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Fullerenes as a *tert*-Butylperoxy Radical Trap, Metal Catalyzed Reaction of *tert*-Butyl Hydroperoxide with Fullerenes, and Formation of the First Fullerene Mixed Peroxides $C_{60}(O)(OO^tBu)_4$ and $C_{70}(OO^tBu)_{10}$

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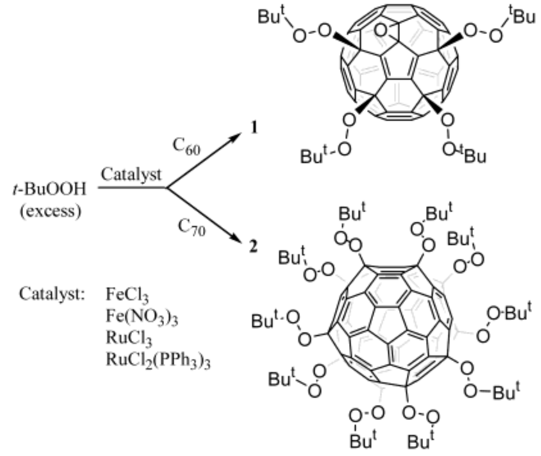
tert-Butyl hydroperoxide (TBHP) has been used extensively in organic synthesis as an oxidant and in biochemical studies as a radical source. The biomimetic oxidation of alkanes by TBHP involves both *tert*-butylperoxy and *tert*-butoxyl radicals.[1] Fullerenes are well-known efficient radical scavengers. Extensive ESR studies have been carried out on their reactivity toward radicals such as carbon and alkoxy radicals.[2] A number of radical derived halogenofullerenes have been isolated and well characterized.[3] To our knowledge, so far peroxy radical addition to fullerenes has not been studied, and there is no peroxy fullerene derivative known in the literature. Here we report the reaction of C_{60} and C_{70} with TBHP and characterization of the title compounds.

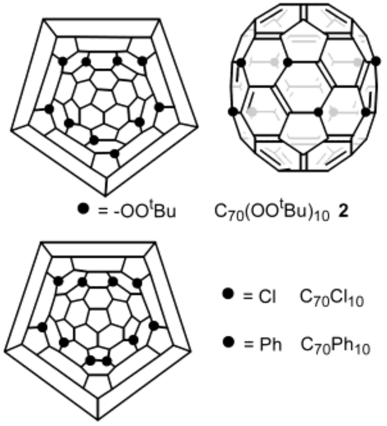
A catalytic amount of $Ru(PPh_3)_3Cl_2$ (or other catalysts in Scheme 1) was added to a benzene solution of C_{60} or C_{70}, followed by excess TBHP. The mixture was stirred at room temperature in the dark. Products were purified by chromatography on silica gel. Yields of the mixed peroxides $C_{60}(O)(OO^tBu)_4$ **1** and $C_{70}(OO^tBu)_{10}$ **2** are 30 and 8%, respectively. Both compounds are readily soluble in common organic solvents. Their excellent solubility greatly facilitates the NMR measurement. Less than 50 scans were enough to get a decent ^{13}C NMR spectrum for **1** on a DMX600 spectrometer. Their NMR solutions can be stored at room temperature in the dark for weeks without noticeable change.

NMR data agree with the structures as depicted in Scheme 1. The ^1H NMR spectrum of **1** showed two methyl signals at room temperature and 10 °C. Heating the solution to 50 °C did not cause any change. Thus, the *tert*-butyl groups rotate fast under these conditions. Hindered rotation of the *tert*-butyl group has been observed in the anionic intermediate $t\text{-}BuC_{60}^-Li^+$ and in the radical $t\text{-}BuC_{60}^\bullet$.[4] ^{13}C NMR showed 32 fullerene skeleton carbon signals. Four of the signals, two in the sp^2 C region and two in the sp^3 C region, are half intensity as compared to the rest, indicating C_s symmetry. All four tertiary *tert*-butyl carbons appear as a single peak at 81.90 ppm at room temperature. It is separated into two peaks (81.92 and 81.94 ppm) at 283 K as expected for the C_s symmetric structure.

Scheme 1. Reaction of TBHP with C_{60} and C_{70}



Scheme 2. Schlegel Diagram of $C_{70}X_{10}$ with C_2 and C_s Symmetry and Schematic Structure of $C_{70}(OO^tBu)_{10}$ Showing the C_2 Symmetry (Only One Enantiomer Is Shown Here)



The NMR spectrum of the C_{70} derivative **2** indicates C_2 symmetry (Scheme 2). The ^{13}C NMR is well separated at 283 K. There are 35 fullerene signals, 30 of which are in the sp^2 C region (all with equal intensity) and five in the sp^3 C region (84.23, 83.88, 83.79, 83.55, 81.33 also with equal intensity). This is in agreement only with a C_2 symmetric structure. The 10 *tert*-butyl groups showed five separate tertiary C signals and four methyl signals with an intensity ratio 1:2:1:1 due to overlapping. The ^1H NMR at 283 K shows four methyl signals with an integral ratio of 1:1:1:2 due to overlapping. At room temperature, the NMR signals are not as well resolved as a result of rotation of the addends.

