

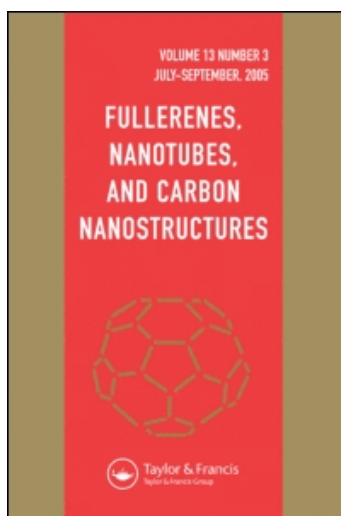
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## Fullerenes, Nanotubes and Carbon Nanostructures

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## OXIDATION OF FULLERENES BY OZONE

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**ABSTRACT** Like typical alkenes, fullerenes can be oxidized by ozone. Epoxidation reaction takes place on  $C_{60}$ , and  $C_{60}O_n$  ( $n=1-5$ ) are formed. Mass spectrometry and chromatography identified the stable existence of two isomers for the dioxides and three for the trioxides in the product mixtures. At lower temperatures, fragmentation occurs and results in the formation of the polar products.  $C_{70}$  and carbon nanotubes also react with ozone but at a much slower rate.

### Introduction

Since the success in preparation and isolation in macroscopic quantities of fullerenes<sup>1</sup>, the chemical and physical properties of these cage-like molecules have attracted much detailed studies. It has been well established that they possess partial carbon-carbon double-bond characters<sup>2</sup>. Consistent with this, oxidation of fullerenes by ozone has been demonstrated to be a facile process. Fullerene oxides, the oxidation products of fullerene, play some important roles in fullerene chemistry. For example, fullerene oxides have been demonstrated to form dimer and trimer under mild reaction conditions<sup>3,4</sup>. Also, degradation occurs spontaneously, though slowly, when fullerene

is stored without careful exclusion of light and oxygen<sup>5</sup>. The degradation is speculated to involve the formation of fullerene oxides. Here, we report that fullerene cages can be controlled to be modified or completely fragmented, depending on the reaction conditions with ozone. And different reactivities toward ozone are compared between C<sub>60</sub>, C<sub>70</sub> and carbon nanotubes.

### Epoxidation

The reaction of C<sub>60</sub> with low concentrations of O<sub>3</sub> was first studied. O<sub>3</sub> was generated from a discharge generator with a 5% O<sub>3</sub> (balanced with Ar) gas mixture and slowly bubbled through a toluene solution at room temperature, in which C<sub>60</sub> was dissolved. Under typical reaction conditions, toluene is considered as inert toward O<sub>3</sub> because the reaction rate of C<sub>60</sub> with O<sub>3</sub> is much faster. Over the entire course of the reaction, the 533 nm absorption peak of C<sub>60</sub> was observed to undergo a blue-shift. Mass spectra obtained by electrospray ionization mass spectrometry (ESI-MS) indicate that the reaction mixture was composed of C<sub>60</sub> and C<sub>60</sub>O<sub>n</sub> (n=1-5). With preparative reversed-phase high-performance liquid chromatography (HPLC), we submitted each isolated component of the reaction mixture to ESI-MS analysis. The results clearly identified one product peak as a monoxide, two as dioxides and three as trioxides<sup>6</sup>.

The C<sub>60</sub>O product was identified by <sup>13</sup>C-NMR spectroscopy to have C<sub>2v</sub> symmetry as previously reported<sup>7</sup>. It is an epoxide with the oxygen atom attached to a C-C bond between two adjacent 6,6- rings. However, both semiempirical (MNDO) calculations and density functional studies suggested a more stable ether form where the oxygen atom had inserted into the C-C bond originally shared by adjacent 6,5-rings<sup>8,9</sup>. A large energy barrier separating these two isomers has already been

documented<sup>10</sup>. The competition between kinetic and thermodynamic controls can be understood by scrutinizing the reaction mechanism where C<sub>60</sub> reacts with O<sub>3</sub> to form a cyclic molozonide as an intermediate, followed by releasing a O<sub>2</sub> molecule to produce C<sub>60</sub>O. Semiempirical (AM1) calculations show that the C<sub>2v</sub> molozonide isomer, in which O<sub>3</sub> is across the C-C bond between 6,6-rings, has a lower reaction barrier than that of the C<sub>s</sub> molozonide, in which O<sub>3</sub> is added to a 6,5-junction, by 19.3 kcal/mole<sup>11</sup>. The difference may result from the higher double bond character of the 6,6 bond and the associated higher electron density. Therefore, the kinetic products (epoxide forms) were observed under our reaction conditions, and it explains why the other more stable isomer is not formed in our reaction.

