

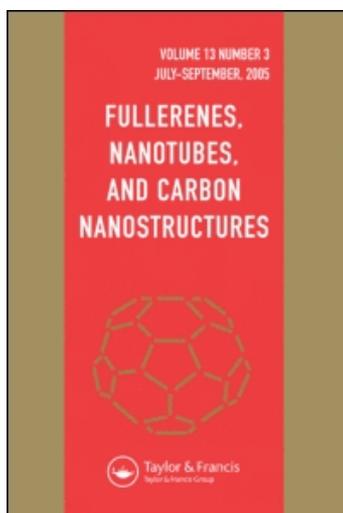
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Fullerenes, Nanotubes and Carbon Nanostructures

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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 fullerenes¹, 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 characters². 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^{3,4}. Also, degradation occurs spontaneously, though slowly, when fullerene

is stored without careful exclusion of light and oxygen⁵. 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 C₆₀, C₇₀ and carbon nanotubes.

Epoxidation

The reaction of C₆₀ with low concentrations of O₃ was first studied. O₃ was generated from a discharge generator with a 5% O₃ (balanced with Ar) gas mixture and slowly bubbled through a toluene solution at room temperature, in which C₆₀ was dissolved. Under typical reaction conditions, toluene is considered as inert toward O₃ because the reaction rate of C₆₀ with O₃ is much faster. Over the entire course of the reaction, the 533 nm absorption peak of C₆₀ 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 C₆₀ and C₆₀O_n (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 trioxides⁶.

The C₆₀O product was identified by ¹³C-NMR spectroscopy to have C_{2v} symmetry as previously reported⁷. 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^{8,9}. A large energy barrier separating these two isomers has already been

documented¹⁰. The competition between kinetic and thermodynamic controls can be understood by scrutinizing the reaction mechanism where C₆₀ reacts with O₃ to form a cyclic molozonide as an intermediate, followed by releasing a O₂ molecule to produce C₆₀O. Semiempirical (AM1) calculations show that the C_{2v} molozonide isomer, in which O₃ is across the C-C bond between 6,6-rings, has a lower reaction barrier than that of the C_s molozonide, in which O₃ is added to a 6,5-junction, by 19.3 kcal/mole¹¹. 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 C₆₀ 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 C₆₀ oxide with dioxygen in the absence of irradiation can be considered as negligible⁶. Previously, Heymann et al. reported that the rate of photo-transformation of the dioxide is faster than that of the monoxide¹², so the quantity of the dioxides in the photo-transformation reaction of C₆₀O with O₂ 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 C₆₀O₂ isomers are more polar than that of C₆₀O, we thus infer that these two oxygen atoms must reside close to each other on the same hemisphere of the C₆₀ cage. Figure 2 shows the UV-VIS spectrum of the two isomers of C₆₀O₂. They all display the absorption peak near 420 nm characteristic of adducts formed across a double bond shared by 6,6-rings in C₆₀.

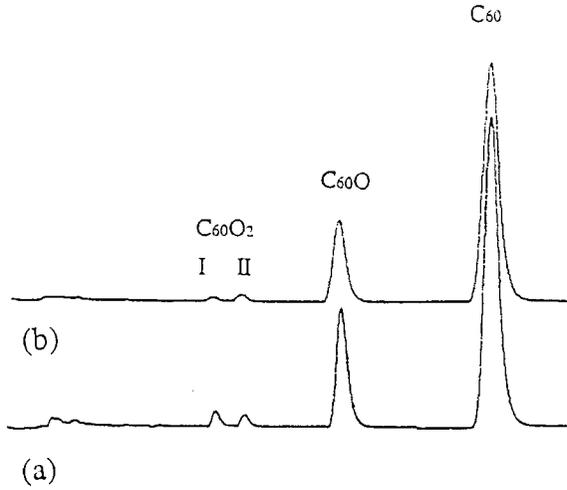


FIG 1 HPLC chromatograms of C₆₀ oxides solution before (a) and after (b) photo-oxidation.

