



Investigation of the photooxidation of [60]fullerene for the presence of the [5,6]-open oxidoannulene C₆₀O isomer

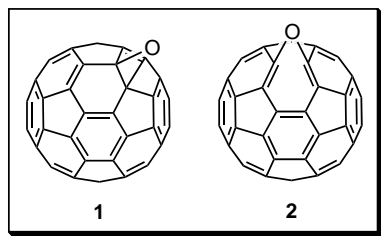
Jorge O. Escobedo, Amy E. Frey and Robert M. Strongin*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

Received 12 June 2002; revised 2 July 2002; accepted 3 July 2002

Abstract—The study of [60]fullerene oxidation reactions has played a major role in fullerene science. The parent fullerene epoxide (**1**) has been the subject of extensive experimental and theoretical study. A recent report described the discovery of a new monooxide isomer, [5,6]-open oxidoannulene (**2**). We have reinvestigated the photooxygenation of [60]fullerene to determine whether **2** forms in addition to epoxide **1**. Isomer **2** is not detected via ¹³C NMR and HPLC analysis in the singlet oxygen sensitized [60]fullerene photolysis reaction. © 2002 Elsevier Science Ltd. All rights reserved.

The study of fullerene oxides has been an active area of research for over a decade. In 1991 Diederich reported the isolation of minor amounts of C₇₀O from a fullerene synthesis reaction involving the resistive heating of graphite.¹ Wood observed C₆₀O under similar fullerene production conditions.² Thorpe showed that oxides of [60]fullerene containing up to four oxygen atoms could be generated electrochemically.³ In 1992, Smith and co-workers reported the first controlled synthesis, isolation and complete characterization of C₆₀O via the photooxygenation of [60]fullerene.⁴ The structure (**1**) was unambiguously assigned as the epoxide based on detailed spectroscopic evidence. Balch later reported the single crystal X-ray structure of an organometallic derivative of **1** which exhibited the epoxide moiety.⁵



In 2001 Weisman et al. reported the first synthesis and isolation of the [5,6]-open C₆₀O annulene **2** (oxa-homo[60]fullerene) isomer.⁶ They obtained **2** upon photolysis of C₆₀O₃,⁷ the [60]fullerene [6,6]-closed ozonide.

They also found that C₆₀O₃ converts to **1** upon thermolytic loss of O₂. The researchers postulated that oxidoannulene **2** may have been present as an undetected contaminant in previous work involving epoxide **1**. They stated that a reevaluation of prior research involving **1** was warranted. This prompted us to undertake the current study.

Since the 1992 photooxygenation reaction,⁴ epoxide **1** has been synthesized and isolated via methods including the reaction of [60]fullerene with dimethyldioxirane,⁸ O₃,⁹ and MCPBA.¹⁰ Compound **1** has served as a substrate for novel fullerene reactions.¹¹ It has been of long-standing interest due to its unique physical and materials properties.¹² Importantly, if **2** has gone undetected in [60]fullerene epoxidation reactions it would potentially impact a number of extensive prior efforts. Isomers **1** and **2** were reported to display significant overlap on columns routinely used to separate fullerenes.⁶

We examined the photooxidation⁴ of [60]fullerene for the presence of **2**. Photooxygenation of [60]fullerene (24 mM, 10–15% randomly enriched with carbon-13) in an oxygenated benzene (200 mL) solution containing benzil (0.2 equiv.) for 8 h led to ca. 10% conversion to **1**, based on the HPLC integral area ratio. In order to observe all possible products, the crude mixture was concentrated and not subjected to any purification steps.

The mixture was dissolved in a 1:1 solution of *o*-dichlorobenzene-*d*₄ and toluene-*d*₈ (the same solvent mixture used to acquire the NMR spectrum of **2**⁶) for

* Corresponding author. Tel.: 225-578-3238; fax: 225-578-3458; e-mail: rstrong@lsu.edu

analysis via 125 MHz ^{13}C NMR (40,960 scans). We expanded regions of the spectrum where resonances corresponding to **2** would not overlap with those of **1**. For instance, according to the published spectrum,¹³ compound **2** exhibits 15 resonances between 137.2 and 139.6 ppm. The NMR spectrum of the crude photooxygenation reaction product displays only one resonance in this region (137.4 ppm) which overlaps with a resonance of **2**. In addition, peaks at 151.9, 147.8, 144.1, 143.8, 143.5, 143.4, 141.0 and several resonances appearing between 134.7 and 136.4 corresponding to **2** are not observed in the NMR spectrum of the crude photooxygenation mixture. Compound **2** is thus not detected in the [60]fullerene photooxygenation reaction by ^{13}C NMR.

