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# Fullerene peroxides

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## Abstract

*t*-Butylperoxy radical adds to fullerenes to form a number of stable fullerene mixed peroxides. The reaction follows the stepwise radical addition mechanism, and usually gives a mixture of products with different numbers of *t*-butylperoxy groups attached on the fullerene cage. Sequential para-addition on the hexagons is the dominant addition pattern. The peroxy groups and fullerene carbons around them exhibit facile reactivity towards various Lewis acids and nucleophiles. The fullerene peroxides can be easily separated by normal column chromatography. Single-crystal X-ray analysis confirmed the presence of peroxy groups. **To cite this article L. Gan C.R. Chimie 9 (2006).**

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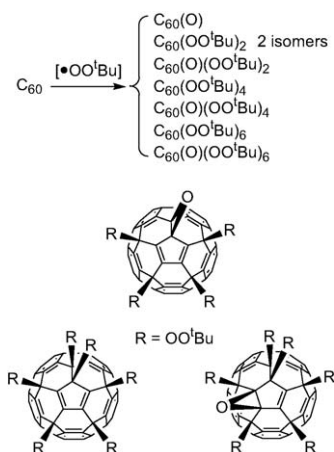
**Keywords:** Fullerene; Peroxide; Hemiketal

The chemistry of peroxide is of significance in many areas such as chemical and biochemical synthesis. Many oxidation reactions involve intermediates containing O–O bonds [1]. Epoxidation of fullerenes with peroxy acids is the most efficient method [2]. Singlet oxygen has been used for ring opening reactions of fullerenes in which a dioxetane intermediate is proposed [3]. Surprisingly the oxidation of a C<sub>60</sub> diol derivative with Pb(OAc)<sub>4</sub> only gave the dioxetane not the cage opened diketone [4]. Further derivatization of addends in some fullerene derivatives also form peroxide species with the peroxy group attached on the addends [5]. But stable and well-characterized fullerene peroxide is rare. We have found that *t*-butylperoxy

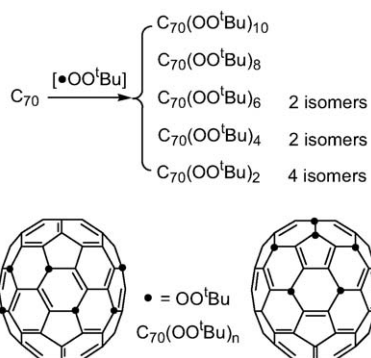
radicals add to fullerenes to form stable fullerene mixed peroxides [6], which exhibits interesting reactions [7–9]. This report summarizes some of the results.

Fullerene is known to be excellent radical scavengers. This is well demonstrated in their reactions with *t*-butylperoxy radical <sup>t</sup>BuOO•. A number of fullerene mixed peroxides have been isolated with different number of *t*-butylperoxy groups. For C<sub>60</sub> the reaction gave adducts with the general formula C<sub>60</sub>(O)<sub>m</sub>(OO<sup>t</sup>Bu)<sub>n</sub>. Low concentration, long reaction time and irradiation of visible light favor the epoxides formation. High concentration of *t*-butylperoxy radical favors homo-peroxy adducts. Under optimized conditions C<sub>60</sub>(O)(OO<sup>t</sup>Bu)<sub>4</sub>, C<sub>60</sub>(OO<sup>t</sup>Bu)<sub>6</sub>, C<sub>60</sub>(O)(OO<sup>t</sup>Bu)<sub>6</sub> adducts can be prepared in 45%, 40% and 57%, respectively [10].

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The addition to  $C_{70}$  is slightly different. Only the homo-peroxo adducts is formed with the general formula  $C_{70}(OO^tBu)_n$  with  $n$  varies from 2 to 10. There is no epoxy moiety in the products. Due to its  $D_{5h}$ -symmetric nature,  $C_{70}$  gave more isomers in particular for those with fewer addends. Thus four isomers were identified for the bis-adduct, two isomers for the tetrakis- and hexakis-adducts, and one isomer for the octakis- and decakis-adducts. The decakis-adduct is the major product (30%) under optimized conditions [8].



