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The role of singlet oxygen in the photochemical formation of $C_{60}O$

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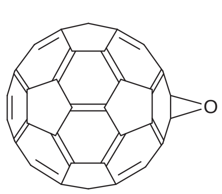
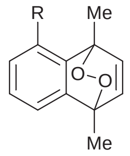
Ground state C_{60} does not give $C_{60}O$ in the presence of singlet oxygen generated thermally from endoperoxides; evidence is presented that the photochemical formation of $C_{60}O$ from C_{60} proceeds *via* reaction of singlet oxygen with the lowest triplet excited state of C_{60}.

Since its synthesis and characterization in 1992 by Smith *et al.*,[1] several studies on $C_{60}O$ **1** have appeared, showing that oxide **1** can be generated through both thermal[2] and photochemical[1] pathways. Dimethyldioxirane,[2a] ozonolysis,[2b–d,f] MCPBA,[2e] P450 cytochrome models,[2g] and a methyltrioxorhenium–H_2O_2 system[2h] all successfully convert C_{60} to **1**. Oxide **1** can also be isolated from the byproducts of fullerene synthesis[3a] and by extended irradiation of C_{60} in an oxygen atmosphere.[1] Although much is known about the photophysical and chemical properties of fullerenes, both the thermal and photochemical mechanisms for the formation of fullerene oxides largely remain a mystery.[3]



Oxide **1**



Endoperoxide **2** R = H
3 R = Me

Foote and co-workers reported in 1991[4] that C_{60} is a very efficient sensitizer for formation of singlet oxygen ($\Phi = 0.96 \pm 0.02$ at 532 nm), and that C_{60} also quenches $^1O_2$, as shown by the shortening of the decay time of $^1O_2$ luminescence at 1270 nm[5] ($k_q = 5 \pm 2 \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$).[4] However, no loss of C_{60} or appearance of new products was observed in the presence of oxygen following hundreds of laser pulses,[3b,4] suggesting that $^1O_2$ does not add to ground state C_{60} in solution. We have confirmed that $C_{60}O$ **1** is not formed upon reaction of C_{60} in toluene with $^1O_2$ when the latter is generated *via* the thermolysis of endoperoxides **2** and **3**.[6] Using an authentic sample of oxide **1**, we verified by HPLC analysis[7] that **1**, if formed, could be present in quantities no more than 0.01% of the total amount of C_{60} present in the solution. The presence of $^1O_2$ in this reaction system was verified by monitoring its emission at 1270 nm, which completely disappeared upon addition of β-carotene.[5,8] When cyclohexa-1,3-diene was added to toluene solutions of C_{60} and endoperoxide **2**, the conversion of the diene to its corresponding 1,4-endoperoxide[9] was detected by HPLC,[7] confirming that $^1O_2$ had indeed been generated under these reaction conditions. We also showed that C_{70} as well as several functionalized derivatives of C_{60} were also uneffected by $^1O_2$ generated thermally from endoperoxide **2**, according to HPLC analysis.[7] Juha *et al.* showed some time ago that C_{60} in fullerene–solvent clathrate microcrystallites was unreactive to a stream of chemically generated $^1O_2$.[10]

The question then remains as to the role played by $^1O_2$ in the photochemical formation of **1**. Could an *electronically excited* state of C_{60} lead to $C_{60}O$ by reaction with $^1O_2$? This question was addressed by photoexciting C_{60} in the presence of endoperoxides **2** and **3** as external sources of $^1O_2$. While endoperoxide **2** releases $^1O_2$ readily at temperatures above 0 °C, endoperoxide **3** does not release $^1O_2$ at room temperature.[6a,b] Thus, no emission at 1270 nm was observed from a toluene solution of **3** at room temperature. Thus, we were able to assess the reactivity of photoexcited C_{60} in the presence of two endoperoxides with very different thermal stabilities. In these reactions, 50 equiv. of endoperoxide were added to a 20 mM solution of C_{60} in benzene-d_6. The solutions were thoroughly degassed on a vacuum line by several freeze-pump-thaw cycles, and were then irradiated for 18 h.[11]

In the case of endoperoxide **2**, HPLC analysis revealed the formation of $C_{60}O$ **1** in 10% yield, higher than that (7%) reported from irradiation of C_{60} in an oxygen atmosphere under analogous conditions.[1] We also observed (HPLC) two additional minor products, presumably isomers of $C_{60}O_2$, as well as a brown precipitate, which were previously observed in the direct photooxygenation reaction.[1] The yield of **1** was far lower (2%) using endoperoxide **3**; furthermore, the higher oxidation products were not observed by HPLC in this case.

