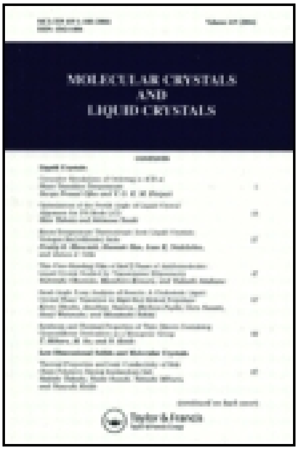

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Efficient Preparation of Poly-Oxygenated [60]Fullerene

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Efficient Preparation of Poly-Oxygenated [60]Fullerene

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A novel method for the production of poly-oxygenated [60]fullerene was developed. Visible light irradiation of the [60]fullerene in the presence of methyl 2-furoate in toluene solution under a sufficient O_2 atmosphere efficiently oxygenates the [60]fullerene. The mass spectrometry of the reaction mixtures showed the formation of $C_{60}O_n$ (n>5).

Keywords: C_{60}; furan peroxide; bond order; regioselective oxygenation

INTRODUCTION

Since the first detection of $C_{60}O_n$ (n≥1) *via* mass spectrometry in the fullerene mixture generated by the arc discharge of graphite in 1991[1], many studies on $C_{60}O_n$ have been carried out for the purpose of new material development. Mono- and poly-oxides of [60]fullerene were produced in benzene-oxygen flames[2], by the ozonolysis of [60]fullerene[3], by the *m*-chloroperoxybenzoic acid (*m*-CPBA) oxidation of [60]fullerene[4], and so on. Among these methods, peroxy acid produces a highly oxygenated [60]fullerene in large quantities. The highest oxygenated [60]fullerene, $C_{60}O_{18}$, has been synthesized by gas-phase ion/molecule reactions between the [60]fullerene anion and ozone[5]. In solution, on the other hand, $C_{60}O_5$ was previously observed by mass spectroscopy as the highest oxygenated [60]fullerene for the synthesis of $C_{60}O_n$[6]. No experimental evidence for the production of the higher oxides of the [60]fullerene with six or more oxygen atoms has so far been reported.

Recently, we found that the peroxide of some furan derivatives quite efficiently oxygenated fullerene, $C_{60}O_n$ ($n>5$)[7]. So far, little is experimentally known about the structures of $C_{60}O_n$ except for the mono-, di-, and tri-epoxy [60]fullerenes. Our quantum calculation predicts that some of the $C_{60}O_n$ have interesting features as novel functional materials based on their unique structures. For instance, it is contemplated that the oxygen atoms on $C_{60}O_n$ ($n>5$) concentrate on one side of the fullerene sphere due to the regioselective oxygenation of the [60]fullerene[8]. We report the formation of poly-oxygenated [60]fullerene, 6-10 oxygen atoms added to one C_{60} molecule by the efficient oxygenation in solution.

EXPERIMENTAL

[60]fullerene (≥99.98%) was purchased from the Term Co. and used without further treatment. Methyl 2-furoate (Tokyo Kasei) was purified by vacuum distillation. A toluene solution containing 1×10^{-3} mol dm^{-3} of the [60]fullerene and 1×10^{-1} mol dm^{-3} of methyl 2-furoate was irradiated by a 150 W Xenon arc lamp through a Pyrex filter to eliminate the ultraviolet light under the condition of O_2 bubbling. The products were detected using high performance liquid chromatography (HPLC, Waters) with a reversed-phase C_{18} column. The detection wavelength was set at 330 nm and a mixture of methanol and toluene at 75:25 (v/v) was used as the eluent. A flash column using FC40 silica gel

(Wako) with toluene as the eluent was used for the separation of the products.

