JOURNAL OF
Materials
CHEMISTRY
Communication

Polysiloxane-supported fullerene derivative as a new heterogeneous sensitiser for the selective photooxidation of sulfides to sulfoxides by $^1O_2$

Daniel Latassa,[a] Olivier Enger,[a] Carlo Thilgen,[a] Tilo Habicher,[a] Heribert Offermanns[b] and François Diederich[a]

[a]*Laboratorium für Organische Chemie, ETH-Hönggerberg, CH-8093 Zürich, Switzerland.*
E-mail: diederich@org.chem.ethz.ch; Fax: (+41) 1-632-1109; Tel: (+41) 1-632-2992
[b]*Grünaustrasse 2, D-63457 Hanau, Germany*

Received 31st January 2002, Accepted 18th February 2002
First published as an Advance Article on the web 28th February 2002

A heterogeneous photosensitiser for the generation of singlet oxygen was synthesized by covalent attachment of a methanofullerene derivative to polysiloxane-based Deloxan® DAP beads and its performance in the photo-oxidation of sulfides to sulfoxides was investigated. As opposed to C_{60} and many of its derivatives, the heterogeneous sensitiser can be readily used in protic solvents such as methanol which makes the photooxygenation highly selective, affording good to excellent yields of sulfoxides with aliphatic and benzylic sulfides. Moreover, the sensitiser is easily recovered at the end of the reaction by simple filtration.

Recent improvements in the functionalisation of fullerenes[1] have significantly accelerated and broadened research on C_{60}-based advanced materials.[2] The carbon cages have been known for nearly a decade to be among the most efficient sensitisers for the generation of singlet oxygen.[3] In terms of chemical applications, a few literature reports are found on ene[4,5] and [4 + 2]cycloaddition[5,6] reactions of olefins with $^1O_2$ generated in the presence of fullerenes or fullerene derivatives as photosensitisers. An interesting reaction which has not received any particular attention in this context is the photooxygenation of sulfides[7] which, depending on the conditions, affords sulfoxides or sulfones.[8,9] Our interest in this chemical transformation was raised by the observation that a mono-adduct of C_{60} having thioether functionality was cleanly converted to the corresponding sulfone upon standing in CH_2Cl_2 solution under ambient conditions.[10] Chemical uses of $^1O_2$ produced by fullerenes are often hampered, however, by the limited solubility of the carbon cages in most solvents[11] or the difficult recovery of soluble fullerene derivatives at the end of the reaction. In contrast, polymer-based solid catalysts are easy to isolate and to recycle after use and they are currently a hot topic in both academic research and industrial applications.[12] We became interested in applying this concept to a fullerene-based heterogeneous photosensitiser[13] in a systematic study on the selective photooxidation of sulfides to sulfoxides by $^1O_2$. This reaction is best performed in polar solvents such as methanol[14] which is, however, a very poor solvent for fullerenes. Therefore, heterogeneous sensitisation by polymer-supported derivatives of C_{60} in methanol seemed quite advantageous.

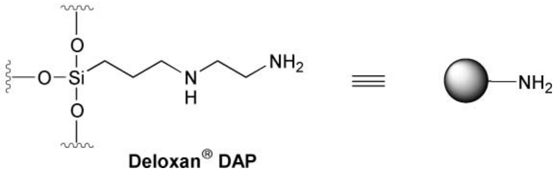


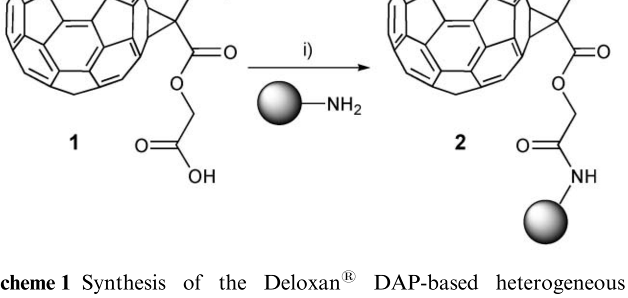
Fig. 1 Structural and schematic representation of Deloxan® DAP beads.

