$C_{120}O_n$ from $C_{60}Br_{24}$

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Abstract

Microcrystalline mixture of fullerene dimer oxides ($C_{120}O_n$, $n = 1, 2, 3, \ldots$) was extracted from decomposed $C_{60}Br_{24}$. Low-temperature FTIR studies of the product showed the absence of orientational ordering transitions indicating freezing of C_{60} rotations due to inter-cage bonding and epoxidation. Characteristic features due to inter-cage vibrations are seen in the far IR spectrum. Bond cleavages in MS/MS leave all the oxygen atoms of the dimer oxide with one fullerene molecule. We propose that dimers are formed by $[3 + 2]$ cycloaddition of C_{60} with its oxides, $C_{60}O_n$ rather than cycloaddition of the monomeric oxides. Results are discussed based on the possible reaction sequences. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Fullerenes can be manipulated in a variety of ways to yield new materials and chemical reactivity of C_{60} is an area of intense research [1]. Fullerene oxides were first identified in the carbon soot generated by the resistive heating of graphite during the bulk preparation of fullerenes [2]. Oxidation of C_{60} by photochemical [3] and electrochemical [4] methods and with strong oxidising agents such as ozone [5], *m*-chloroperoxybenzoic acid [6], etc. results in C_{60} epoxides in which up to six oxygen atoms can be bridged to the C_{60} sphere. Recently fullerene dimer oxides [7] have caught the attention, being the precursors for odd numbered all carbon fullerene dimers such as C_{119} [8,9]. $C_{120}O$ is formed in thermal conditions by the $[3 + 2]$ cycloaddition of C_{60} with $C_{60}O$ [10,11].

Gromov et al. [12] proposed structures for two isomers of the dimeric fullerene $C_{120}O_2$, one with fullerene cages bis-linked by furanoid rings and one with a single furanoid bridge. Deng et al. [13] have prepared V-shaped fullerene trimer oxides, $C_{180}O_n$, along with dimer oxides $C_{120}O_n$ by simple heating of a mixture of C_{60} and C_{60} oxides and characterised them by electrospray ionisation mass spectrometry (ESI-MS). There are reports on the matrix-assisted laser-induced aggregation of C_{60} [14] and C_{70} [15] oxides giving rise to dimeric species. Fullerene dimer oxides have been extracted from fullerene soot by a special method called 'hydrothermally initiated dynamic extraction' or HIDE technique by Takahashi et al. [16]. $C_{120}O$ undergoes thermal reactions with sulphur forming $C_{120}OS$ [17]. The electrochemical and EPR studies on $C_{120}O$ throw more light into the electronic structures of fullerene dimer oxides [18]. Theoretical calculations on the structure and energetics of fullerene dimer oxides also exist in the literature [19,20]. $C_{120}O$ upon decarbonylation

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produces C_{119}, which has been isolated and characterised [8]. Infrared spectroscopic studies by Taylor et al. [21] confirm CO and CO_2 losses from fullerene dimer oxides by thermal means. Because fullerene oxides can easily liberate attached oxygen atoms as CO and CO_2, the established techniques for their mass spectrometric studies are laser desorption mass spectrometry (LD-MS) and electrospray techniques (ESI-MS), often in the negative ion mode [13]. During matrix-assisted laser desorption ionisation (MALDI), laser-induced aggregation of C_{60} [14] and C_{70} oxides [15] occurs giving dimeric species. Recently, it was shown that the narrow line-width signal appearing in the electron paramagnetic resonance (EPR) spectrum of $C_{60}O^-$ is due to $C_{120}O^-$ formed from the unavoidable $C_{120}O$ impurity in air exposed C_{60} [22].

Halogen compounds are well known as important synthetic intermediates due to their reactivity towards various nucleophiles. Chlorinated [23] and fluorinated [24] fullerenes have been used in the preparation of various derivatives.

In this Letter we show that C_{60} formed by the solid state thermal decomposition of $C_{60}Br_{24}$ readily undergoes oxidation reactions with atmospheric oxygen which otherwise happens only with strong oxidising agents like ozone or by using photochemical or electrochemical methods. The fullerene epoxides thus formed undergo dimerisation reactions forming fullerene dimer oxides. Based on the observations and the available literature reports, possible reaction sequences during fullerene bromide decomposition have been proposed.