In order to confirm the NMR results we analyzed mixtures of **1** and **2** by HPLC. We prepared a standard sample of **2** for analysis according to the reported method⁶ via ozonation of [60]fullerene (5 mM) in *o*-xylene at -16°C in the dark for 7 min, followed by purging with N_2 . We found that the [60]fullerene monoozonide eluted at 12.3 min on a Cosmosil Buckyprep column (4.6 \times 250 mm, toluene mobile phase, 1 mL/min, $\lambda=330$ nm, 0°C). The ozonide solution was cooled to -16°C and irradiated with a fluorescent desk lamp for several minutes. The irradiation was stopped after ca. 95% conversion to **2** (9.3 min retention time) based on HPLC peak areas. ^{13}C NMR analysis of the crude ozonation/photolysis reaction mixture confirmed the presence of **2**.

In order to study mixtures of the two oxide isomers we employed an HPLC mobile phase gradient (1:4 toluene:hexane to 100% toluene over 35 min, 1.8 mL/min, rt). Under these conditions **2** elutes at 20.5 min and **1** elutes at 21.2 min. We found no trace of **2** in the crude photooxygenation reaction mixture via HPLC. In addition, we collected the first ca. 25% of the epoxide eluent since **2** elutes prior to **1**. This latter fraction of **1** exhibited no trace of **2** via HPLC. The first 25% of this early eluting fraction was then collected and reinjected. No trace of **2** was observed, even after a double recycle of epoxide-containing forerun material (Fig. 1).

The [60]fullerene ozonide C_{60}O_3 is analogous to the dipolar cycloadducts formed via the reaction of [60]fullerene and diazoalkanes or azides. These latter materials, upon loss of N_2 , typically afford [6,6]-open and/or [5,6]-closed cyclopropane or annulene (homo-fullerene) one atom bridged isomers, depending on reaction conditions.¹⁴ Thermolysis of C_{60}O_3 affords **1**. Photolytic extrusion of O_2 from the [60]fullerene ozonide affords **2**. To date, ozonide photolysis is the only known reaction in which [5,6]-open **2** has been observed experimentally.^{6,15}

In summary, we have employed carbon-13 labeling in conjunction with ^{13}C NMR spectroscopy and an HPLC mobile phase gradient technique to analyze the [60]fullerene monooxide isomers. We found no trace of oxidoannulene **2** in the singlet oxygen sensitized photol-

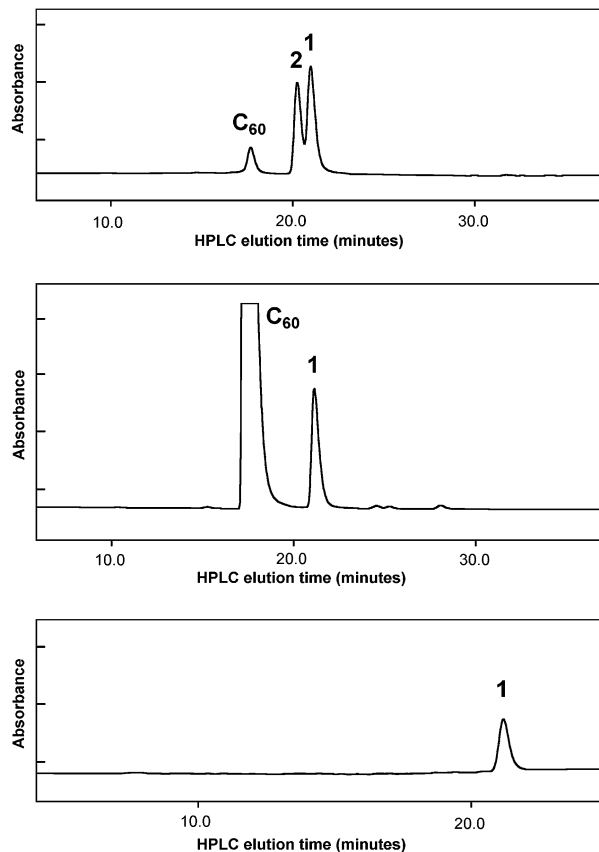


Figure 1. HPLC traces: a prepared mixture of [60]fullerene, **1** and **2** (top), the crude reaction mixture obtained via the photolysis of [60]fullerene in an O_2 -saturated benzene solution containing benzil (middle) and recycled epoxide **1** early-eluting fractions from the [60]fullerene photolysis reaction (bottom).

ysis of [60]fullerene, a major preparative method used for the synthesis and study of epoxide **1**.

