[60]Fullerene Supported on Silica and γ-Alumina Sensitized Photooxidation of Olefins: Chemical Evidence for Singlet Oxygen and Electron Transfer Mechanism

Georgios C. Vougioukalakis,^a Yiannis Angelis,^a John Vakros,^b George Panagiotou,^b Christos Kordulis,^b Alexis Lycourghiotis,^b Michael Orfanopoulos^{*a}

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Abstract: Fullerene C_{60} supported on silica and γ -alumina (2% w/w C_{60} /SiO₂ and C_{60} /Al₂O₃) sensitizes the photooxidation of alkenes via singlet oxygen and/or electron transfer mechanism, depending on the solvent and the substrate.

Key words: heterogeneous photooxidations, fullerene C_{60} , alkenes, singlet oxygen, electron transfer

Fullerene C_{60} is an electron-deficient compound with rich photophysical and photochemical properties.¹ The triplet-excited state of C_{60} is formed almost quantitatively with a lifetime, in solution, between 40 and 280 µs.² In the presence of molecular oxygen, energy transfer from the triplet-excited state of C_{60} to the ground state oxygen produces singlet oxygen with quantum yield near unity (Equation 1).¹

$$C_{60} \xrightarrow{hv} {}^{1}C_{60} \xrightarrow{ISC} {}^{3}C_{60} \xrightarrow{3O_{2}} {}^{1}O_{2}$$

Equation 1

This useful photochemical property characterizes C_{60} as an efficient sensitizer for the mild homogeneous photooxygenation of unsaturated substrates such as alkenes and dienes.³ Additionally, fullerenes are easily reduced and quenching of their triplet states by electron donors occurs efficiently in polar solvents. An electron transfer mechanism has been proposed in order to rationalize these results.⁴

Furthermore, fullerene C_{60} derivatives that bear an oxidizable group are easily oxidized in the presence of oxygen and light. A self-sensitized photooxygenation mechanism rationalizes the formation of the oxygenated adducts.⁵ However, the very small solubility of C_{60} in medium polar to polar solvents limits its utility as a photosensitizer.⁶ In previous studies, fullerene-coated beads have been prepared and used as photocatalyst for the production of singlet oxygen. However, in all cases, fullerene was derivatized and bound to the surface by a chemical reaction.⁷ Herein we report the generation and trapping of ${}^{1}O_{2}$ in a 'two phase' system, by using Silica and γ -Alumina-bound fullerene C₆₀ as sensitizer and a well characterized singlet oxygen olefin (2-methyl-2-heptene) acceptor. We also report the photooxygenation of suitable aryl substituted olefins by both singlet oxygen and/or electron transfer mechanism.⁸

Supported photosensitizers were prepared by depositing C_{60} on γ -Al₂O₃ [Akzo, specific surface area: 265 m²g⁻¹, size: 100–150 mesh powder, pore volume: 0.76 mLg⁻¹] and SiO₂ [Alfa Aesar, specific surface area: 175–200 m²g⁻¹, size: ca. 325 mesh powder, pore volume: 1.6 mLg⁻¹] surfaces.⁹ Incipient wetness impregnation was used for the above deposition. The impregnating solution was prepared by dissolving the necessary amount of C_{60} in 1,2-dichloro-benzene in order a loading of 2% w/w C_{60} to be achieved in the final catalysts. The impregnated samples were dried at 180 °C for 4 hours in air. Impregnated and/or final (dried) samples were characterized using UV/Vis diffuse reflectance spectroscopy, nitrogen physioroption for specific surface area measurements and carbon analysis.¹⁰

Photosensitized oxygenations were carried out in a 4 mL Pyrex cell containing a 0.03 M solution of 2-methyl-2-heptene (**1**) in various solvents in the presence of 3.6 mg of the insoluble catalyst (2% C_{60} on Al_2O_3 or 2% C_{60} on SiO_2 , 10^{-4} M in C_{60}) in 1 mL of solvent. The solution mixture was irradiated for a period of 30 min, using a 300W xenon lamp as the light source, while bubbling dry oxygen at 0 °C. The photooxygenation reaction was monitored by GC-MS (after reduction of the allylic hydroperoxides to the corresponding alcohols with triphenyl phosphine) and the products were identified by GC-MS and ¹H NMR spectroscopy. Allylic hydroperoxides **1a** and **1b** were the only detected products by ¹H NMR. The results are summarized in Table 1.

As seen in Table 1, the ratio of the allylic hydroperoxides **1a:1b** in non polar solvents is similar, within experimental error, to those observed with conventional singlet oxygen sensitizers such as tetraphenyl-porphyrine (TPP) or rose bengal (RB).