Our choice of solid support was Deloxan® DAP,[15] a macroporous (2.0–2.8 ml g^{-1}) polysiloxane bead (0.2–0.5 mm) with a high loading (1.7 mmol g^{-1}) of functionalisable primary amino groups developed by Degussa AG (Fig. 1). It has a high specific surface area (350–500 m^2 g^{-1}), can be handled in organic solvents as well as in water, and shows very good mechanical and chemical stability.

Concerning the sensitising moiety, fullerene-derived carboxylic acid **1** was synthesised as previously reported.[16] It was attached to the primary amino groups of Deloxan® DAP beads by DCC–HOBt-mediated coupling, thus affording the heterogeneous sensitiser **2** (Scheme 1). The well defined and homogeneous photoactive units consist of a mono-cyclopropanated derivative of C_{60} with a π-system that is only slightly perturbed, an important aspect with regard to the quantum yield of singlet oxygen production.[17]

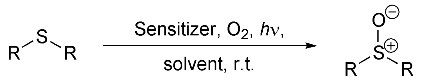
Attachment of the fullerene to the Deloxan® DAP beads was confirmed by IR and MALDI-TOF spectroscopies. According to the method of Berendsen and De Galan,[18] the fullerene loading of the beads **2** was determined from the micro-analytically measured percentage of carbon to be 3.7×10^{-4} mol g^{-1}, which corresponds to 22% of functionalised amino groups.

The performance of the heterogeneous sensitiser **2** in the photooxidation of sulfides to sulfoxides (Scheme 2) was tested on a variety of thioethers with alkyl, benzyl, or phenyl substituents. Methanol was used as the solvent of choice according



Scheme 1 Synthesis of the Deloxan® DAP-based heterogeneous photosensitiser **2**. *Reagents and conditions*: i) DCC, HOBt, THF, 0 °C → 25 °C, 3 d.

DOI: 10.1039/b201141g



Scheme 2 Photosensitised oxidation of sulfides to sulfoxides.

to the observation of Foote and Peters that protic solvents, minimising the physical quenching of singlet oxygen, afforded better yields of sulfoxides than aprotic ones.[8] Irradiation was carried out with a 150 W medium pressure Hg lamp and the progress of the reaction monitored by ^{1}H-NMR spectroscopy.

After filtration of the sensitiser beads **2** at the end of the reaction, the oxidation product was easily isolated from the starting material by flash chromatography. In each case, the sulfoxide was identified as the exclusive reaction product by comparison of its ^{1}H-NMR spectrum to that of an authentic sample.

Photooxygenation of di(*n*-octyl), dibenzyl, and benzyl methyl sulfides, sensitised by **2**, afforded the corresponding sulfoxides in good to very good yields (Table 1, Entries 1, 6, and 8). It is remarkable that no side or cleavage reactions were observed with the benzylic substrates, in particular the Pummerer rearrangement which is often described in this context.[19] Noticeably lower yields of sulfoxide were obtained from the five-membered heterocycle tetrahydrothiophene (52%, Table 1, Entry 5) and from diisopropyl sulfide (28%, Table 1, Entry 4).

In accordance with many literature reports[20] almost complete lack of reactivity was observed for diphenyl sulfide which afforded only traces of sulfoxide (Table 1, Entry 7). The markedly reduced nucleophilicity of sulfur in this case, combined with an increase in steric hindrance as compared to di(*n*-alkyl) sulfides may account for this result. Replacement of one aryl group by an alkyl group activates the substrate to some extent as observed for methyl phenyl sulfide (27%, Table 1, Entry 9).

At the end of the reaction, the heterogeneous sensitiser **2** was easily recovered by filtration and recycled by washing (MeOH, CH_2Cl_2, Et_2O) and drying. Reuse in subsequent runs still afforded clean sulfoxides but in noticeably lower yields, showing that the effectiveness of the sensitiser gradually decreases. As an example, di(*n*-octyl) sulfide provided 98% of the corresponding sulfoxide in the first run, and after recycling of **2**, 60% and 54% in a second and third run, respectively. This may be related to progressive oxidation of the active chromophore[21] or to cleavage of fullerene units from the beads.[22]

