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Synthesis and Characterization of the “Missing” Oxide of C_{60}: [5,6]-Open $C_{60}O$

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In 1992, Creegan et al. synthesized and studied one of the first fullerene derivatives, the [6,6]-closed epoxide isomer of $C_{60}O$.[1] Although theoretical calculations suggest that it should be possible to isolate another $C_{60}O$ isomer of comparable stability,[2−4] that [5,6]-open oxidoannulene (an ether structure) has remained unobserved to date. We describe here the photochemical synthesis and characterization of [5,6]-open $C_{60}O$ (oxa-homo[60]fullerene).

We have found that this oxidoannulene isomer of $C_{60}O$ is readily formed by photolysis of $C_{60}O_3$, a [6,6]-closed ozone adduct. As in our previous report, $C_{60}O_3$ was prepared by ozonating a 3 mM solution of C_{60} in *o*-xylene at −16 °C in darkness.[5] While shielding the sample from light, the product $C_{60}O_3$ was then separated from C_{60} and other species on a Cosmosil PYE HPLC column cooled to 0 °C. Several minutes of irradiation under a fluorescent desk lamp was sufficient to convert the chilled $C_{60}O_3$ fraction to the new fullerene derivative with a yield of nearly 100%.

HPLC peaks of the photoproduct and $C_{60}O$ epoxide overlap strongly for Cosmosil Buckyprep or PBB columns and toluene eluent, although the retention order changes from photoproduct first on Buckyprep to epoxide first on PBB. LDI-TOF mass spectrometry of the photoproduct shows a parent isotopic cluster at 736 to 739 amu and a smaller C_{60} cluster from 720 to 723 amu. These observations clearly suggest that the photoproduct is an isomer of $C_{60}O$.

Figure 1 shows the UV−vis absorption spectrum of the new $C_{60}O$ isomer, along with the corresponding spectrum of [6,6]-$C_{60}O$ epoxide for comparison. Several differences are apparent. The new isomer has a near-UV peak at 336 nm, closely matching that of C_{60} but 8 nm red-shifted from the epoxide and 4 nm blue-shifted from [5,6]-$C_{60}CH_2$. In addition, the new isomer shows no sharp feature analogous to the 424 nm peak of the epoxide, which is characteristic of [6,6]-closed C_{60} adducts.[6] In the visible region, the broad minimum and maximum are red-shifted from 435 and 494 nm in the epoxide to 447 and 535 nm in the new isomer, nearly matching features of [5,6]-$C_{60}CH_2$. Both oxide isomers show weak $S_1 \leftarrow S_0$ origin bands near 680 nm. Except for this, the spectrum of the new $C_{60}O$ isomer resembles a broadened C_{60} spectrum. Such similarity is consistent with [5,6]-derivatization, which preserves 60 electrons in the fullerene π-system. The 680 nm band is more intense here than in other [5,6]-adducts, probably because of stronger symmetry-breaking. Absorptivities in Figure 1 were determined using a new kinetics-based method that will be described in a separate report.[7]

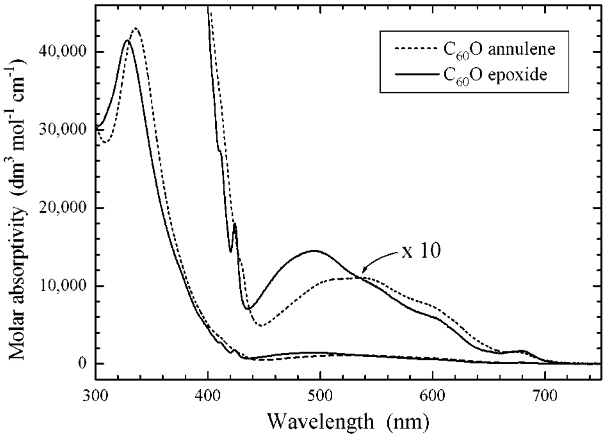

Figure 1. Molar absorptivity spectra of [5,6]-$C_{60}O$ annulene (dashed line) and [6,6]-$C_{60}O$ epoxide (solid line). To show features at longer wavelengths, the curves marked “× 10” have been multiplied by 10. Spectra were measured in toluene on a Cary 400 spectrophotometer.