LETTER

^a Department of Chemistry, University of Crete, 71409 Iraklion, Crete, Greece Fax +30(2810)393601; E-mail: orfanop@chemistry.uoc.gr

^b Department of Chemistry, University of Patras and Institute of Chemical Engineering and High-Temperature Chemical Processes (ICE/HT), 26500 Patras, Greece

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 Table 1
 Sensitized Photooxidation of 2-Methyl-2-heptene

>	+ ноо					
1	1a	1b				
Sensitizer	Solvent	Conversion (%) ^{a,b}	1a:1b ^d			
C ₆₀ /SiO ₂	Hexanes	46	46:54			
C_{60}/Al_2O_3	Hexanes	24	46:54			
C ₆₀ /SiO ₂	MeCN	16	52:48			
C_{60}/Al_2O_3	MeCN	38	52:48			
C ₆₀ /SiO ₂	MeOH	7	47:53			
C_{60}/Al_2O_3	CH ₃ OH	30	47:53			
C ₆₀ /SiO ₂	DMSO	15	54:46			
C_{60}/Al_2O_3	DMSO	21	54:46			
C ₆₀ /SiO ₂ ^c	H_2O	65	43:57			
C ₆₀ /Al ₂ O ₃ ^c	H ₂ O	76	43:57			
C ₆₀ /SiO ₂ ^c	D ₂ O	94	43:57			
C ₆₀ /Al ₂ O ₃ ^c	D ₂ O	100	43:57			
RB	MeCN	100	50:50			
TPP	Hexanes	100	52:48			

^a All measurements were taken after 30 min of irradiation.

^b Determined by GC-MS after reduction to allylic alcohols with Ph_3P : error $\pm 1\%$.

 $^{\rm c}$ A small amount of MeCN (H2O or D2O/MeCN: 15/1) was used as a co-solvent in order to dissolve the alkene in H2O and D2O.

^d Determined by ¹H NMR: error $\pm 3\%$.

Unlike the regioselectivity observed in intrazeolite¹¹ photooxidations, at the present system, there is no notable change in regioselectivity with that of the ${}^{1}O_{2}$ homogeneous solution behavior. A reasonable explanation of this result is that the mean pore diameter of silica and alumina surfaces, used in this work, is in the order of 70–80 Å, much larger than the corresponding zeolites of ca. 8 Å. This fact, as well as the absence of cations in the present system that could develop cation- π interactions, lead to the absence of any induced special conformational effects in the corresponding substrates.

In deuterated water the reaction conversion is higher than that in non-deuterated water. It is well established that the lifetime of ${}^{1}O_{2}$ is significantly longer in deuterated than protiated solvents. This solvent isotope effect has been used in the past as strong evidence for the involvement of ${}^{1}O_{2}$ in the reaction mechanism.¹²

The results from the irradiation of 2-(*E*)-2-phenyl-butene (2) with a variety of sensitizers and solvents are shown in Table 2. C_{60} on SiO₂ and C_{60} on Al₂O₃ effectively sensitize the photooxidation of 2 both in hexane and aceto-

nitrile. In hexane the allylic hydroperoxides **2a** and **2b** were formed exclusively, in 9:1 ratio, whereas in acetonitrile, along with allylic hydroperoxides **2a** and **2b**, small amounts of acetophenone (**2c**), and 1-phenyl-1,2-dimethyloxirane (**2d**) were formed. For comparison reasons, sensitized photooxygenations of **2** were also performed in the presence of three conventional sensitizers, rose Bengal (RB), methylene blue (MB) and 9,10-dicyanoanthracene (DCA). The first two, RB and MB, are well known singlet oxygen photosensitizers, while DCA, an electron deficient sensitizer, catalyzes the photooxidation reaction by both electron transfer and/or singlet oxygen mechanism depending on solvent polarity and substrate.¹³

Irradiation of **2** in the presence of MB or RB as the sensitizers gave exclusively a mixture of the two allylic hydroperoxides **2a** and **2b** in a ratio 9:1. Hydroperoxides **2a** and **2b** are typical singlet oxygen products. The ratio of the allylic hydroperoxides **2a** and **2b** has been shown to be independent on solvent polarity or the *para*-substitution of the phenyl ring of arylalkene **2**.¹⁴ These results are indicative of ¹O₂ mechanism. Addition of DABCO, which quenches the triplet state of C₆₀ as well as singlet oxygen,¹⁵ retarded the photocatalytic activity of both C₆₀/SiO₂ and C₆₀/Al₂O₃.

Furthermore, the DCA-sensitized photooxygenation of **2** in acetonitrile gave, apart of the allylic hydroperoxides **2a** and **2b**, appreciable amounts of acetophenone **2c**, (Table 2).