Acknowledgements

Support was provided by Louisiana State University. J.O.E. is the recipient of Fulbright and CONACYT Foundation Fellowships.

References

- Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sehsharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548.
- Wood, J. M.; Kahr, B.; Hoke, S. H., II; Dejarme, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* **1991**, *113*, 5907.
- Kalsbeck, W. A.; Thorpe, H. H. *J. Electroanal. Chem.* **1991**, *314*, 363.
- Creegan, K. M.; Robbins, J. L.; Win, K.; Millar, J.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103.

5. Balch, A. L.; Costa, D. A.; Lee, J. W.; Noll, B. C.; Olmstead, M. M. *Inorg. Chem.* **1994**, *33*, 2071.
6. Weisman, R. B.; Heymann, D.; Bachilo, S. M. *J. Am. Chem. Soc.* **2001**, *123*, 9720.
7. Heymann, D.; Bachilo, S. M.; Weisman, R. B.; Cataldo, F.; Fokkens, R. H.; Nibbering, N. M. M.; Vis, R. D.; Chibante, L. P. F. *J. Am. Chem. Soc.* **2000**, *122*, 11473.
8. Elmes, Y.; Silverman, S. K.; Sheu, C.; Kao, M.; Foote, C. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 351.
9. (a) Heymann, D.; Chibante, L. P. F. *Chem. Phys. Lett.* **1993**, *207*, 339; (b) Malhotra, R.; Kumar, S.; Satyam, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1339.
10. Balch, A. L.; Costa, D. A.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1995**, *117*, 8926.
11. Precursor to odd-numbered carbon clusters and isolated dimeric fullerenes, for example: (a) McElvany, S. W.; Callahan, J. H.; Ross, M. M.; Lamb, L. D.; Huffman, D. R. *Science* **1993**, *260*, 1632; (b) Deng, J.-P.; Ju, D. D.; Her, G.-R.; Mou, C.-Y.; Chen, C.-J.; Lin, Y.-Y.; Han, C.-C. *J. Phys Chem.* **1993**, *97*, 11575; (c) Taylor, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1629; (d) Beck, R. D.; Brauchle, G.; Stoermer, C.; Kappes, M. M. *J. Chem. Phys.* **1995**, *102*, 540; (e) Smith, A. B., III; Tokuyama, H.; Strongin, R. M.; Furst, G. t.; Romanow, W. J.; Chait, B. T.; Mizra, U. A.; Haller, I. *J. Am. Chem. Soc.* **1995**, *117*, 9359; (f) Lebedkin, S.; Ballenweig, S.; Gross, J.; Taylor, R.; Krätschmer, W. *Tetrahedron Lett.* **1995**, *36*, 4971.
12. For example: (a) Vaughan, G. B. M.; Heiney, P. A.; McGhie, A. R.; Jones, D. R.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III *Chem. Phys.* **1992**, *168*, 185; (b) Cheng, A.; Klein, M. I. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1949; (c) Maliszewskyj, N. C.; Heiney, P. A.; Jones, D. R.; Strongin, R. M.; Cichy, M. A.; Smith, A. B. *Langmuir* **1993**, *9*, 1439; (d) Cheng, A.; Klein, M. I. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 253; (e) Fedurco, M.; Costa, D. A.; Balch, A. I.; Fawcett, W. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 194; (f) Meingast, C.; Roth, G.; Pintschovius, L.; Michel, R. H.; Stoermer, C.; Kappes, M. M.; Heiney, P. A.; Brard, L.; Strongin, R. M.; Smith, A. B., III *Phys. Rev. B* **1996**, *54*, 124; (g) Illescas, B. M.; Martin, N. *J. Org. Chem.* **2000**, *65*, 5986.
13. See Ref. 6, Supporting Information.
14. For example: (a) Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243; (b) Prato, M.; Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148.
15. The initial synthesis, isolation and characterization of an oxahomofullerene was of a fluorinated fullerene (C₆₀F₁₈O) in which the oxygen bridges fluorinated carbons on a flattened, significantly π -depleted molecule: Boltalina, O. V.; de La Vaissiere, B.; Fowler, P. W.; Hitchcock, P. B.; Sandall, J. P. B.; Troshin, P. A.; Taylor, R. *J. Chem. Soc., Chem. Commun.* **2000**, 1325.