Reactivity of Fullerenes with Chemically Generated Singlet Oxygen

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Non-reactivity of fullerene C_{60} in its ground state with electronically excited molecular oxygen, $O_2(^1\Delta_g)$, chemically generated externally, has been observed, which could contribute to a better understanding of the fullerene photooxidation mechanisms.

The formation of fullerene–oxygen adducts in fullerene samples containing oxygen irradiated by ultraviolet or visible radiation has been observed in solution[1–3] as well as in the solid state.[4,5] According to majority opinion, these adducts have epoxide structures.[2,3] However, oxa-bridged [10]annulene[6,7] and cage-opened dicarbonyl[4] structures respectively, have also been proposed. These results indicate that the nature of fullerene–oxygen adducts depends strongly on the experimental conditions of their formation and on elementary steps in the oxidation mechanisms. Taliani *et al.*[4] have proposed a relatively simple mechanism of fullerene photooxidation, in which the formation of fullerene–oxygen adducts during the irradiation of a thin film of C_{60} by means of an Ar^+ laser is caused by the reaction of C_{60} with the electronically excited oxygen in a singlet delta state, $O_2(^1\Delta_g)$ (hereafter abbreviated as $^1O_2$), which is generated in fullerene films *via* laser-excited C_{60} triplet energy transfer to the ground state of molecular oxygen $O_2(^3\Sigma_g)$ in the surrounding atmosphere. It is expected that $^1O_2$ cleaves a C=C bond, thus opening the fullerene cage with an entrance with two adjacent carbonyl groups. A more complex view has been presented by Kroll *et al.*,[8] which has been confirmed by Ito *et al.*[9] They[8] speculated that the fullerene cages are attacked by reactive oxygen species (O, O^-, O_2^*) created through the decay of O_2^- produced by the capture of low-energy electrons generated in oxygen–fullerene films during irradiation by a focused projector lamp.

We now report the results of experimental work aimed to prove the above mechanism of fullerene oxidation, thus determining whether the singlet oxygen can react with fullerenes in their ground state only or whether electronic excitation of the fullerene cage is necessary for an observable reaction. We exposed small crystallites of fullerenes to a high concentration of $^1O_2$ which was chemically generated externally. Similar experiments were carried out in the 1960s to study the role of $^1O_2$ in dye-photosensitized autooxidation of various organic molecules in solution.[10–12]

We used μm sized crystallites of fullerene–solvent clathrates grown from 5 ml of either toluene or *n*-hexane solutions of a fullerene mixture (Aldrich: 90% C_{60}, 10% C_{70}, with small amounts of higher fullerenes and $C_{60}O$; concentration 1.4×10^{-5} mol l^{-1} C_{60}) by evaporation in a Petri dish under atmospheric pressure. These samples were exposed to a stream of singlet oxygen produced in a generator, described elsewhere,[13,14] by the reaction of gaseous chlorine with an alkaline solution of hydrogen peroxide. The rate of chlorine production was 1.5 mmol s^{-1} and the partial pressure of singlet oxygen at the sample was 25 Pa. The sample exposure time was 90 minutes. The concentration of singlet oxygen was determined by measurement of its fundamental emission at 1.27 μm.

The exposed, and unexposed (reference), samples were dissolved in 6 ml of the corresponding solvent and analysed by UV–VIS spectrometry and HPLC [C18 reverse phase column; toluene–methanol (1 : 1); detection at 330 nm]. The spectra and the chromatograms of the exposed and the unexposed samples for both the solvents were identical. Fig. 1 shows liquid chromatograms of *n*-hexane samples (*a*) exposed and (*b*) unexposed to singlet oxygen. The areas of the peaks at 4.7 min corresponding to $C_{60}O$ are identical. This peak arises from the $C_{60}O$ formed in the fullerene sample during the early stages of its production, preparation and handling. Chromatogram (*c*), shown for comparison only, is of a fullerene solution in toluene through which ground state molecular oxygen had been bubbled for 30 minutes, followed by irradiation by 1000 shots of an XeCl laser (the energy of a 30 ns long single pulse was 130 mJ and the power density at a quartz cell window was 4.1 MW cm^{-2}). The $C_{60}O$ concentration in this case was twice as large as in (*a*) and (*b*). As the use of a lamp can lead to irreproducible photochemical behaviour of fullerenes in solution,[15] the results in Fig. 1(*c*) were obtained by use of an excimer laser.[16]