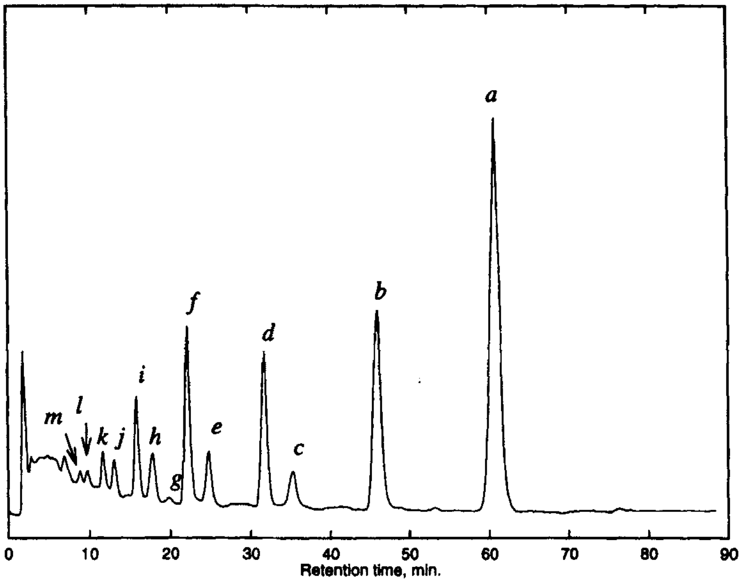


FIGURE 1 High-performance liquid chromatogram (toluene:methanol = 25:75, 330nm detection) for the peroxide oxidation products of [60]fullerene. The mass number of the peaks *a* to *m* were measured by LC-ESI-MS.

Identification of the mass number was carried out using HPLC coupled with electrospray ionization mass spectrometry (LC-ESI-MS, Jasco Co.) and matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS, Bruker Biflex). In the LC-ESI-MS analysis, the sample solution was eluted with methanol and toluene (75:25,v/v) at a flow rate of 1 ml/min. The negative ions of the substances were observed under the scan mode that ranged between 600 and 1000 a.m.u. In the MALDI-MS analysis, the analyte with 9-nitroanthracene as a matrix substance was applied to a stainless steel probe tip and air-dried before the mass spectrometric analysis.

RESULTS AND DISCUSSION

The photoreaction of C_{60} with methyl 2-furoate was examined under O_2 bubbling. Irradiation of C_{60} in the presence of a 100-fold molar excess of methyl 2-furoate in toluene at 25 °C for 5h produced a brown solution and brown precipitate. HPLC analysis of the products yielded the chromatogram shown in Fig. 1. Thirteen clearly separated peaks labeled *a-m* are present between 9 and 65 min. The mass numbers corresponding to each peak were determined by LC-ESI-MS. Unreacted [60]fullerene and the mono-oxygenated [60]fullerene, $C_{60}O$, are the last two peaks (*a* and *b* in Fig. 1). The other peaks at the shorter elution times (*c-m* in Fig. 1) were the poly-oxygenated [60]fullerene, $C_{60}O_n$ with $n \geq 2$. The product peaks *c* and *d* were isomers of $C_{60}O_2$ and *e* and *f* corresponded to $C_{60}O_3$. The other peaks were higher oxides, *i.e.*, $C_{60}O_4$ (*g*, *h*, *i*) and $C_{60}O_5$ (*j*, *k*). We could not assign the mass number of the peaks *l* and *m*, but these peaks are likely to correspond to the hexa-oxygenated [60]fullerene. Based on the elution at times shorter than $C_{60}O$ regardless of the larger mass number, the polarities of these products are higher than that of $C_{60}O$. The treatment of the product using flash column chromatography with FC40 silica gel made the filtrate separable into three different color fractions. The results of the MALDI-TOF-MS measurements of these fractions showed different spectra. The mass spectrum of the first fraction (reddish-purple solution) contained six peaks corresponding to $C_{60}O_n$ (n=0-5). In the second fraction (dark brown solution), mass peaks corresponding to n=2-8 (m/z=752-848) were clearly identified. Finally, the mass peaks corresponding to at least n=3-10 (m/z=768-880) were identified in the third fraction (brown solution) as shown in Fig. 2. Though there are 5 peaks beyond m/z=880, these deviate from the expected mass numbers for n=11-15. There may be other products such as a hydride that intervened in the formation process of the poly-oxygenated [60]fullerene. This trend shows that the order of separation using flash column chromatography with FC40 silica gel depends on the degree of oxygenation. No evidence for the synthesis of poly-oxygenated [60]fullerene $C_{60}O_n$ (n>5) using peroxide has been reported even by mass spectroscopy. It has been believed that further oxygen could not be added to $C_{60}O_5$ without cage opening[6]. Nevertheless, we succeeded in observing up to deca-oxygenated [60]fullerene, *i.e.*, $C_{60}O_{10}$, by MALDI-MS analysis from the result of the photo-oxidation in the presence of methyl 2-furoate.