A few control reactions were run to ascertain the relevance of the chosen combination of the heterogeneous photosensitiser **2** and the protic solvent methanol. When the photooxygenation of di(*n*-octyl) sulfide was carried out in the presence of crystalline C_{60} powder which is virtually insoluble in methanol,[11] the yield of sulfoxide was only 7% as compared to 98% obtained with sensitiser **2** (Table 1, Entries 2 and 1). This result can be explained by the very small amount of solubilised fullerene or the limited accessible surface of the C_{60} crystallites. In contrast, the total surface of the macroporous sensitiser **2**, carrying the photoactive C_{60} units, is very much larger and, in addition, the appended fullerenes are presumably not aggregating, which makes them easily accessible to the reagents. When toluene, which is a much better solvent for fullerenes, was used in combination with pure C_{60} as sensitiser, small amounts of sulfoxide and sulfone were produced (Table 1, Entry 3). Finally, photooxygenation of di(*n*-butyl) sulfide in the presence of unmodified Deloxan® DAP beads—*i.e.* not carrying any fullerene residues—afforded only traces of sulfoxide. This clearly shows that the beads themselves, or any impurity that might be included, did not have a photosensitising effect.

Table 1 Oxidation of sulfides to sulfoxides by $^1O_2$ generated in the presence of **2** or C_{60} as photosensitisers.[a]

Entry	Substrate	Sensitiser	Solvent	Time/h	Yield (%)[b]
1	$(n\text{-}C_8H_{17})_2S$	**2**	MeOH	2	98
2	$(n\text{-}C_8H_{17})_2S$	C_{60} (cryst.)	MeOH	6	7
3	$(n\text{-}C_8H_{17})_2S$	C_{60}	Toluene	3	Mixture[d]
4	Pr^i_2S	**2**	MeOH	4	28
5	THT[c]	**2**	MeOH	6	52
6	Bn_2S	**2**	MeOH	8	98
7	Ph_2S	**2**	MeOH	4	Traces
8	BnMeS	**2**	MeOH	4	90
9	MePhS	**2**	MeOH	4	27

[a] Conditions: see experimental part. [b] Isolated yields of sulfoxide. [c] THT = Tetrahydrothiophene. [d] Minor amounts of sulfoxide and sulfone.

In summary, we have prepared a polysiloxane-supported fullerene derivative (**2**) as a new heterogeneous photosensitiser for the generation of singlet oxygen and proven its effectiveness in the photooxygenation of sulfides. Preliminary studies have shown that these substrates are converted to sulfoxides with high selectivity and in excellent to fair yields by singlet oxygen generated in methanol in the presence of **2**. The protic solvent methanol plays a decisive role in terms of product selectivity. This emphasises the utility of a heterogeneous fullerene-derived sensitiser combining the high quantum yields for $^1O_2$ generation of mono-functionalised C_{60} with its dispersion at the molecular level. In addition, the heterogeneous sensitiser **2** can easily be recycled, but the gradual decrease in activity observed in subsequent reactions needs to be addressed in further studies.

Typical experimental procedure exemplified by the photooxidation of di(n-octyl) sulfide to di(n-octyl) sulfoxide. Molecular oxygen was bubbled through a suspension of the heterogeneous photosensitiser **2** (13 mg beads ≡ 4.9 μmol functionalised fullerene ≡ 1 mol% in relation to sulfide) in MeOH (25 ml) at 25 °C. Di(*n*-octyl) sulfide (0.49 mmol) was added and the mixture stirred and irradiated with a continuously water-cooled Heraeus TQ 150 W medium pressure mercury lamp located at 5 cm of the pyrex glass reactor. After 2 h, **2** was filtered off, washed with MeOH (2 × 25 ml), CH_2Cl_2 (25 ml), and Et_2O (25 ml) and dried prior to reuse (10^{-5}–10^{-7} mbar, 25 °C, 12 h). The filtrate was evaporated *in vacuo* and the sulfoxide was separated from the starting material by flash chromatography (SiO_2, hexane–AcOEt 3 : 2). White solid (132 mg, 98%). Mp 71–72 °C (lit.[23] 71–72 °C). IR (KBr): 2911m, 2844w, 1466s, 1088m, 1005s, 933w, 722m. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.87 (t, J = 6.9, 6 H, CH_3), 1.27–1.29 (m, 16 H, CH_2), 1.34–1.45 (m, 4 H, CH_2), 1.72–1.79 (m, 4 H, CH_2), 2.59–2.70 (m, 4 H, CH_2). ^{13}C-NMR ($CDCl_3$, 75MHz): 14.07, 22.65 (×2), 28.96, 29.07, 29.22, 31.79, 52.58. FAB-MS: 275.2 (89, MH^+), 297.2 (100, $[M + Na]^+$).