Thus, not only does the initial presence of $^1O_2$ in the photochemical reaction system increase the yield of fullerene oxide **1**, the absence of $^1O_2$ significantly decreases the efficiency of formation of **1**. This clearly identifies $^1O_2$ as the key species in the mechanism for fullerene oxide formation under photochemical reaction conditions, and suggests that $C_{60}O$ results from reaction of $^1O_2$ (lifetime 24 μs in benzene, 25 μs in toluene)[12] with an excited state of C_{60}. Such a mechanism was previously suggested[10] but no supporting evidence was presented. Given the very short lifetime of the S_1 state of C_{60} (*ca.* 1.2 ns),[13] and the long lifetime of the corresponding T_1 state (variously reported as 40 to 133 μs),[4,14] the triplet excited state is the obvious choice. If **1** were arising from reaction of C_{60} triplets directly with ground state endoperoxide, the yield of **1** should be similar using **2** and **3**. The large disparity in the yields of **1** suggests that this is at best a minor reaction pathway. We therefore conclude that the dominant photochemical pathway to $C_{60}O$ from C_{60} involves the reaction of C_{60} triplet excited states with singlet oxygen.

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Notes and references

1 K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith III, J. P. McCauley Jr., D. R. Jones and R.T. Gallager, *J. Am. Chem. Soc.*, 1992, **114**, 1103.

2 (*a*) Y. Elemes, S. K. Silverman, C. Sheu, M. Kao, C. S. Foote, M. M. Alvarez and R. L. Whetten, *Angew. Chem., Int. Ed. Engl.*, 1992, **3**, 351; (*b*) J. P. Deng, D. D. Ju, G. R. Her, C. Y. Mou, C. J. Chen, Y. Y. Lin and C.C. Han, *J. Phys. Chem.*, 1993, **97**, 11575; (*c*) R. Malhotra, S. Kumar and A. Satyam, *J. Chem. Soc., Chem. Commun.*, 1994, 1339; (*d*) J. P. Deng, C. Y. Mou and C. C. Han, *J. Phys. Chem.*, 1995, **99**, 14907; (*e*) A. L. Balch, D. A. Costa, B. C. Noll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1995, **117**, 8926; (*f*) S. Lebedkin, S. Ballenweg, J. Gross, R. Taylor and W. Krätschmer, *Tetrahedron Lett.*, 1995, **28**, 4971; (*g*) T. Hamano, T. Mashino and M. Hirobe, *J. Chem. Soc., Chem. Commun.*, 1995, 1537; (*h*) R.W. Murray and K. Iyanar, *Tetrahedron Lett.*, 1997, **38**, 335.

3 (*a*) A. Hirsch, *The Chemistry of Fullerenes*, G. Thieme Verlag, Stuttgart, New York, 1994; (*b*) C. S. Foote, *Top. Curr. Chem.*, 1994, **169**, 347; (*c*) D. I. Schuster, *Inter-American Photochemical Society Newsletter*, 1996, **19**, 35.

4 J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz and R. L. Whetten, *J. Phys. Chem.*, 1991, **95**, 11; J. L. Anderson, Y.-Z. An, Y. Rubin and C. S. Foote, *J. Am. Chem. Soc.*, 1994, **116**, 9763.

5 A. U. Khan and M. Kasha, *Proc. Natl. Acad. Sci. U.S.A.*, 1979, **76**, 6047; A. U. Khan, *J. Photochem.*, 1984, **25**, 327; P. R. Ogilby and C. S. Foote, *J. Am. Chem. Soc.*, 1982, **104**, 2069; 1983, **105**, 3423.

6 (*a*) H. H. Wasserman and D. L. Larsen, *J. Chem. Soc., Chem. Commun.*, 1972, 253; (*b*) N. J. Turro, M.-F. Chow and J. Rigaudy, *J. Am. Chem. Soc.*, 1981, **103**, 7218; (*c*) T. Wilson, A. U. Khan and M. M. Mehrotra, *Photochem. Photobiol.*, 1986, **43**, 661.

7 HPLC was performed on a Buckyclutcher-1 column (C. J. Welch and W. H. Pirkle, *J. Chromatogr.*, 1992, **609**, 89); eluent: 70:30 toluene–hexanes; detection 354 nm.

8 Singlet oxygen luminescence at 1270 nm was studied using a previously described ultrasensitive Ge-based near-IR detector: A. U. Khan, *J. Am. Chem. Soc.*, 1981, **103**, 6516; A. U. Khan, *ACS Symp. Ser.*, 1987, **339**, 58.

9 C. Kaneko, A. Sugimoto and S. Tanaka, *Synthesis*, 1974, 876.

10 L. Juha, V. Hamplová, J. Kodymová and O. Spalek, *J. Chem. Soc., Chem. Commun.*, 1994, 2437.

11 The light source was a Hanovia 450 W medium pressure Hg arc lamp cooled by a quartz jacket fitted with a Pyrex filter between the lamp and the inner wall of the jacket.

12 P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, 1972, **94**, 1029; A. A. Gorman, G. Lovering and M. A. Rodgers, *J. Am. Chem. Soc.*, 1978, **100**, 4527.

13 T. W. Ebbesen, K. Tanigaki and S. Kuroshima, *Chem. Phys. Lett.*, 1991, **181**, 501.

14 M. R. Fraelich and R. B. Weisman, *J. Phys. Chem.*, 1993, **97**, 11 145.

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