystals exposed to O<sub>3</sub> at room temperature became less soluble in toluene in a matter of days, but oxides were apparently not formed.

The discovery of C<sub>60</sub> and C<sub>70</sub> 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<sub>3</sub> rather than O<sub>2</sub> might be the dangerous chemical in air, we exposed C<sub>60</sub> and C<sub>70</sub> in solution to O<sub>2</sub> gas containing 2.6 volume % O<sub>3</sub>. The gas mixture was bubbled through the solutions. Figure 1 shows the decrease of C<sub>60</sub> concentration as a function of ozone dose. Within about 3 minutes, C<sub>60</sub> is essentially destroyed and a buff colored precipitate has formed. Treatment with ozone-free O<sub>2</sub> (a total of 0.1 mole) showed no decomposition of the C<sub>60</sub>. 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<sub>70</sub> to C<sub>70</sub>O is about 0.7 that of C<sub>60</sub> to C<sub>60</sub>O. Figure 3 is an HPLC chromatogram of the solution in which 0.66% and 2.10% of the original C<sub>60</sub> and C<sub>70</sub> had remained. The substance labels are certain except for C<sub>60</sub>O<sub>4</sub> and C<sub>70</sub>O<sub>2</sub>. The oxides are well-soluble in toluene. Figure 4 shows the areas of the C<sub>60</sub>O and C<sub>60</sub>O<sub>2</sub> 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<sub>60</sub> to C<sub>60</sub>O to C<sub>60</sub>O<sub>2</sub> to C<sub>60</sub>O<sub>3</sub>, etc to insoluble matter. We cannot deduce for which value of n in C<sub>60</sub>O<sub>n</sub> 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<sub>60</sub> 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<sub>60</sub> 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.

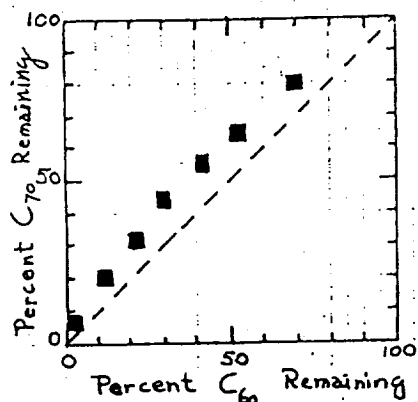
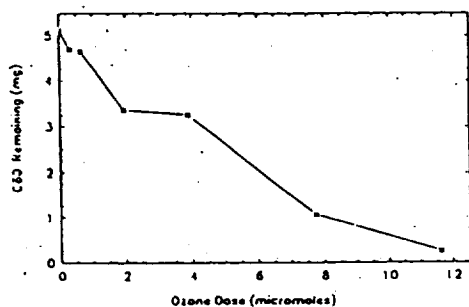


Figure 2

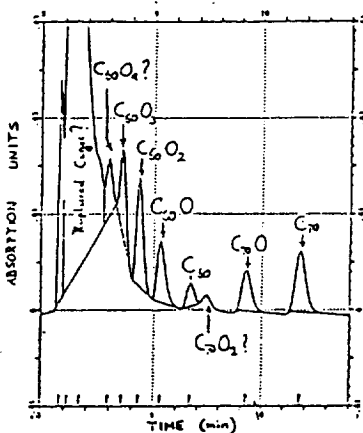


Figure 3

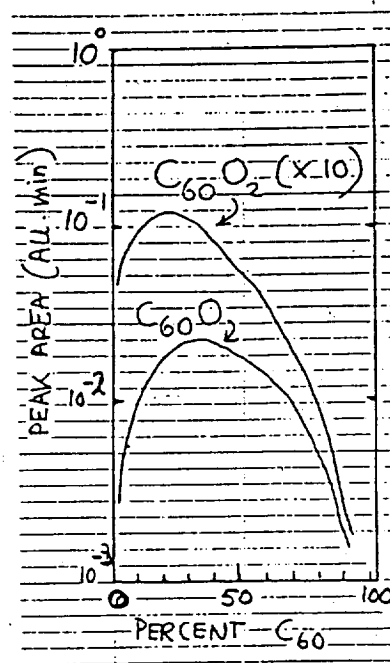


Figure 4

**SOME CHEMISTRY.** It is generally believed that the O-atoms bridge C-C bonds between two adjacent 6-membered C-rings. For C<sub>70</sub> it has been postulated that the O occurs in a bridged annulene-like structure. For C<sub>60</sub>, an epoxide structure has been proposed. In principle, C<sub>60</sub>O can have two isomers and C<sub>70</sub>O can have eight; in each case equal to the number of different C-C bonds. C<sub>60</sub>O<sub>2</sub> 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<sub>60</sub> oxides decompose on dry neutral alumina, which can, therefore, not be used as a substrate for their separation by liquid chromatography.