C_{60} degrades to $C_{120}O$

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At ambient temperature and in the solid state C_{60} degrades to $C_{120}O$ which is present in up to *ca.* 1% concentration in each of thirteen differently sourced samples examined; traces of $C_{120}O_2$ have also been detected.

When pure [60]fullerene was first obtained,[1] it was observed that films which had been left on the surface of a flask for a few days would not redissolve easily, successive extracts being increasingly dilute and more pink in colour relative to the magenta of the pure fullerene.[2] Oxidation was suspected, but further analysis was not possible at that time.

Recently, we have found that completely insoluble products are formed from fullerenes (especially higher fullerenes) on standing.[3,4] These were provisionally described as graphitic due to this insolubility,[3] but more recent work showed that graphitic planes are absent, and moreover, heating KBr discs of them produces matrix-isolated CO_2.[4] Evidently these derivatives contained oxygen, but no further details of the structures could be deduced.

[60]Fullerene, available now from numerous suppliers, comes with a stated purity. Given this assurance, fullerene researchers have had no need to examine the purity of the material. This has not been problematical because purification is usually affected at the derivative stage. Recently however, we found it necessary to check by HPLC (4.6 mm × 25 cm Cosmosil Buckyclutcher column, toluene eluent at 1 ml min^{-1}) the [70]fullerene level in a new batch of [60]fullerene. While the amount of [70]fullerene was virtually undetectable we were surprised to find a significant peak with a retention time of 14.6 min compared with [60]fullerene at 7.4 min, Fig. 1 ([70]fullerene elutes at 11.8 min under these conditions). The retention time was identical to that for an authentic sample[5] of $C_{120}O$ under our conditions. (NB. The retention times for fullerenes and derivatives vary slightly according to the ambient temperature, column condition, and injection volume, and for the above column/eluent/flow have been described[6] as 7.8 and 15.8 min for C_{60} and $C_{120}O$, respectively.) The eluent solution was straw-coloured, and removal of the toluene produced a brown film, which was much less soluble in toluene than either C_{60} or its oxides, further indicating it to be a dimeric species. Examination of twelve commercial samples from various suppliers, and also one of our own dating from 1990, showed that this component is present in *all* of them, with varying concentrations.

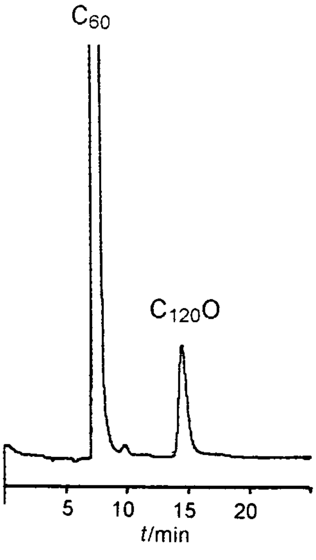
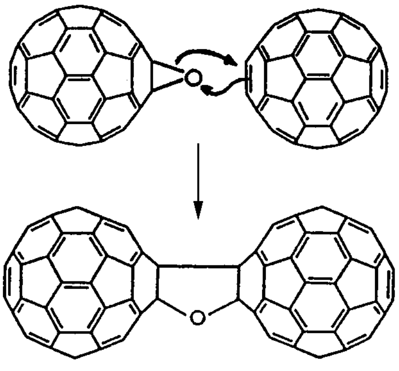


Fig. 1 HPLC of a 1 ml injection of a saturated toluene solution of C_{60}, showing $C_{120}O$ andthe absence of C_{70}.

Although an EI mass spectrum of the component showed just C_{60}, a MALDI-TOF mass spectrum proved it to be $C_{120}O$ (*m/z* 1457), and this was confirmed by comparison of the IR spectrum with that of an authentic sample.[5] The common bands are at 1632m, 1463m, 1456sh, 1429, 1384, 1307, 1218, 1183, 1166, 1101m, 1063, 1033m, 1016sh, 960, 849, 831, 807, 780, 765, 746, 711, 606, 589, 574, 551, 527 and 479 nm. The main bands in our spectrum have also been reported very recently.[7]

It is thus ironic that although various groups have gone to some trouble to prepare and isolate $C_{120}O$,[5,8,9] this was actually unnecessary because it is readily available in the first place, and we have been able to extract multimilligram quantities (which crystallise from carbon disulfide as black needles) from commercial C_{60} The literature preparation method consists of converting C_{60} to $C_{60}O$ which was separated and purified, the two reagents being then heated together for many hours, either in the solid state, or under reflux in 1,2-dichlorobenzene, which results in combination to give $C_{120}O$.