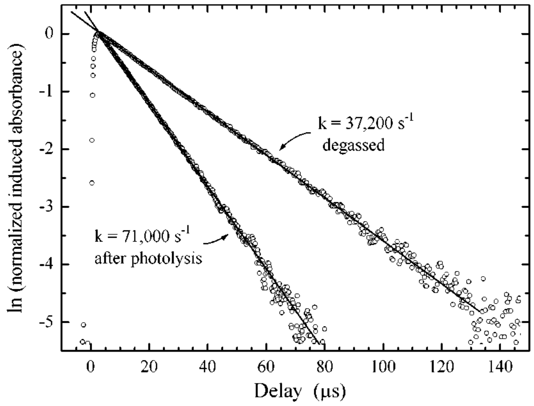

Figure 2. Semilog plot of triplet decay kinetics in a sample of photolyzed $C_{60}O_3$. The difference between the decays reveals quenching from O_2 produced in photolysis.

To confirm that the photoproduct is a mono-oxide of C_{60}, we measured the release of oxygen in photolysis. A chilled sample of $C_{60}O_3$ in toluene was quickly vacuum degassed to remove dissolved oxygen, sealed, and then photolyzed with an intense incandescent light source. Using a homemade apparatus, we measured the triplet-state lifetime of the fullerene photoproduct in the cell. The sample was then degassed again, and the triplet lifetime was remeasured for comparison. As shown in Figure 2, the second degassing reduced the triplet decay constant from 71 000 s^{-1} to 37 200 s^{-1}. The difference of 33 800 s^{-1} reflects triplet quenching from O_2 released in photolysis and removed by degassing. Estimating a quenching constant of 1.65×10^9 M^{-1} s^{-1},[8,9] we deduce an O_2 concentration of 20.5 μM. Because the ozonide concentration was near 25 μM, we find that ca. 0.8 molecules of O_2 were produced per photolyzed $C_{60}O_3$ molecule. This result falls within experimental uncertainty of 1, confirming

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that the photolysis reaction is

$$C_{60}O_3 \xrightarrow{h\nu} C_{60}O + O_2$$

On the basis of the stoichiometry, our spectroscopic findings, and the absence of plausible alternatives, we conclude that the photoproduct is the oxidoannulene isomer of $C_{60}O$.

The two $C_{60}O$ isomers show distinct photophysical properties apart from their absorption spectra. In contrast to the epoxide, the fluorescence spectrum of the oxidoannulene shows a first peak (at 727 nm) less intense than its second peak (at 792 nm). We estimate that the oxidoannulene S_1 origin energy in toluene is 14 500 cm^{-1}. The isomers also differ in their triplet lifetimes. Measurements on carefully degassed samples dissolved in toluene at 297 K show that the intrinsic triplet lifetime of the oxidoannulene isomer is 31 μs. By contrast, the epoxide triplet lifetime was found to be approximately 4 μs in hexane solution at a similar temperature.[10]

^{13}C NMR spectroscopy was performed on a sample of [5,6]-$C_{60}O$ containing 4% ^{13}C. The solvent was a 1:1 mixture of toluene-d_8 and *o*-dichlorobenzene-d_4 with $Cr(acac)_3$ added as a spin relaxant and TMS as a shift reference. While no signals characteristic of sp^3 carbons were detected, there was a signal at 152.0 ppm that likely arose from the two bridgehead carbon atoms. In comparing to the spectrum of [5,6]-$C_{60}CH_2$,[11,12] deshielding by the oxygen atom appears to be less than 5 ppm, an unusually small value. All other [5,6]-$C_{60}O$ resonances fell between 133.3 and 145.4 ppm. Approximately twice as many signals were observed as for the epoxide isomer,[1] as is consistent with C_s symmetry of [5,6]-$C_{60}O$.

To better understand the formation of C_{60} oxides from $C_{60}O_3$ dissociation, we have used kinetic spectrophotometry to extend and refine our previous thermolysis study.[5] The results, which are consistent with those from HPLC, give an Arrhenius prefactor of $1.9 \pm 1 \times 10^{12}$ s^{-1} and an activation energy of 87.2 ± 1.2 kJ mol^{-1} in toluene solution. The exponential thermolysis lifetime of $C_{60}O_3$ is therefore 22 min at 23 °C and 7.2 h at 0 °C. We find that thermolysis produces only the epoxide isomer of $C_{60}O$.

