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# Fullerene $C_{60}$ and $C_{70}$ Photosensitized Oxygenation of Olefins

**Michael Orfanopoulos* and Spiros Kambourakis**

Department of Chemistry, University of Crete, 71110 Iraklion, Crete, Greece.

***Abstract:*** *$C_{60}$ and $C_{70}$ sensitize the photooxygenation of 2-methyl-2-butene as well as (E)-2-methyl-2-pentene-1,1,1-$d_3$ by the intermediacy of singlet oxygen. Addition of DABCO reduces substantially the rate of photooxygenation. The regio- and stereoselectivity of these reactions are reported.*

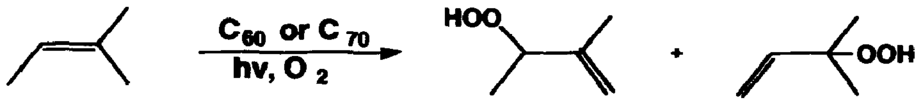
The discovery[1] of the spherical all-carbon "buckminsterfullerene" $C_{60}$ molecule has attracted much attention and its availability in macroscopic quantities[2,3,4] has led to remarkable discoveries of its chemical reactivity and physical properties in the last three years. The unusual geometry of this molecule may be responsible for some unique photochemical properties. It was shown recently that its triplet state is formed nearly quantitatively and produces very high yields[5] of singlet oxygen (measured by luminescence at 1268 nm.).

$$C_{60} \xrightarrow{hv} {}^{1}C_{60} \xrightarrow[\text{crossing}]{\text{Intersystem}} {}^{3}C_{60} \xrightarrow{{}^{3}O_2} {}^{1}O_2$$

We wish to report here the first case of using $C_{60}$ and $C_{70}$ as sensitizers to photooxygenate olefins by singlet oxygen. These results are summarized in Table 1.

The photooxidations were carried out in NMR tubes containing a solution of the olefin in deuterochloroform or benzene-$d_6$ with $C_{60}$ or $C_{70}$ as sensitizers, by bubbling dry oxygen, at room temperature. A Varian-Eimac Cermac 300-W xenon lamp was used as the light source and a $K_2Cr_2O_7$ solution (0.05M) as the cut-off filter, path length 3.5 cm (<400nm).

As seen from Table 1, the ratio of the allylic hydroperoxides **1a**:**1b** is independent of solvent polarity, as it was expected[6], and similar within experimental error to those observed when tetraphenylporphyrine (TPP) or rosebengal (RB) are used as sensitizers.



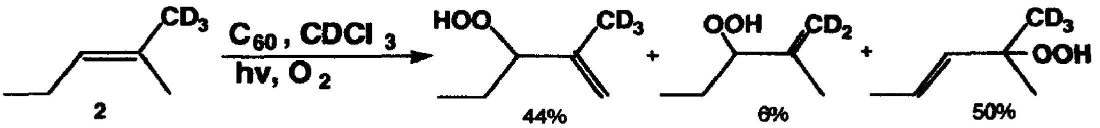
**1** **1a** **1b**

Table 1. Sensitized Photooxygenation[a] of Trimethylethylene 1[b].

| Sensitizer[c] | M | Solvent | T(min) | % Conversion | 1a:1b | DABCO M |
|---|---|---|---|---|---|---|
| $C_{60}$ | $1\times10^{-3}$ | Benzene | 20 | 85 | 52:48 | - |
| | $2\times10^{-4}$ | " | 40 | 45 | 50:50 | - |
| | " | $CDCl_3$ | 45 | 40 | 51:49 | - |
| | " | " | 40 | 22 | - | $2\times10^{-3}$ |
| $C_{70}$ | " | " | 180 | 23 | - | - |
| | $2\times10^{-3}$ | " | 40 | 4 | - | $2\times10^{-2}$ |
| | " | " | 40 | 47 | 48:52 | - |
| TPP | $2\times10^{-4}$ | " | 15 | 90 | 50:50 | - |
| RB | " | Acetone | 15 | 32 | 52:48 | - |

[a]The reaction was monitored by $^1H$ NMR spectroscopy by frequent interruptions of the photooxygenation experiment. The product ratio was determined by integration of the proper peaks and the error was ± 5%. [b]Solutions of 0.4 M. [c]$C_{60}$ and $C_{70}$ were purified from the soot (Polygon Enterprise Inc.) by a literature method[3]. HPLC analysis showed >99% purity for both $C_{60}$ and $C_{70}$.

Similarly the side selectivity of the trisubstituted olefins follows similar trends with that observed earlier[7,8]. This was demonstrated by the $C_{60}$ sensitized photooxygenations of (E)-2-methyl-2-pentene-1,1,1-d3, 2[9], where the less substituted side of the olefinic double bond is less reactive[10].



After the completion of the photooxidation, the UV/Vis spectrum of $C_{60}$ showed no visible change from its spectrum before the photooxidation. However, careful HPLC analysis (C18 reverse phase, acetonitrile/toluene 50:50 v:v, detection at 254nm, 1 ml/min) showed that a small portion of $C_{60}$ (~10%) was oxidized to an epoxide [11]. The addition of $2.5\times10^{-3}$ M 1, 4-Diazabicyclo[2.2.2]octane (DABCO), an excellent $^1O_2$ quencher[14], to the $C_{60}$ sensitized photooxidation of 0.4 M trimethylethylene in $CDCl_3$, reduced product formation by a factor of 2-3. This finding provides strong additional support for the intermediacy of $^1O_2$.

The $C_{70}$ fullerene also sensitizes the photooxygenation of **1** to produce allylic hydroperoxides **1a** and **1b** in the same ratio, as did $C_{60}$. Again the presence of DABCO reduced the rate of photooxygenation, indicating the $^1O_2$ intermediacy. This interesting result shows that $C_{70}$ also produces singlet oxygen in large quantities.

However, the photooxygenation of 1 in the presence of $C_{70}$ as the sensitizer is slower than that in the presence of $C_{60}$ by a factor of 3-4, indicating a slower rate of production of singlet oxygen.

In our quest to produce endo-peroxides, a sample of cyclopentadiene was photooxygenated with $C_{60}$ as the sensitizer. Within 10 minutes the light purple solution of $C_{60}$ turned brown and the characteristic peak of $C_{60}$ (HPLC) disappeared. Three new peaks with shorter retention times appeared. Very likely a 4+2 adduct of $C_{60}$ with pentadiene was formed[15], along with two other products. This reaction mixture also photosensitized the oxidation of olefin **1**, and is currently under further investigation.

In summary, we have shown that $C_{60}$ and $C_{70}$ a) photosensitize the oxidation of unsaturated compounds b) are relatively inert to photooxidation conditions c) are attractive sensitizers for laboratory use, because of their stability and the easy separation from the reaction mixture by changing the solvent polarity and d) Diels-Alder fullerene adducts also sensitize photooxygenations.

The environmental consequences of the photodynamic effect of the spectacular family of all carbon molecules remains to be investigated.

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