2. Experimental

$C_{60}Br_{24}$ was prepared by adding excess bromine to about 5 mg of C_{60} and the reaction was allowed to proceed overnight. After pumping away excess bromine, the product was separated as a yellow powder [25]. Purity of the product was checked with the FTIR spectroscopy. For thermal decomposition, the $C_{60}Br_{24}$ sample was kept in air at 200°C for 12 h in an alumina boat. It was then taken out and C_{60} along with monomeric fullerene

oxides was removed by repeated washing with toluene. The dimer oxides were extracted with o-dichlorobenzene (ODCB) and evaporation of the solvent gave a microcrystalline powder. Yield was about 20% (in weight) of the parent C_{60}.

FTIR studies were performed with a Perkin Elmer Spectrum RXI FTIR spectrometer. A 10% (by weight) pellet of the sample was made by mixing it with pure KBr powder. A Leybold commercial cryostat was used for low-temperature FTIR measurements. The UV/VIS absorption spectra were taken with a VARIAN CARY-05 spectrophotometer. ^{13}C NMR measurements were done in CS_2 solutions with $Cr(acac)_3$ as the relaxation agent using a 400 MHz GEOL NMR spectrometer.

Mass spectrometry was performed on a Finnigan LCQ ion trap mass spectrometer (Finnigan MAT, San Jose, CA, USA) with a nano-ESI ion source (Protana A/S, Odense, Denmark). A sample of 1–2 μl solution of the oxides in 1,2-dichlorobenzene was loaded into the metal-coated glass capillary. The capillary was positioned about 1 mm away from the heated capillary. Electrospray was performed in the negative ion mode and the spray voltage was set at 800 V. The heated capillary was kept at 150°C. In the MS/MS mode, the precursor ion was isolated and fragmented at 40% collision energy.

3. Results and discussion

The negative ion electrospray mass spectrum of the products extracted from the reaction mixture using ODCB (Fig. 1) showed peaks corresponding to various fullerene dimer oxides, $C_{120}O$, $C_{120}O_2$, $C_{120}O_3$, $C_{120}O_4$, $C_{120}O_5$, $C_{120}O_6$, $C_{120}O_7$ etc. as well as to the monomeric epoxides of C_{60}, such as $C_{60}O$, $C_{60}O_2$, $C_{60}O_3$, $C_{60}O_4$, $C_{60}O_5$ etc. The MS/MS spectrum of $C_{120}O$ (inset of Fig. 1) showed peaks corresponding to C_{60} and $C_{60}O$ indicating the presence of one furanoid ring system bridging the cages which ruptures on fragmentation in agreement with the literature reports [10,11].

The FTIR spectrum of the mixture of fullerene dimer oxides is shown in Fig. 2 (top trace). The four IR peaks in the C_{60} spectrum at 1430, 1183,
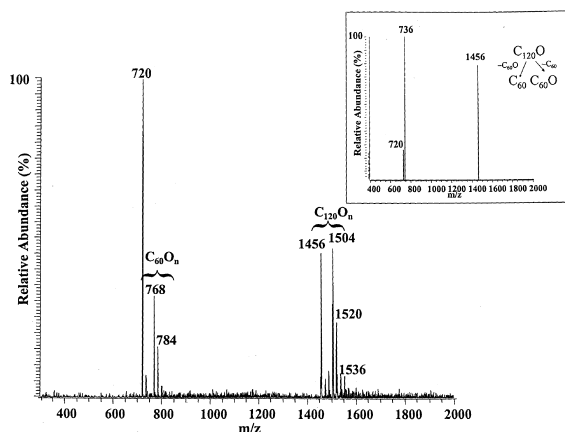
Fig. 1. The negative ion electrospray mass spectrum of the products extracted from the reaction mixture using ODCB. MS/MS data and fragmentation processes of $C_{120}O^-$ are shown in the inset.
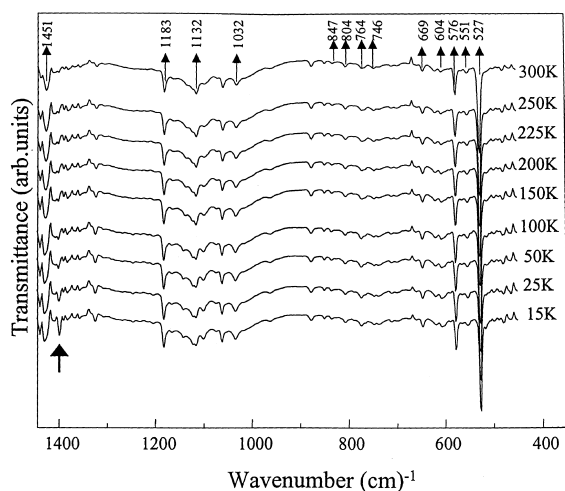