We have also measured the quantum yield for $C_{60}O_3$ photolysis. A solution of $C_{60}O_3$ was added to a magnetically stirred quartz cuvette and then irradiated for timed intervals using the excitation source of a Spex Fluorolog 3-21 spectrofluorometer set to 324 nm. Following each interval, a measured portion of the sample was analyzed by HPLC on a Cosmosil Buckprep column. Using the measured excitation power, the sample's optical density, the total rate of reactant loss, and the thermal rate of reactant loss, we determined a quantum yield of $6.1 \pm 0.8\%$ at 24 °C in air-saturated toluene. The quantum yield is about 5 times lower at 3 °C.

In air-saturated solutions, fullerene triplet-state decay is normally dominated by oxygen quenching with a rate constant near 3.3×10^6 s^{-1}. The measured photochemical quantum yield of 0.061 therefore implies a rate constant for photolysis from the triplet state of 2.0×10^5 s^{-1}. We have also measured the triplet-state kinetics of $C_{60}O_3$ under low-concentration, oxygen-free conditions in 297 K toluene and found a first-order decay lifetime of approximately 6 μs. This value sets the sum of unimolecular photophysical and photochemical decay constants from the triplet state at 1.7×10^5 s^{-1}. The similarity between this value and the deduced rate constant for photolysis indicates that in the absence of bimolecular quenching, essentially every triplet-state $C_{60}O_3$ molecule dissociates into $C_{60}O$ plus O_2. Photolysis of $C_{60}O_3$ appears to produce only the oxidoannulene isomer. Figure 3 illustrates the species and reactions involved in C_{60} ozonation.

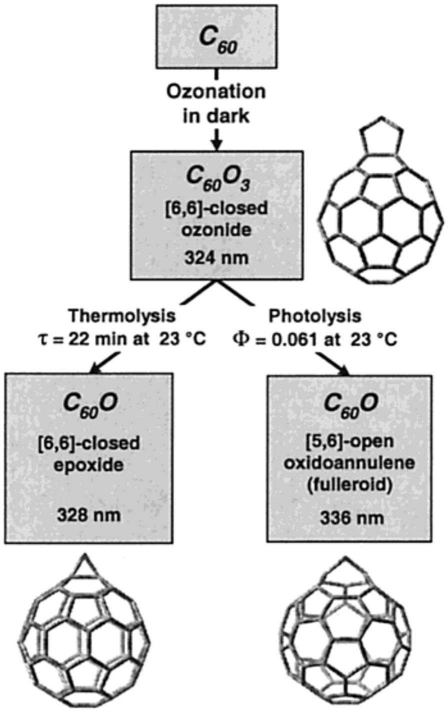

Figure 3. Species, structures, and transformations involved in forming oxides of C_{60} through ozonation.

The new oxidoannulene isomer of $C_{60}O$ is stable enough to persist in dilute solution for several days in laboratory light at room temperature. We estimate that its exponential thermolysis lifetime in toluene is near 100 hours at 65 °C in darkness, and its quantum yield for photochemical decay is at least 2 orders of magnitude lower than that of $C_{60}O_3$. Decay products apparently include $C_{60}O$ epoxide and dimeric and trimeric fullerene species. The thermal and light-induced reactions of [5,6]-open $C_{60}O$ clearly deserve further study.

To our knowledge, the only oxahomofullerene previously reported is $C_{60}F_{18}O$,[13] a compound that differs significantly from [5,6]-open $C_{60}O$ in that its π-system is heavily depleted by fluorination and the oxygen is bonded to fluorinated carbon atoms in a flattened region of the molecule. Our synthesis of [5,6]-open $C_{60}O$ confirms long-standing computational predictions that the epoxide and ether isomers of $C_{60}O$ are both isolable. Some prior studies of $C_{60}O$ epoxide may now require reevaluation for possible sample contamination by the oxidoannulene isomer. Finally, the simple and efficient preparation of [5,6]-open $C_{60}O$ reported here should be useful for synthesizing other novel fullerene compounds, including several new oxides of $C_{70}O$ that are currently under study.[14]

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Supporting Information Available: Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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