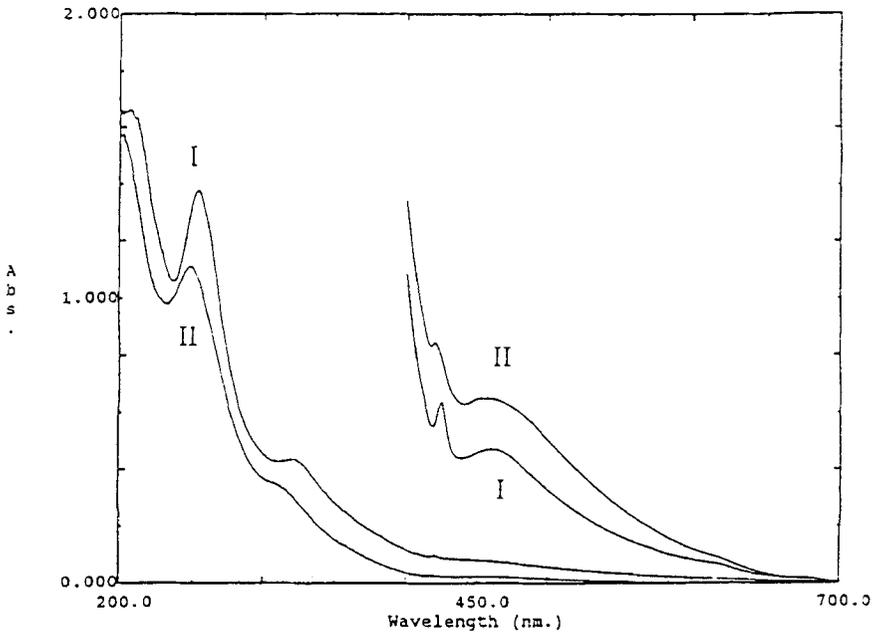


FIG 2 UV-VIS spectrum of the C₆₀O₂ isomers I and II.

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 $C_{60}O$ ¹². ¹³C-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)^{13,14} and a P450 chemical model system¹⁵, respectively. The latter report also proposed two structures for triepoxide isomers.

Ozonolysis

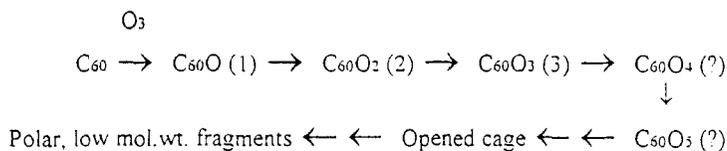
We also studied $C_{60}-O_3$ reactions at -78°C . The solubility of ozone in organic solvents is greatly enhanced at low temperatures. C_{60} was dissolved in dichloromethane instead of toluene, and the gas source was pure dioxygen. The

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 ^1H -NMR of the product in D_2O 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 CH_3OH in deuteriated solvent) to O-H (4.88 ppm) in CD_3OD 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 cm^{-1} characteristic of hydroxyl groups, and two strong absorption bands at 1724 and 1617 cm^{-1} suggest the presence of carbonyl groups and conjugated double bonds, respectively.

The deprotonated molecule, which is obtained with the additions of NaH , could react with excess benzylic chloride to give new derivatives that are soluble in ether. IR, ^1H -, and ^{13}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 C_{60} and O_3 at lower temperatures, the progress and evolution of reaction products was constantly monitored by mass spectrometry. C_{60} , C_{60}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 fullerene¹⁶. 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} reactions¹⁷. 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 desorption¹⁸. 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°C)¹⁹. 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 energies¹¹. 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°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°C results in etching away of the tube caps and thinning of tubes²⁰. From this point, O_3 at low temperatures has the same effect as O_2 at high temperatures.

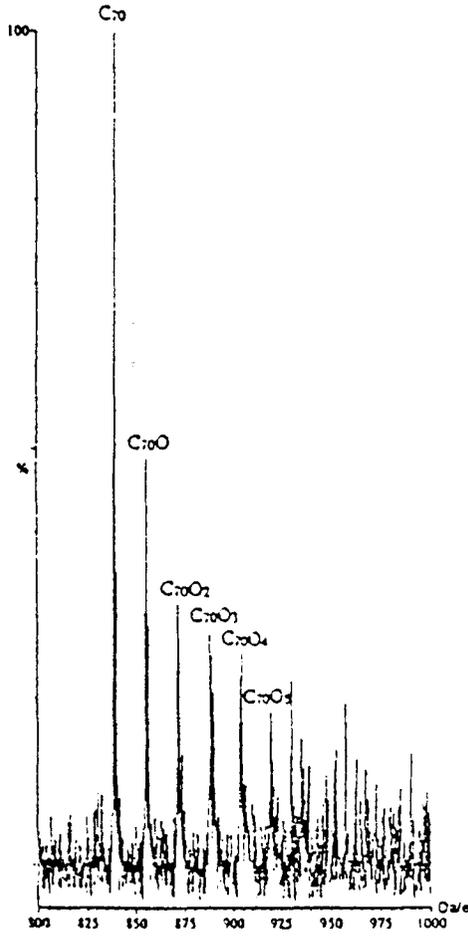


FIG 3 A negative ion mass spectrum of a crude C₇₀-O₃ reaction mixture.



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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