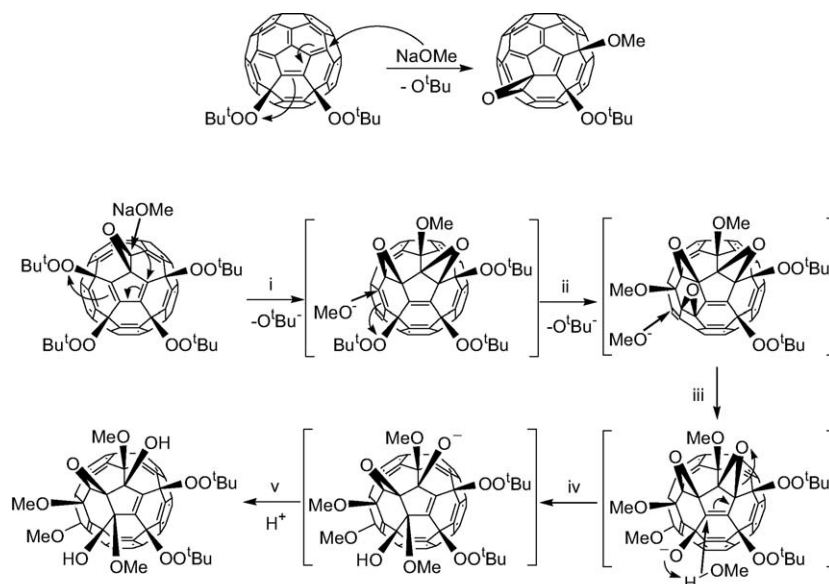
Various literature methods may be used to generate the  $t$ -butyl peroxy radical. Catalysis with Fe or Ru chlorides or coordination complexes requires a relatively large excess of TBHP and longer reaction time. The epoxy containing  $C_{60}(O)(OO^tBu)_4$  is best prepared under this condition. Stoichiometric oxidation with diacetoxyiodobenzene (DIB) or cerium ammonium nitrate (CAN) produces the  $t$ -butylperoxy radical efficiently in high concentration. The reaction is faster than the catalytic reaction and the number of addends on fullerene can be controlled by limiting the amount of DIB or

CAN.  $t$ -Butyl peroxy radical is the best peroxy radical for the formation of fullerene mixed peroxides. Other peroxy radicals such as cumyl peroxy radical  $PhC(Me)_2(OO^\bullet)$  reacts efficiently with  $C_{60}$ , but complex mixtures were formed [7].

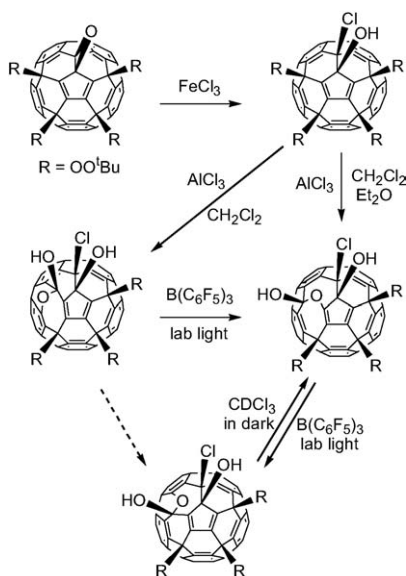
Formation of fullerene peroxides follows the stepwise radical addition mechanism [7,8]. The  $t$ -butylperoxy group already attached to the fullerene cage has a strong effect on the next  $t$ -butylperoxy group as a result of steric hindrance and/or the resulting radical stability. Para-addition on the hexagon is the dominant pattern. For  $C_{60}$  sequential para-addition occurs on the hexagons around a pentagon, i.e. the cyclopentadienyl addition mode [7]. For  $C_{70}$  two types of products are formed [8]: sequential para-addition along the belt and around a pentagon on the side of  $C_{70}$ . The two pentagons on the poles of  $C_{70}$  do not facilitate the cyclopentadienyl mode in the present reactions. Perhaps the pole carbons are too much pyramidalized for effective double bond formation between them [11].

Given the well established peroxide chemistry, fullerene peroxides have much potential for further functionalization. Functional groups on fullerene derivatives usually exhibit unique chemical reactivity due to the influence of the fullerene cage. Trivial transformations readily achieved in classical organic synthesis may not take place or drastic conditions are needed in fullerene chemistry. Further investigation of the fullerene peroxides have revealed some interesting reactions and resulted in a number of other fullerene peroxide derivatives.