Figure 1 shows the reversed-phase HPLC chromatograms of C<sub>60</sub> oxides solution before (a) and after (b) photo-oxidation. The irradiation UV source is a mercury vapor pen-light (254nm) placed outside of the reaction flask. Air was bubbled through the toluene solution. We concluded in our previous study that the reaction rate of C<sub>60</sub> oxide with dioxygen in the absence of irradiation can be considered as negligible<sup>6</sup>. Previously, Heymann et al. reported that the rate of photo-transformation of the dioxide is faster than that of the monoxide<sup>12</sup>, so the quantity of the dioxides in the photo-transformation reaction of C<sub>60</sub>O with O<sub>2</sub> has no chance to be accumulated. Therefore, it can be concluded that isomer I is more prone to photo-transformation than isomer II. Figure 1 suggests both C<sub>60</sub>O<sub>2</sub> isomers are more polar than that of C<sub>60</sub>O, we thus infer that these two oxygen atoms must reside close to each other on the same hemisphere of the C<sub>60</sub> cage. Figure 2 shows the UV-VIS spectrum of the two isomers of C<sub>60</sub>O<sub>2</sub>. They all display the absorption peak near 420 nm characteristic of adducts formed across a double bond shared by 6,6-rings in C<sub>60</sub>.

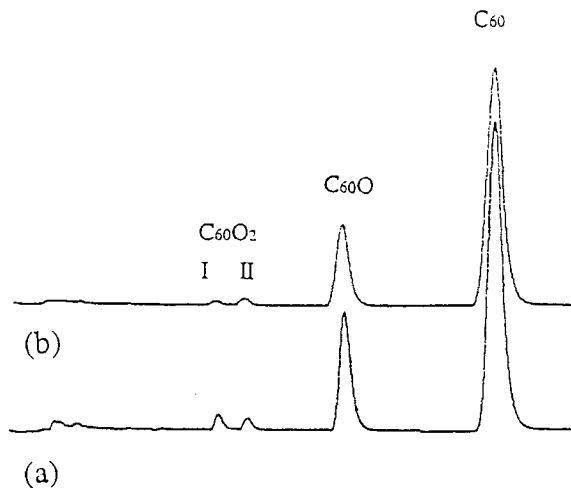


FIG 1 HPLC chromatograms of C<sub>60</sub> oxides solution before (a) and after (b) photo-oxidation.

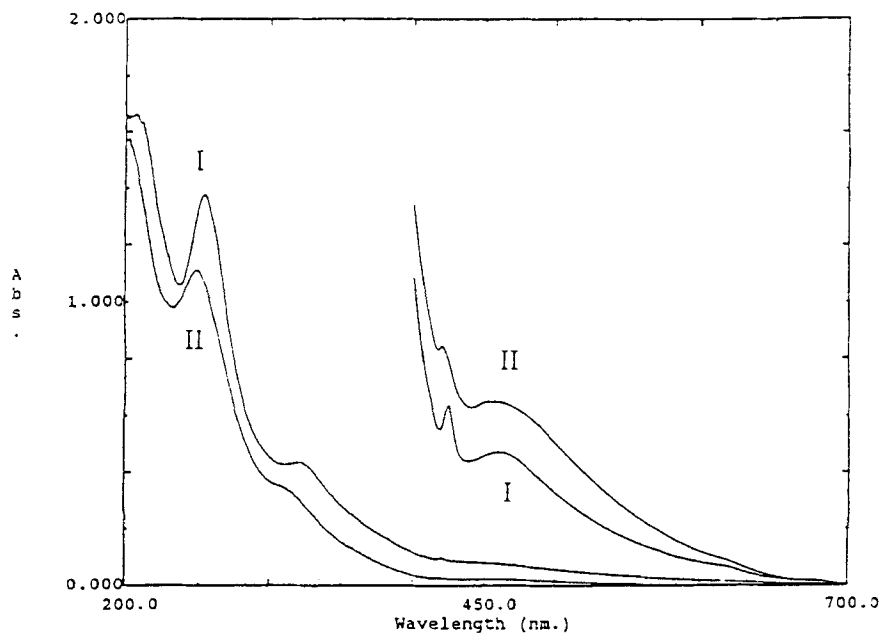


FIG 2 UV-VIS spectrum of the C<sub>60</sub>O<sub>2</sub> isomers I and II.