From these results we can conclude that the reactivity of fullerene–solvent clathrate microcrystallites in their ground state with externally generated singlet oxygen was extremely

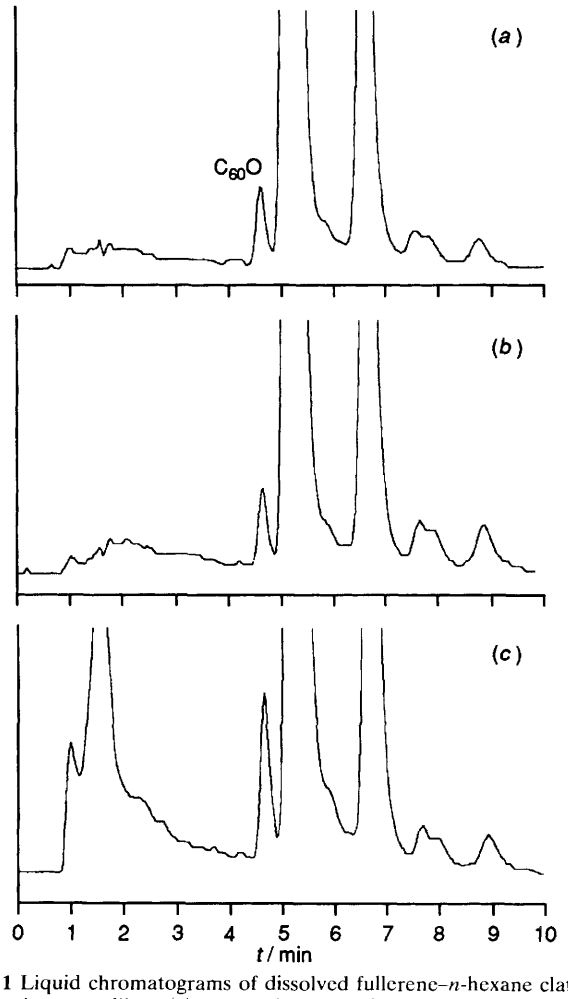

Fig. 1 Liquid chromatograms of dissolved fullerene–*n*-hexane clathrate microcrystallites (*a*) exposed to chemically generated singlet oxygen ($^1O_2$) for 90 min and (*b*) unexposed; (*c*) toluene fullerene solution bubbled for 30 min by ground state molecular oxygen ($^3O_2$), then irradiated by an XeCl laser. The peaks with t_R 5.2 and 6.8 min correspond to C_{60} and C_{70}, respectively; t_R for $C_{60}O$ is 4.7 min. The peaks at 7.9 and 8.9 min are due to higher fullerenes and peaks at low t_R in (*c*) are due to low-molecular mass photodecomposition products.

low at room temperature, despite its high concentration. The fullerene photooxidation mechanism given by Taliani *et al.*[4] should thus be supplemented by the assumption that the fullerene cage must itself be electronically excited to be able to react with singlet oxygen. More generally, the lack of chemical reactivity of fullerene triplets expected by Wilson *et al.*[17] (because they are of low-energy, long-lived and highly delocalized) seems to be questionable. As to the photooxidation by Kroll *et al.*,[8] they allege that highly delocalized electrons of photoexcited C_{60} may not be very effective in the enhancement of fullerene–oxygen reactions either. It is possible that these excitations not only cause 'feeble noise' in the fullerene structure, but under suitable conditions they may 'open the door' into the fullerene cage.[18] On the other hand, the extremely low reactivity of ground-state fullerenes with singlet oxygen may be beneficial for their use as photosensitizers producing singlet oxygen in systems which are relevant to biochemistry[19] and preparative organic chemistry.[20] Our results indicate that irradiation conditions (wavelength, power density, choice of quencher, *etc.*) in this type of experiment could be optimized for the minimum formation of fullerene–oxygen adducts at a relatively high rate of singlet oxygen production.

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