Acknowledgement

We are grateful to Degussa AG and the Swiss National Science Foundation for financial support and to Degussa AG for providing the Deloxan® DAP beads. We also thank Dr. Stephan Wieland for fruitful discussions.

Notes and references

1 *Fullerenes and Related Structures*, ed. A. Hirsch, *Top. Curr. Chem.*, **Vol. 199**, Springer-Verlag, Berlin, 1999, p. 1; S. R. Wilson, D. I. Schuster, B. Nuber, M. S. Meier, M. Maggini, M. Prato and R. Taylor, in *Fullerenes: Chemistry, Physics, and Technology*, ed. K. M. Kadish and R. S. Ruoff, Wiley Interscience, New York, 2000, p. 91.

2 M. Prato, *J. Mater. Chem.*, 1997, **7**, 1097; N. F. Goldshleger, *Fullerene Sci. Technol.*, 2001, **9**, 255.

3 M. Terazima, N. Hirota, H. Shinohara and Y. Saito, *J. Phys. Chem.*, 1991, **95**, 9080; C. S. Foote, *Top. Curr. Chem.*, 1994, **169**,

347; T. Nagano, K. Arakane, A. Ryu, T. Masunaga, K. Shinmoto, S. Mashiko and M. Hirobe, *Chem. Pharm. Bull.*, 1994, **42**, 2291; C. S. Foote, in *Light-Activated Pest. Control*, ACS Symposium Series, American Chemical Society, Washington DC, 1995, **616**, p. 17; M. Orfanopoulos and S. Kambourakis, *Tetrahedron Lett.*, 1995, **36**, 435; N. Tagmatarchis, H. Kato and H. Shinohara, *Phys. Chem. Chem. Phys.*, 2001, **3**, 3200.

4 M. Orfanopoulos and S. Kambourakis, *Tetrahedron Lett.*, 1994, **35**, 1945; Y.-Z. An, A. L. Viado, M.-J. Arce and Y. Rubin, *J. Org. Chem.*, 1995, **60**, 8330; A. Fukuoka, K. Fujishima, M. Chiba, A. Yamagishi, S. Inagaki, Y. Fukushima and M. Ichikawa, *Catal. Lett.*, 2000, **68**, 241.

5 H. Tokuyama and E. Nakamura, *J. Org. Chem.*, 1994, **59**, 1135; Y.-Z. An, G. A. Ellis, A. L. Viado and Y. Rubin, *J. Org. Chem.*, 1995, **60**, 6353; N. Tagmatarchis and H. Shinohara, *Org. Lett.*, 2000, **2**, 3551; N. Tagmatarchis, H. Shinohara, M. Fujitsuka and O. Ito, *J. Org. Chem.*, 2001, **66**, 8026.

6 H. Irngartinger, A. Weber and T. Escher, *Eur. J. Org. Chem.*, 2000, 1647; T. Takabatake, T. Miyazawa, M. Hasegawa and C. S. Foote, *Tetrahedron Lett.*, 2001, **42**, 987.

7 G. O. Schenck and C. H. Krauch, *Angew. Chem.*, 1962, **74**, 510; N. Ishibe, M. Odani and K. Teramura, *J. Chem. Soc., Chem. Commun*, 1970, 371; A. Miyake and M. Tomoeda, *J. Chem. Soc., Chem. Commun.*, 1970, 240; W. Adam and J.-C. Liu, *J. Chem. Soc., Chem. Commun.*, 1972, 73; R. W. Murray and S. L. Jindal, *J. Org. Chem.*, 1972, **37**, 3516; F. E. Stary, S. L. Jindal and R. W. Murray, *J. Org. Chem.*, 1975, **40**, 58; W. Adam and H. J. Eggelte, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 765; W. Ando, S. Kohmoto, H. Miyazaki, K. Nishizawa and H. Tsumaki, *Photochem. Photobiol.*, 1979, **30**, 81.