Based on these clues, we propose that isomer I has the two juxtaposed oxygen atoms, and isomer II has two oxygen atoms separated by two C-C bonds. These proposed structures can reasonably account for the different behavior of the two  $C_{60}O_2$  isomers under photo-oxidation conditions shown in Figure 1. The through-bond inductive effect of the oxygen atom in  $C_{60}O$  enhances the chemical reactivity of the double bonds nearby where another ozone molecule preferentially attacks. This activation effect is expected to increase with the number of close-by epoxides incorporated in the  $C_{60}$  cage, yet, this effect attenuates quickly with increasing distances between the epoxide sites. So, the oxygen atoms in isomer II are so far apart that the two epoxide functional groups exert chemical influence on the molecule more independently and they each behave like the  $C_{60}O$  molecule. Therefore, isomer I with two juxtaposed oxygen atoms is more prone to undergo subsequent photo-oxidation reaction than isomer II. Thus, it is isomer I that contributes most to the rate of photo-oxidation of  $C_{60}O_2$  with a faster rate by a factor of approximately 20 than that of  $C_{60}O$ <sup>12</sup>. <sup>13</sup>C-NMR spectrum showed that isomer I has  $C_s$  symmetry. The result is consistent with the proposed structure. The dioxide isomers I and II have been reported in the reaction of  $C_{60}$  with meta-chloroperbenzoic acid (MCPBA)<sup>13,14</sup> and a P450 chemical model system<sup>15</sup>, respectively. The latter report also proposed two structures for triepoxide isomers.

### Ozonolysis

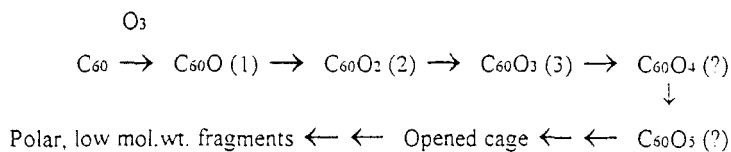
We also studied  $C_{60}-O_3$  reactions at  $-78^\circ\text{C}$ . The solubility of ozone in organic solvents is greatly enhanced at low temperatures.  $C_{60}$  was dissolved in dichloromethane instead of toluene, and the gas source was pure dioxygen. The

reaction time is about 1 h. The product is insoluble in both dichloromethane and toluene, but is soluble in polar solvents such as acetone, methanol and water. The  $^1\text{H}$ -NMR of the product in  $\text{D}_2\text{O}$  shows only a single peak (4.6 ppm) characteristic of O-H groups. On the other hand, we found that the area ratio of C-H (3.3 ppm, from the tiny amount of  $\text{CH}_3\text{OH}$  in deuteriated solvent) to O-H (4.88 ppm) in  $\text{CD}_3\text{OD}$  is less than 3. Intermolecular proton exchange occurred in the solvent medium. We thus concluded that almost all the hydrogen atom in the product are present in O-H groups. Moisture dissolved in the solvent or from air are the likely sources of the hydrogen. IR spectrum of the product shows the broad band at  $3415\text{ cm}^{-1}$  characteristic of hydroxyl groups, and two strong absorption bands at  $1724$  and  $1617\text{ cm}^{-1}$  suggest the presence of carbonyl groups and conjugated double bonds, respectively.

The deprotonated molecule, which is obtained with the additions of  $\text{NaH}$ , could react with excess benzylic chloride to give new derivatives that are soluble in ether. IR,  $^1\text{H}$ -, and  $^{13}\text{C}$ -NMR spectra identify the  $\text{Ph-CH}_2\text{-O}$  structure in the derivatives, however, some  $-\text{OH}$  groups are still present. Mass spectra of the derivatives show that their molecular weights are between  $m/z$  600 to 1200.

During the course of the reaction between  $\text{C}_{60}$  and  $\text{O}_3$  at lower temperatures, the progress and evolution of reaction products was constantly monitored by mass spectrometry.  $\text{C}_{60}$ ,  $\text{C}_{60}\text{O}$  and tiny amounts of higher oxides were observed in the early stages of reaction. Then, high mass molecules appeared and continued to increase with increasing reaction time. To our surprise, the originally opaque and turmoil reaction solution suddenly turned clear and became colorless at a later time. Finally, we could only detect mass peaks below  $m/z$  300. Had the reaction time been limited to just several minutes, mass peaks between  $m/z$  600 and 700 could be observed, in

addition to those of  $C_{60}$  and its oxides. Based on these pieces of evidence, we can infer that the reaction occurs in a way that oxygen atoms are added to  $C_{60}$  cage one by one at kinetically preferred sites. Eventually, the oxygenated rim broke off leaving behind an opening in the cage. Thereafter, further epoxidation and fragmentation continued to reduce the mass of the fullerene molecule. Summarizing our observations, we propose that the reaction of  $C_{60}$  with  $O_3$  proceeds in the following :



The numbers in the parentheses indicate the number of stable isomers we have been able to isolate and characterize for their chemical composition.

