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

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Abstract : Fullerene C₆₀- and C₇₀-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" C₆₀ and C₇₀ have recently received intensive attention.¹⁻³ It was shown recently that the triplet state of C₆₀ sensitizes singlet oxygen formation in high yields¹. We and others reported recently that electron deficient Fullerenes C₆₀ and C₇₀ are useful sensitizers in preparative photooxygenation reactions by the intermediacy of singlet oxygen.^{4,5} Unfortunately the unfunctionalized C₆₀ 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 C₆₀ molecules in polar solvents and particularly in water has been recently achieved by a number of investigators. Cyclodextrins⁸, as well as micellar and lipid systems enhance the solubility of C₆₀ in water.^{9, 10} In two recent reports, the solubility and absorption spectra of C₆₀ 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 C₆₀-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 C₆₀ and C₇₀ 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.

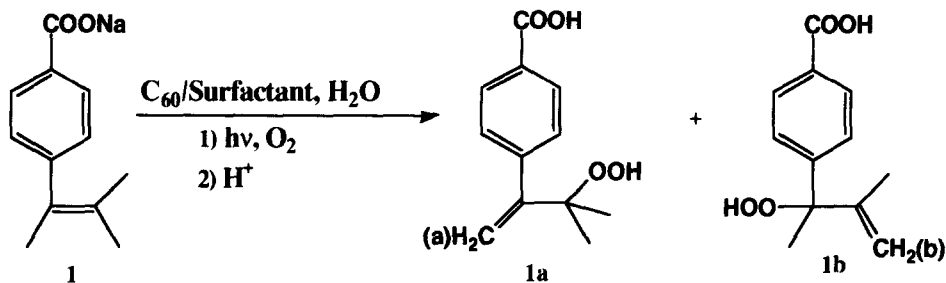
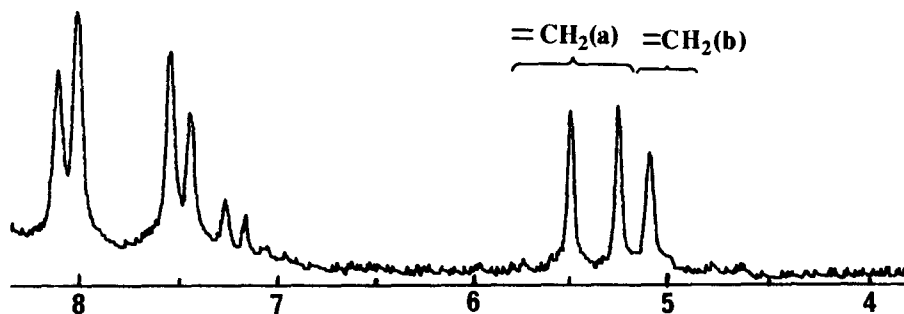


Table 1. Sensitized Photooxygenation of Carboxylic salt **1a**, in H₂O, DMSO and CDCl₃

Sensitizer	Solvent	T(min)	% Conversion	1a : 1b ^b
C ₆₀ ^c /Triton ^d	H ₂ O	150	58	20:80
" "	DMSO	90	95	18:82
C ₆₀ /PVPe	H ₂ O	150	80	30:70
C ₆₀ ^f	CDCl ₃	20	>97	18:82
C ₇₀ ^c /Triton ^g	H ₂ O	150	70	20:80
RB	D ₂ O	120	65	18:82

^a Solutions of 0.2M. ^bThe product ratio was determined by ¹H NMR integration of the olefinic peaks, after acidification, at δ (CDCl₃) 5.51–5.28 of 2Ha and 5.13 ppm of 2Hb. The error was \pm 5%. ^cC₆₀ and C₇₀ were purified from the soot (Polygon Enterprise Inc.) by a literature procedure.¹⁵ HPLC analysis showed >99% purity in C₆₀ and C₇₀. ^dThe ratio of [C₆₀]:[Triton] is 5X10⁻⁴-10⁻⁴. ^e200mg of PVP in 7ml of 3X10⁻⁴M C₇₀ in H₂O. ^fSolutions of 10⁻⁴M. ^gSolutions of 4X10⁻⁴M C₇₀ and 0.4M Triton.



¹H NMR of the C₆₀-PVP/H₂O sensitized photooxygenation products **1a** and **1b** in CDCl₃. 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 C₆₀, the ratio of [C₆₀] : [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 C₆₀ in water passed to colloidal dispersion.¹²

As seen from Table 1, the C₆₀ /Triton sensitized ene photooxygenation¹⁶ of carboxylic salt **1**, proceeds even in polar media such as water and dimethyl sulfoxide. C₆₀ is also solubilized in water in the presense of PVP as the surfactant. Photooxygenation of **1** by C₆₀-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 C₇₀/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 C₆₀ and C₇₀ 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 C₆₀ and C₇₀. This result shows that sensitized photooxygenation by Fullerenes C₆₀ and C₇₀ 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 C₆₀ does not affect either the production of ¹O₂ or the reaction of the latter with the various singlet oxygen acceptors. The fact that the stereoselectivity is independent of the state of C₆₀ (free or surfactant solubilized) indicates that ¹O₂ reacts free of any stereochemical dependence of the C₆₀ sensitizer.

Similarly, photooxygenation of trimethylethylene, sensitized by C₆₀/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 C₆₀-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.

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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, transmetalation with butyllithium and carboxylation with carbon dioxide (dry ice) gave the free acid **1** in good yield. ¹H NMR in CDCl₃, 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 (CH₃)₃CCH₂C(CH₃)₂-C₆H₄(OCH₂CH₂)_xOH, where x=10(avg). Polyvinylpyrrolidone (PVP) is a cross-linked powder, Avg. M. W. 24, 000 (Aldrich).
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