Pergamon

Tetrahedron Letters, Vol. 36, No. 3, pp. 435-438, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(94)02277-1

Chemical Evidence of Singlet Oxygen Production from C60 and C70 in Aqueous and Other Polar Media.

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Abstract : Fullerene C_{60}*- and* C_{70}*-surfactant systems sensitize the photooxygenation of singlet oxygen acceptors in aqueous and other polar media.*

The photochemical and photophysical properties of spheroidal carbon molecules "Fullerenes" C_{60} and C_{70} have recently received intensive attention.[1-3] It was shown recently that the triplet state of C_{60} sensitizes singlet oxygen formation in high yields[1]. We and others reported recently that electron deficient Fullerenes C_{60} and C_{70} are useful sensitizers in preparative photooxygenation reactions by the intermediacy of singlet oxygen.[4,5] Unfortunately the unfunctionalized C_{60} molecules possess poor solubility in nonpolar solvents and not at all in polar solvents.[6] This fact limits their photochemical, electrochemical and synthetic usefulness in many media. However the preparation of polar functional derivatives make possible the indirect study of their properties in polar media. For example, carboxylic Fullerene derivatives have been used to cut DNA and to inhibit enzyme activity under photolytic conditions.[7] Furthermore, the solubilization of C_{60} molecules in polar solvents and particularly in water has been recently achieved by a number of investigators. Cyclodextrins[8], as well as micellar and lipid systems enhance the solubility of C_{60} in water.[9, 10] In two recent reports, the solubility and absorption spectra of C_{60} in water with the aid of surfactants, such as poly vinylpyrrolidone (PVP) and Triton X-100, have been thoroughly studied.[11-12]

We now report the sensitized photooxygenation of 4-[2-(3-methyl-2-butenyl)] benzoic acid-sodium salt **1** and 2-methyl-2-butene by C_{60}-surfactant system in aqueous media as well as in polar solvents, such as dimethylsulfoxide, methanol, acetonitrile and acetone/toluene. The photooxygenations were carried out in a 3.0ml pyrex cell containing a solution of the carboxylic salt **1**[13] in water or DMSO with C_{60} and C_{70} as the sensitizer and Triton X-100 and poly vinylpyrrolidone (PVP) as the surfactants.[14] Dry molecular oxygen was bubbled through the solution at 0°C (ice-water bath), and a Xenon lamp Variac-Eimac Cermax 300-W was used as the light source. At the end of each photolysis, the reaction mixture was extracted three times with ether and dichloromethane to remove the Triton X-100 from the aqueous phase.

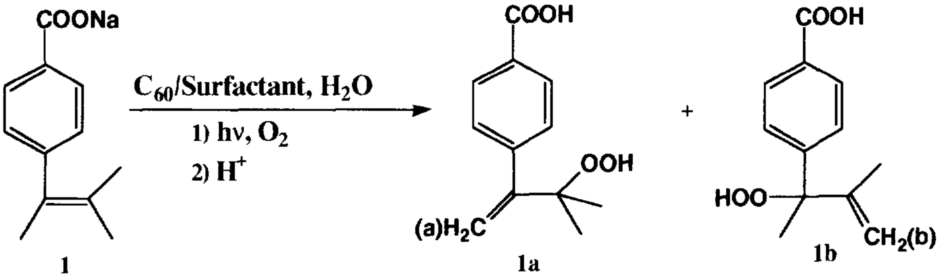
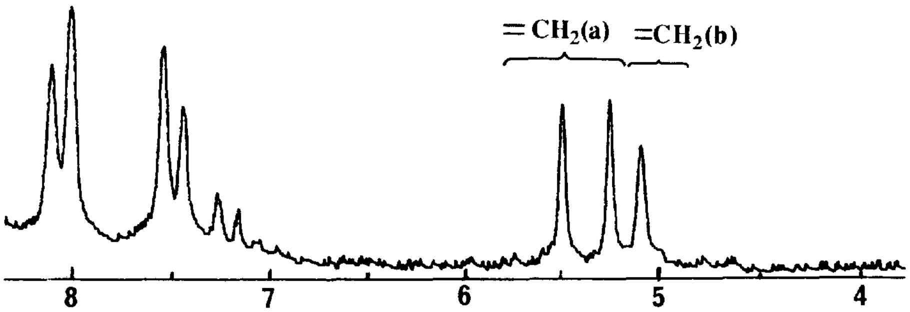


Table 1. Sensitized Photooxygenation of Carboxylic salt **1**[a], in H_2O, DMSO and $CDCl_3$

Sensitizer	Solvent	T(min)	% Conversion	**1a : 1b**[b]
C_{60}[c]/Triton[d]	H_2O	150	58	20:80
" "	DMSO	90	95	18:82
C_{60}/PVP[e]	H_2O	150	80	30:70
C_{60}[f]	$CDCl_3$	20	>97	18:82
C_{70}[c]/Triton[g]	H_2O	150	70	20:80
RB	D_2O	120	65	18:82