Acetophenone (**2c**) is most likely produced from 1,2-dimethyl-2-phenyl-1,2-dioxetane (Equation 2) which, under the reaction conditions, is expected to decompose to cleavage products **2c** and acetaldehyde. Epoxide **2d** could be formed by a mechanism similar to that suggested by Bartlett and Landis (Scheme 1).¹⁶ Analogous mechanistic rationalization has been reported previously on the DCA sensitized photooxygenation of diphenylethylene.¹³ Similarly, the C₆₀/SiO₂ and C₆₀/Al₂O₃ sensitized photooxygenation of **2** in acetonitrile gave, in addition to allylic hydroperoxides **2a** and **2b**, small amounts of epoxide **2d**. These results are consistent with both singlet oxygen and electron transfer mechanism.





To probe the C_{60}/SiO_2 and C_{60}/Al_2O_3 sensitized photooxygenation mechanism further and obtain additional information on the electron transfer efficiency of these surfaces, we photooxidized 1-methoxy-4-[1-(4-methoxyphenyl)vinyl]benzene (**3**).

Substrate **3** is appropriate for an electron transfer test since it is an electron rich olefin, not reactive under singlet oxygen conditions. As presented in Equation 3, the C_{60} /SiO₂ and C_{60} /Al₂O₃ sensitized photooxygenation of **3** in

Table 2 Sensitized Photooxidation of 2-(E)-2-Phenyl-butene (2)^a



Sensitizer ^b	Solvent	Irradiation time (min)	Conversion (%) ^c	Relative yields (%)		
				$2\mathbf{a} + 2\mathbf{b}^{c,d}$	2c ^c	2d ^c
Methylene blue	CHCl ₃	30	97	100	_	_
Rose bengal	MeCN	30	93	100	_	-
DCA	MeCN	30	99	80	20	_
C ₆₀ /SiO ₂ ^e	Hexanes	20	100	100	_	-
C ₆₀ /SiO ₂	MeCN	60	100	89	7	4
C ₆₀ /SiO ₂ (DABCO)	MeCN	80	0	_	_	-
C ₆₀ /Al ₂ O ₃ ^e	Hexanes	60	100	100	_	-
C ₆₀ /Al ₂ O ₃	MeCN	60	100	94	4	2
C ₆₀ /Al ₂ O ₃ (DABCO)	MeCN	80	0	_	_	-

^a Solutions of 0.03 M.

^b Solutions of 10⁻⁴ M.

^c The reaction was monitored by GC-MS on a Supelco capillary column (SPB-5, 30m) in a Shimatzu GCMS-QP5050 (CI mass detector). The error was 1%.

^d The product ratio **1a:1b** is, constant at 9:1, within experimental error.

^e Photocatalysts were prepared by literature methods.^{9,10}

acetonitrile gave exclusively and quantitatively the cyclic endoperoxide **3a**. In a previous work Gollnick and coworkers showed that DCA photosensitizes the exclusive formation of *endo*-peroxide **3a** under similar conditions to these reported here and shown in Equation $3.^{17}$ In a control experiment, free fullerene C₆₀ under identical conditions to those reported in Equation 3, gave no oxygenated dimer **3a**. Additionally, the production of **3a** was quenched when a small amount (<10% of the corresponding alkene) of 1,2,4-trimethoxybenzene was added to the reaction. This result is consistent with an electron transfer









mechanism, involving a donor **3** radical cation and the sensitizer radical anion, since it is well established that donor molecules with oxidation potentials lower than that of the oxidizing alkene, quench the electron transfer path from the alkene to DCA.¹³ It is not clear, at the moment, why the irradiation of C_{60} supported silica and alumina surfaces in acetonitrile promote electron transfer mechanism to arylalkene substrates whereas free C_{60} , under similar conditions, does not. It is reasonable to assume that special interactions may develop between C_{60} and alumina or silica surfaces. These interactions may play a crucial role on the electronic properties of the absorbed C_{60} molecule. In summary, we have shown that C_{60} supported on SiO₂ or Al₂O₃ sensitizes heterogeneously the photooxygenation of alkenes. With simple alkenes, which can undergo only singlet oxygen reactions, this mechanism operates efficiently producing allylic hydroperoxides. With arylalkenes, which can undergo electron transfer to give radical ions, both ${}^{1}O_{2}$ and/or ET mechanisms can operate. Which of these mechanisms will predominate depends on the particular arylalkene and the solvent polarity. Finally, we believe the fullerene C₆₀ supported on silica or alumina surfaces may be of general utility for laboratory use because a) it photosensitizes the oxidation of a variety of unsaturated compounds, b) the photoreaction is heterogeneous and therefore the catalyst can be easily removed by a simple filtration, c) the heterogeneous nature of the photoreactions overcome solubility problems of the photosensitizers, and d) remains stable at the photooxidation conditions.

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