Nucleophiles react with the fullerene peroxides according to either  $S_N1$  or the extended  $S_N2'$  or  $S_N2''$  pathway. Thus addition of sodium methoxide results in the loss of a  $t$ -butoxide from the 1,4-bis-adduct  $C_{60}(OO^tBu)_2$  to give the epoxy containing product  $C_{60}(O)(OMe)(OO^tBu)$ . The same reaction with  $C_{60}(O)(OO^tBu)_4$  is more complicated. Multi-addition of methoxy groups takes place resulting four isolable products, one of which is  $C_{60}(O)(OH)_2(OMe)_4(OO^tBu)_2$ . Coordination of  $Na^+$  with the epoxy oxygen probably initiates its opening to leave a positive fullerene carbon for the first methoxide addition, a process similar to the classical  $S_N1$  reaction. The oxygen anion formed here through the epoxide opening then induces the loss of another  $t$ -butoxide through a  $S_N2''$  route forming the first intermediate  $C_{60}(O)_2(OMe)(OO^tBu)_3$ . Further reactions with sodium methoxide and methanol eventually gave the final product  $C_{60}(O)(OH)_2(OMe)_4(OO^tBu)_2$ , the structure of which is confirmed by single crystal X-ray analysis [7].



Various Lewis and Bronsted acids can also react with the fullerene peroxides. Ferric chloride opens the epoxide effectively to give the vicinal hydroxyl chloride. In the presence of boron trifluoride addition of methanol, *t*-butylhydroperoxide and hydrogen peroxide yielded the corresponding epoxide opened derivatives. Aluminum chloride results in heterolysis of the peroxy O–O bond and formation of hemiketals after rearrangement. The hemiketals have similar stability and can be interconverted under milder conditions [9].



Most of the fullerene peroxides were characterized by their spectroscopic data. In a few cases structures were confirmed by single crystal X-ray analysis [9]. The fullerene peroxides are readily soluble in both polar and non-polar solvents due to presence of the *t*-butylperoxy groups. The relatively high solubility greatly facilitates the separation by normal flash chromatography with more choice of solvents, and in particular reduces the time of obtaining  $^{13}\text{C}$  NMR spectra. The compounds are stable under atmospheric conditions. Most samples can be stored at r.t. for months without noticeable decomposition. We have carried out the reaction with up to 1 g  $\text{C}_{60}$  and never had any problem. But considering the high local concentration of the peroxy groups, one must take great care in dealing with such fullerene peroxides to avoid possible explosion.

We have shown that fullerene peroxides can be readily prepared. Such compounds react with various acids and sodium methoxide to give characterizable products. Preliminary work with other nucleophiles, such as primary and secondary amines and carbon anions, indicates that atoms other than oxygen can be added to these fullerene peroxides. Many of the compounds prepared here are racemic mixtures. Chirality is another aspect to be addressed in the future [12]. Cleavage of the C–C and C=C bonds by peroxides are classical reactions in organic synthesis. Work is in progress to open up the fullerene cage starting from fullerene peroxides.

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## References

- [1] S. Patai, in: *The Chemistry of Peroxides*, John Wiley and Sons, Chichester–New York–Brisbane–Toronto–Singapore, 1983.
- [2] A.L. Balch, D.A. Costa, B.C. Noll, M.M. Olmstead, *J. Am. Chem. Soc.* 117 (1995) 8926.
- [3] J.C. Hummelen, M. Prato, F.J. Wudl, *J. Am. Chem. Soc.* 117 (1995) 7003.
- [4] I. Lamparth, A. Herzog, A. Hirsch, *Tetrahedron* 52 (1996) 5065.
- [5] N. Chronakis, G.C. Vougioukalakis, M. Orfanopoulos, *Org. Lett.* 4 (2002) 945.
- [6] L.B. Gan, S.H. Huang, X. Zhang, A.X. Zhang, B.C. Cheng, H. Cheng, X.L. Li, G. Shang, *J. Am. Chem. Soc.* 124 (2002) 13384.
- [7] S.H. Huang, Z. Xiao, F.D. Wang, L.B. Gan, X. Zhang, X. Q. Hu, S.W. Zhang, M.J. Lu, J.Q. Pan, L. Xu, *J. Org. Chem.* 70 (2004) 2442.
- [8] Z. Xiao, F.D. Wang, S.H. Huang, L.B. Gan, J. Zhou, G. Yuan, M.J. Lu, J.Q. Pan, *J. Org. Chem.* 69 (2005) 2060.
- [9] S.H. Huang, Z. Xiao, F.D. Wang, J. Zhou, G. Yuan, S. W. Zhang, Z.F. Chen, W. Thiel, P.R. Schleyer, X. Zhang, X. Q. Hu, B.C. Chen, L.B. Gan, *Chem. Eur. J.* 11 (2005) 5449.
- [10] Unpublished results.
- [11] S.I. Troyanov, A.A. Popov, *Angew. Chem., Int. Ed. Engl.* 44 (2005) 4215.
- [12] C. Thilgen, F. Diederich, For a leading reference in this area see, *Top. Curr. Chem.* 99 (1999) 135.