[a] Solutions of 0.2M. [b] The product ratio was determined by ^1H NMR integration of the olefinic peaks, after acidification, at δ ($CDCl_3$) 5.51–5.28 of 2Ha and 5.13 ppm of 2Hb. The error was ± 5%. [c] C_{60} and C_{70} were purified from the soot (Polygon Enterprise Inc.) by a literature procedure.[15] HPLC analysis showed >99% purity in C_{60} and C_{70}. [d] The ratio of [C_{60}]:[Triton] is $5X10^{-4}$-10^{-}.[4] [e] 200mg of PVP in 7ml of $3X10^{-4}$M C_{70} in H_2O. [f] Solutions of 10^{-4} M. [g] Solutions of $4X10^{-4}$M C_{70} and 0.4M Triton.



^1H NMR of the C_{60}-PVP/H_2O sensitized photooxygenation products **1a** and **1b** in $CDCl_3$. Aromatic region shows a 80% conversion of **1** to **1a** and **1b**.

Subsequent acidification and extraction of the aqueous phase with ether gave various amounts of photooxygenation products **1a**, **1b** and starting material, as the free acids. To avoid any aggregation of C_{60}, the ratio of $[C_{60}]$: [Triton] concentration was kept at low values, about $10.^{-4}$ In a recent study, UV-Vis spectra and "small angle neutron scattering" (SANS) experiments have shown that as the concentration of Triton X-100 decreases, the monomeric state of C_{60} in water passed to colloidal dispersion.[12]

As seen from Table 1, the C_{60} /Triton sensitized ene photooxygenation[16] of carboxylic salt **1**, proceeds even in polar media such as water and dimethyl sulfoxide. C_{60} is also solubilized in water in the presense of PVP as the surfactant. Photooxygenation of **1** by C_{60}-PVP in aqueous media is also efficient. PVP is a more attractive surfactant because it requires much lower quantities than that of Triton surfactant and the separation from the reaction mixture is easier. Similar results have been obtained when a C_{70}/Triton system has been used as the sensitizer. Furthermore, all these ene reactions show a strong preference for hydrogen abstraction on the methyl group that is geminal to the larger phenyl substituent of the alkene. Similar geminal selectivity in non polar solvents with singlet oxygen producing sensitizers has been recognized recently and rationalized by invoking a number of mechanisms.[17-19]

As with C_{60} and C_{70} as sensitizers, photooxygenation of **1** in the presence of Rose Bengal (RB) gave as the only observable products **1a** and **1b** in the same ratio as with C_{60} and C_{70}. This result shows that sensitized photooxygenation by Fullerenes C_{60} and C_{70} is identical with that by RB, a well known sensitizer for the generation of singlet oxygen. It is constructive to note that the surfactant solubilizing sphere around C_{60} does not affect either the production of $^1O_2$ or the reaction of the latter with the various singlet oxygen acceptors. The fact that the stereoselectivity is independent of the state of C_{60} (free or surfactant solubilized) indicates that $^1O_2$ reacts free of any stereochemical dependence of the C_{60} sensitizer.

Similarly, photooxygenation of trimethylethylene, sensitized by C_{60}/Triton in polar solvents such as methanol, acetonitrile and toluene/acetone in a ratio 1:2, is also efficient. The reaction was monitored by GC analysis and the characteristic ene adducts were observed,[4] after reduction with triphenylphosphine.In conclusion, we have shown that C_{60}-surfactant system is an efficient water soluble sensitizer. Its stability under the photolysis conditions and its high efficiency in preparative scale photooxygenations, rank it among the few useful water soluble sensitizers.

Acknowledgments. We thank professor G. J. Karabatsos for valuable comments and professor C. S. Foote for a generous donation of 100g of Fullerenes soot. The financial support of M & S. Hourdakis SA. and NATO grant No CRG 931419 are also acknowledged.

Dedicated to Professor Charles W. Jefford on the occasion of his 65th birthday.

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13. The free acid of **1** was prepared by coupling of the Grignard reagent of 2-bromopropionate with 4-bromo-acetophenone. Subsequent dehydration with p-toluenesulfonic acid, transmetallation with butylithium and carboxylation with carbon dioxide (dry ice) gave the free acid **1** in good yield. ^1H NMR in $CDCl_3$, δ(ppm) : 1.61 (s, 3H), 1.84 (d, 3H), 1.98 (s, 3H), 7.22 (d, 2H), 8.06 (d, 2H).
14. Triton X-100 (Merck) is a non-toxic detergent $(CH_3)_3CCH_2C(CH_3)_2\text{-}C_6H_4(OCH_2CH_2)_xOH$, where x=10(avg). Polyvinylpyrrolidone (PVP) is a cross-linked powder, Avg. M. W. 24, 000 (Aldrich).
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(*Received in UK* 15 *July* 1994; *accepted* 16 *November* 1994)