8 C. S. Foote and J. W. Peters, *J. Am. Chem. Soc.*, 1971, **93**, 3795.

9 C. L. Gu and C. S. Foote, *J. Am. Chem. Soc.*, 1982, **104**, 6060; F. Jensen and C. S. Foote, *J. Am. Chem. Soc.*, 1987, **109**, 1478; E. L. Clennan and X. Chen, *J. Am. Chem. Soc.*, 1989, **111**, 8212; E. L. Clennan, K. A. Oolman, K. Yang and D.-X. Wang, *J. Org. Chem.*, 1991, **56**, 4286; A. Greer, F. Jensen and E. L. Clennan, *J. Org. Chem.*, 1996, **61**, 4107; E. L. Clennan, D. Wang, C. Clifton and M.-F. Chen, *J. Am. Chem. Soc.*, 1997, **119**, 9081; S. M. Bonesi and A. Albini, *J. Org. Chem.*, 2000, **65**, 4532.

10 O. Enger and F. Diederich, unpublished results.

11 M. V. Korobov, in *Fullerenes: Chemistry, Physics, and Technology*, ed. K. M. Kadish and R. S. Ruoff, Wiley Interscience, New York, 2000, p. 53, and references cited therein.

12 F. Balkenhohl, C. von dem Bussche-Hünnefeld, A. Lansky and C. Zechel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2288; J. S. Früchtel and G. Jung, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 17; L. A. Thompson and J. A. Ellman, *Chem. Rev.*, 1996, **96**, 555; S. R. Wilson and A. W. Czarnik, in *Combinatorial Chemistry*, ed. K. M. Kadish and R. S. Ruoff, Wiley, New York, 1997; D. J. Maly, L. Huang and J. A. Ellman, *ChemBioChem*, 2002, **3**, 16.

13 J. L. Bourdelande, J. Font and R. González-Moreno, *Helv. Chim. Acta*, 2001, **84**, 3488.

14 E. L. Clennan and K. Yang, *Tetrahedron Lett.*, 1993, **34**, 1697.

15 Trademark of Degussa AG, Düsseldorf, Germany; U. Deschler, P. Kleinschmit and P. Panster, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 236.

16 J.-F. Nierengarten, A. Herrmann, R. R. Tykwinski, M. Rüttimann, F. Diederich, C. Boudon, J.-P. Gisselbrecht and M. Gross, *Helv. Chim. Acta*, 1997, **80**, 293; J.-F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J.-P. Gisselbrecht, C. Boudon and M. Gross, *Helv. Chim. Acta*, 1997, **80**, 2238.

17 F. Prat, R. Stackow, R. Bernstein, W. Qian, Y. Rubin and C. S. Foote, *J. Phys. Chem. A*, 1999, **103**, 7230.

18 G. E. Berendsen and L. De Galan, *J. Liquid Chromatogr.*, 1978, **1**, 561.

19 E. J. Corey and C. Ouannès, *Tetrahedron Lett.*, 1976, **47**, 4263; S. M. Bonesi, M. Mella, N. d'Alessandro, G. G. Aloisi, M. Vanossi and A. Albini, *J. Org. Chem.*, 1998, **63**, 9946; S. M. Bonesi, R. Torriani, M. Mella and A. Albini, *Eur. J. Org. Chem.*, 1999, 1723; S. M. Bonesi, M. Freccero and A. Albini, *J. Phys. Org. Chem.*, 1999, **12**, 703; A. Toutchkine and E. L. Clennan, *J. Am. Chem. Soc.*, 2000, **122**, 1834.

20 W. Ando and T. Takata, in *Singlet* O_2, ed. A. A. Frimer, CRC Press, Boca Raton, 1985, p. 1, and references cited therein.

21 D. I. Schuster, P. S. Baran, R. K. Hatch, A. U. Kahn and S. R. Wilson, *Chem. Commun.*, 1998, 2493.

22 T. Hamano, K. Okuda, T. Mashino, M. Hirobe, K. Arakane, A. Ryu, S. Mashiko and T. Nagano, *Chem. Commun.*, 1997, 21.

23 M. Hirano, S. Yakabe, S. Itoh, J. H. Clark and T. Morimotoa, *Synthesis*, 1997, 1161.