$C_{60}O$, which has been produced by oxidation of [60]fullerene under a variety of conditions *viz.* using photosensitizers,[10] chemically generated singlet oxygen,[11] dimethyldioxirane,[12] iodosobenzene/metal catalysts,[13] methyltrioxorhenium–hydrogen peroxide,[14] ozone,[15] 3-chloroperbenzoic acid,[16] and electrochemistry.[17] It is widely assumed that C_{60} undergoes oxidation to $C_{60}O$ on exposure to air, but we believe this has never been demonstrated. We consider that this does indeed happen, but given that the mono-oxide is strained and predicted to be unstable relative to $C_{120}O$,[18] it is quickly captured by a further C_{60} molecule in a [2 + 2] reaction (Scheme 1) to produce $C_{120}O$.



Scheme 1 Conjectured [2 + 2] cycloaddition mechanism for the formation of $C_{120}O$ from C_{60} and $C_{60}O$.

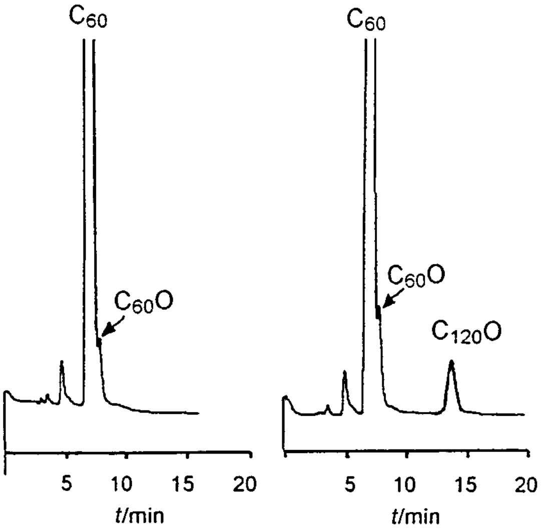


Fig. 2 HPLC traces of saturated toluene solutions (50 μl each) of a C_{60} sample: (a, left) HPLC purified; (b, right) the same material after exposure of the solid to daylight for 40 h.

The possibility that the observed $C_{120}O$ is formed during the arc-discharge process may be discounted since it elutes after [70]fullerene, yet samples in which it is present are entirely free of the latter. Removal of [70]fullerene by chromatographic purification would remove the later-eluting oxide as well. Moreover, given the different separation regimes used by different manufacturers (and none use alumina which was employed to purify our original in-house sample) it would be most surprising that no-one managed to remove any pre-existing $C_{120}O$. In order to provide further information on this point and to confirm our belief that the oxide results from a solid state reaction that occurs at ambient temperature, we exposed a sample of solid HPLC-purified C_{60} to air and daylight for 40 h. Fig. 2(a) and (b) show consecutive HPLC traces for saturated solutions of the solid before and after this exposure. The presence of the $C_{120}O$ peak in the exposed material is apparent, as is the increased intensity of the $C_{60}O$ peak. (The trace of the latter in the purified material arises during the handling and concentration of the HPLC eluent.)

Atmospheric oxidation of [60]fullerene beyond the monoxide stage is likely, giving *e.g.* $C_{60}O_2$ with capture by a further [60]fullerene to give $C_{120}O_2$. Indeed we find evidence of $C_{120}O_2$ in some of the samples, with a peak of retention time under our conditions of 16.9 min, identical to that of an authentic[6] sample. The concentration is however lower than that of $C_{120}O$ despite its formation being energetically more favourable.[18] We believe this is because $C_{60}O$, the $C_{60}O_2$ precursor, is rapidly converted to $C_{120}O$ before further oxidation can occur.

We suggest that $C_{120}O$ may add on further oxygens or $C_{60}O$ molecules (probably remote from the initial addition site, because of steric considerations) to give ultimately a polymer, which is very likely the insoluble oxygen-containing material that we have isolated from various fullerene samples.[3,4] In this connection we find that after a film of HPLC purified C_{60} had stood in daylight during four days, most (*ca.* 70%) would not redissolve readily in toluene (and some not at all). HPLC of the slightly soluble material showed the presence of four components with retention times either similar to, or considerably longer than, the dimeric species described above. This suggests that a mixture of oxygenated dimers and trimers is produced by the more aggressive oxidation, and we hope subsequently to examine these further.

Because the absorption coefficient of $C_{120}O$ is not known (and difficult to measure with any accuracy due to the extremely low solubility in hexane) the percentage present in the examined samples (which varies by a factor of *ca.* 5) is uncertain, but we visually estimate the maximum levels to be around 1%.

These results have consequences. First, they make it difficult to account for the reports[19] that C_{60} has been found to occur naturally. Secondly, the purity levels quoted by suppliers refer to the as-produced material, and are not characteristic of the condition at the time it is used. Thirdly, they make it essential to study the stability of products towards oxidation, if uses are to be found for fullerenes. We know from our own studies that some fullerene derivatives, such as phenylated fullerenes rapidly acquire oxygen on standing,[20] and this may be true for many other derivatives, whilst by contrast, some addends may actually inhibit oxidation. Resolution of this problem must feature amongst the goals of fullerene chemists.

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