Besides our study, there have been several reports concerning  $O_3$ - $C_{60}$  reaction. Heymann et al. observed the formation of  $C_{60}O_n$  ( $n=1-3$ ) and proposed that the existence of ozone in ambient air is responsible for degradation of fullerene<sup>16</sup>. McElvany et al. observed that the odd-numbered carbon clusters ( $C_{119}$ ,  $C_{129}$  and  $C_{139}$ ) in the mass spectra of the products of  $O_3$ - $C_{60}$  reactions<sup>17</sup>. At the same time, we showed that  $C_{60}O$ , by ozone reacting with  $C_{60}$ , can undergo decarbonylation to give  $C_{59}$  in the process of laser desorption<sup>18</sup>.  $C_{59}$  is the active species and can subsequently react with  $C_{60}$  to give  $C_{119}$ . Malhotra et al. studied the reaction at lower temperatures ( $-35$  and  $-78^\circ\text{C}$ )<sup>19</sup>. They obtained a mixture of the oxidized products having ketone, ester and epoxide functionalities. Mass spectrum of the products showed the peaks corresponding to  $C_{60}O_n$  ( $n=1-5$ ). They concluded that carbonyl oxide could be an



intermediate which transferred an oxygen to aromatic compound. In this paper, we propose another mechanism for the formation of  $C_{60}O_n$ .

### $C_{70}$ and Carbon Nanotube

$C_{70}$ , a member of fullerene family, can be also oxidized by ozone. Figure 3 is a typical negative ion mass spectrum of a crude reaction mixture. The reaction conditions were the same as for  $C_{60}$  at room temperature. In addition to  $C_{70}$ , mass peaks corresponding to  $C_{70}O_n$ ,  $n=1-5$ , can be clearly identified. We observed that the reaction rate of  $C_{70}$  is slower than that of  $C_{60}$ . HPLC chromatogram indicates that two products were formed in similar amount in the beginning of the reaction, then new polar products appeared, followed by the formation of precipitation. Given that  $C_{70}$  proceeds by the same mechanism (via molozonide intermediate) as we discussed above for  $C_{60}$ , semiempirical (AM1) computational results show that the two most stable  $C_{70}O$  isomers have their oxygen atoms bridging across the double bond shared by 6,6-rings at the long axis of the  $C_{70}$  cage, and that both isomers have almost the same energies<sup>11</sup>. This theoretical prediction of two low energy isomers of  $C_{70}O$  agrees with our experimental observation.

Figure 4 is the transmission electron micrograph of a carbon nanotube which has reacted with ozone at  $-78^\circ\text{C}$  for 12 h. The tip of the carbon nanotube is seen to have been sharpened by ozone. Compared with  $C_{60}$  and  $C_{70}$ , carbon nanotube is less reactive toward ozone. Iijima et al. reported that the oxidation of carbon nanotubes in air for short durations above about  $700^\circ\text{C}$  results in etching away of the tube caps and thinning of tubes<sup>20</sup>. From this point,  $O_3$  at low temperatures has the same effect as  $O_2$  at high temperatures.

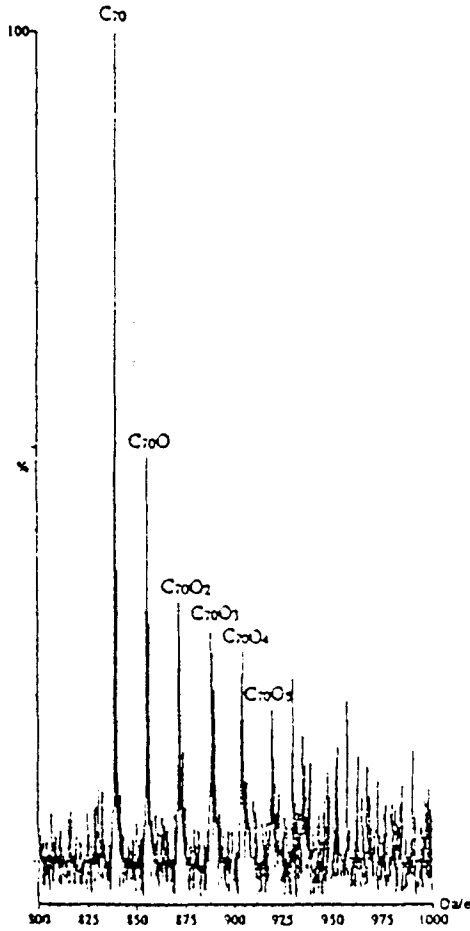


FIG 3 A negative ion mass spectrum of a crude C<sub>70</sub>-O<sub>3</sub> reaction mixture.



FIG 4 Transmission electron micrograph of a carbon nanotube after reaction with  $O_3$  for 12 h.

In summary, fullerenes, with their partial double-bond characters, can undergo oxidative reaction with ozone.  $C_{60}$  produces  $C_{60}O_n$  ( $n=1-5$ ) before cage opening occurs, and followed by further fragmentation if the reaction allowed to continue. This is the first report on chemical reaction in solution that resulted in cage shrinkage to produce low mass fragments.  $C_{70}$  and carbon nanotubes react with ozone at much slower rates; this reactivity difference probably results from the increase of hexagons in their structures.

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