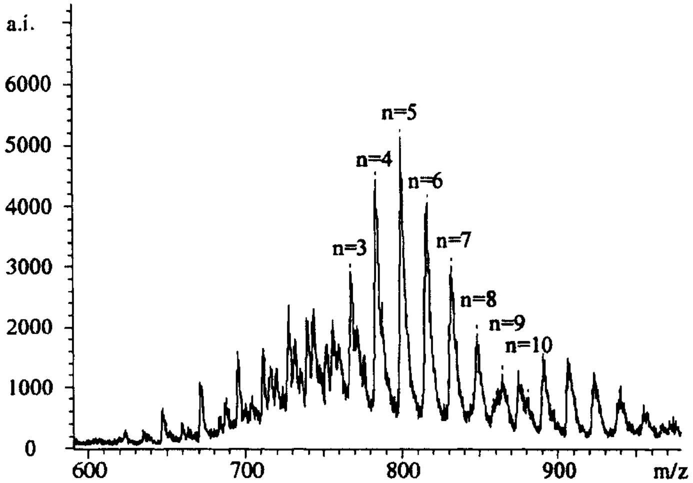
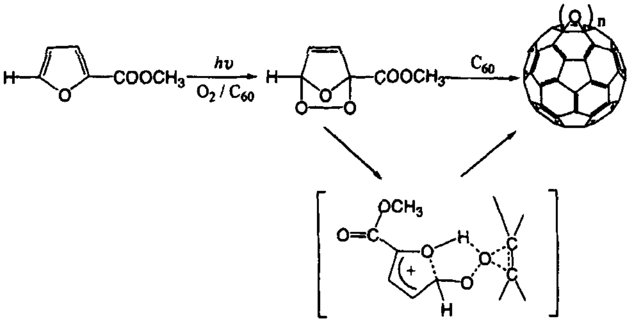


FIGURE 2 MALDI-TOF-mass spectrum of the third fraction separated using the flash column.

The reason for the efficient formation of the poly-oxygenated [60]fullerene with methyl 2-furoate is considered as follows. Since the excitation of [60]fullerene leads to the generation of singlet oxygen, methyl 2-furoate was oxidized to generate the endo-peroxide as an intermediate which was believed to acted as a strong oxidizing agent for the [60]fullerene. The oxidation mechanism often includes the cyclic transition state between peroxide and alkenes[9]. It is reasonable to assume that the reaction proceeds *via* the transition state shown in scheme 1, because the existence of the transition state was confirmed by our quantum calculations, and the obtained reaction barrier of 14.9 kcal/mol was appropriate for a peroxide epoxidation[10].

We have shown that poly-oxygenated [60]fullerene with up to 10 oxygen atoms could be synthesized in solution. The isolation of each $C_{60}O_n$ (n=4-10) is currently under way using chromatographic techniques.



SCHEME 1

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[8] Generally, it shows a tendency to add an oxygen atom to the double bond having a large electron density, because the oxygenation of the olefin by the peroxide is an electrophilic reaction. The electron density of each oxygenated [60]fullerene was calculated using the PM3 method.

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