Taylor's group pioneered the [70]fullerene multiadduct chemistry. They have unequivocally determined the structure of $C_{70}Cl_{10}$ and $C_{70}Ph_{10}$ to have the C_s symmetry (Scheme 2).[5] Even though two groups are adjacent in these compounds, the C_s structure is the most stable isomer according to theoretical calculation.[6] As the size of

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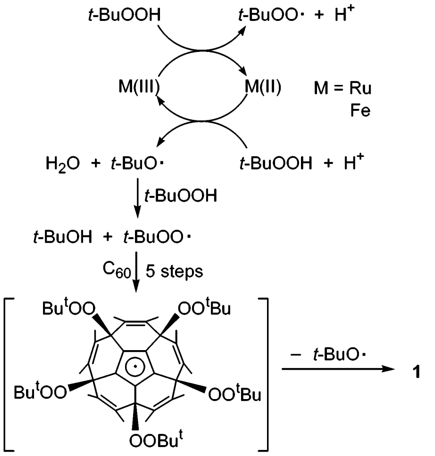
Scheme 3. Possible Mechanism for the Formation of **1**



the addend increases, the C_2 structure becomes favored. Theory predicts the C_2 isomer of $C_{70}(t\text{-Bu})_{10}$ is about 55 kcal mol^{-1} more stable than the corresponding C_s isomer.[6] The *tert*-butylperoxy group in the present system is certainly bulky enough and leads to the experimentally unprecedented addition pattern.

Three methods, ESI, MALDI-TOF, and SIMS, have been employed to obtain the mass spectra for the mixed peroxides. Molecular ion signals are observed as the most prominent signals in the positive ESI-MS spectra for both compounds, the base peak being 1115 ($M^+ + Na$) for **1** and 1754 ($M^+ + Na$) for **2** in addition to the $M^+ + K$ signals with less intensity as was commonly observed with other compounds. MALDI-TOF spectra show only the fullerene multioxides $C_{60}(O)_n$ or $C_{70}(O)_n$. For compound **1**, oxides with *n* up to 12 can be detected with successive loss of O, and the most intense peak is *n* equal to 4. A similar spectrum is observed for **2** with $C_{70}(O)_4$ as the most intense species and *n* up to 9. The laser at 337 nm used in the MALDI-TOF is very effective at breaking peroxide bonds.[7] SIMS spectra did not show the molecular ion signal either, but signals resulting from fragmentation of the fullerenes become evident besides the fullerene multioxides. Fragmentation signals for the C_{70} derivative **2** range from 576 to 840 at 24 amu intervals. The peak at 720 (C_{60}) is the strongest among the fragmentation signals. For the C_{60} derivative **1**, the fullerene skeleton fragmentation peaks range from 576 to 720 at 24 amu intervals. Multioxide signals similar to the MALDI-TOF spectrum are also present. In addition, several other intriguing signals resulting from successive loss of 28 amu (CO) are observed in the SIMS spectrum of **1**. These peaks seem to indicate the presence of $C_{58}O$, $C_{58}O_2$, $C_{58}O_3$, $C_{59}O_2$, $C_{59}O_3$, and $C_{59}O_4$. Similar $C_{58}(O)_{1-3}$ species have been observed in the LDI spectrum of $C_{60}(O)$.[8]

Scheme 3 shows the possible mechanism for formation of the C_{60} mixed peroxide **1**. Steps regarding the generation of the *tert*-butylperoxy radical including the reaction of *tert*-butoxyl radical with TBHP are the same as those proposed by Barton and Le Gloahec.[1a] *tert*-Butoxyl radical can also add to C_{60} as shown by Lunazzi et al.[2b] Yet in a toluene solution, the *tert*-butoxyl radical abstracts a methyl hydrogen atom from the solvent, and addition of the resulting benzyl radical to C_{60} is the only observed reaction.[2a] In the present reaction, TBHP, used in a large excess, reacts apparently more rapidly with the *tert*-butoxyl radical than C_{60} (but unidentified products may involve the *tert*-butoxyl radical). By increasing the amount of trapping agent, Barton and Le Gloahec were able to trap the *tert*-butoxyl radical in the Fe(III) and TBHP system.[1a] If less TBHP is added in the present reaction or if toluene is used as the solvent, more complicated products are observed perhaps as a result of competing reactions of *tert*-butoxyl radicals.

The addition pattern of the five *tert*-butylperoxy radicals in Scheme 3 has been reported before in the ESR study of reactions between fullerene and $R^\bullet$, $RS^\bullet$, $RO^\bullet$ radicals.[2] Preference of such an addition pathway is well explained on the basis of steric hindrance, radical pairing, and the likely participation of the more reactive double bonds.[2a] The penta-*tert*-butylperoxy [60]fullerene radical is a perfect precursor to **1**. It loses a *tert*-butoxyl radical to form the neutral **1** with an epoxide unit as in many classical epoxidation reactions. Oxygen may be produced in the solution by the combination of two *tert*-butylperoxy radicals.[1] It may react with a neutral tetra adduct $C_{60}(OO\text{-}t\text{-}Bu)_4$ to form **1** as well. In the presence of oxygen, some secondary amines react with C_{60} to give epoxide derivatives with structures analogous to **1**.[9]

A similar mechanism should apply for the formation of the C_{70} mixed peroxide **2**. In this case, the 1,4-stepwise addition of *tert*-butylperoxy radicals results in a neutral deca adduct. Thus, loss of a *tert*-butoxyl radical and formation of an epoxide unit are not necessary.

Fullerene oxides, $C_{60}(O)_n$ and $C_{70}(O)_n$, have attracted much attention due to their many possible applications.[10] Ring opening is expected as the number of O increases on the fullerene surface.[11] Yet selective preparation of such compounds is a challenging task. The mass spectra suggest that the mixed peroxides prepared here may serve as precursors to fullerene multioxides with defined structures. Further work is in progress toward this direction.

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Supporting Information Available: Detailed experimental procedure and NMR, MS, IR, and UV−vis spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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