Fig. 2. Variable temperature IR spectra of the mixture of the fullerene dimer oxides in the 1440–1450 cm^{-1} region, in the temperature range 300–315 K. The temperatures are marked. The top trace gives the room temperature data. Some of the important peaks are labelled. The thick arrow shows the emergence of a band near 1400 cm^{-1} around 50 K indicating a phase transition. Note that no changes in the spectra are observed around the orientational ordering temperature of C_{60}.

576 and 527 cm^{-1} (the F_{1u} modes) are shown up almost at the same positions for the dimer oxides, indicating that the fullerene cages are intact in these dimers. The presence of the 527 cm^{-1} band, although at reduced intensity, seems to suggest

that complete C_{60} removal has not been achieved. However, the weakening of this signal and persistence of the other F_{1u} modes suggest that 1,2-functionalisation has occurred. The peak at 1032 cm^{-1} can be attributed to the C–O stretching of the epoxide moieties. Several additional bands are observed in the spectrum, all of which can be attributed to the various intra-cage vibrations arising due to the removal of the I_h symmetry of the C_{60} cage due to epoxidation and dimerisation. A detailed study on the vibrational properties of $C_{120}O$ and $C_{120}O_2$ is reported by Krause et al. [20]. Our IR spectrum is consistent with the reported spectra of $C_{120}O$ and $C_{120}O_2$ and based on this, tentative assignments of the bands are given in Table 1. The far IR spectrum of the $C_{120}O_n$ mixture shows several vibrations in the 300–100 cm^{-1} region which correspond to the various inter-cage vibrations of the fullerene dimer oxides. Because the spectrum was taken for the mixture of compounds, a complete and clear assignment of the vibrational bands is difficult. Raman spectroscopic investigations on the cage–cage vibrations of fullerene dimer oxides have been reported by Eisler et al. [26].

The low-temperature FTIR study of the fullerene dimer oxides (Fig. 2) shows the absence of orientational ordering transitions in these materials, found in pristine C_{60} around 247 K which manifest in the IR spectra as a splitting of the 1429 cm^{-1} band and a substantial narrowing of the other bands. None of these changes are observed in the spectrum of the dimeric oxides down to 50 K. Below 50 K a new peak is found to emerge in the 1400 cm^{-1} region, indicating a phase transition. But this cannot be compared with the orientational ordering transition of C_{60} found at 247 K [27]. From the low-temperature FTIR study, it is evident that the C_{60} balls in these dimers are not free to rotate unlike the case of pristine C_{60} and C_{60} derivatives such as $C_{60}O$ [28] and $C_{60}Br_{24}$ [29] which also show the orientational ordering transition. Thus, it can be concluded that at least two C atoms from each fullerene ball are involved in inter-cage bonding restricting the free rotation.

Fig. 3 shows the comparison of the UV–visible absorption spectra of fullerene dimer oxides with pure C_{60} in ODCB. The C_{60} bands at 338 and 404

Table 1
Infrared frequencies and their assignments for the fullerene dimer oxides[a]

Frequency (cm^{-1})	Assignments
527	$F_{1u}(1)$
551, 576, 604	$F_{1u}(2)$
644, 669, 690, 727, 746, 764, 804, 847	$H_g(3)$ and $H_g(4)$
1032	Furanoid ring vibration
1100	$H_g(5)$
1183	$F_{1u}(3)$
1384, 1430, 1451	$F_{1u}(4)$

[a] The notations $F_{1u}(1)$, $F_{1u}(2)$, $F_{1u}(3)$ and $F_{1u}(4)$ represent the vibrational modes derived from the F_{1u} modes and $H_g(2)$, $H_g(3)$, $H_g(4)$ and $H_g(5)$ represent the vibrational modes derived from the H_g modes of C_{60}.

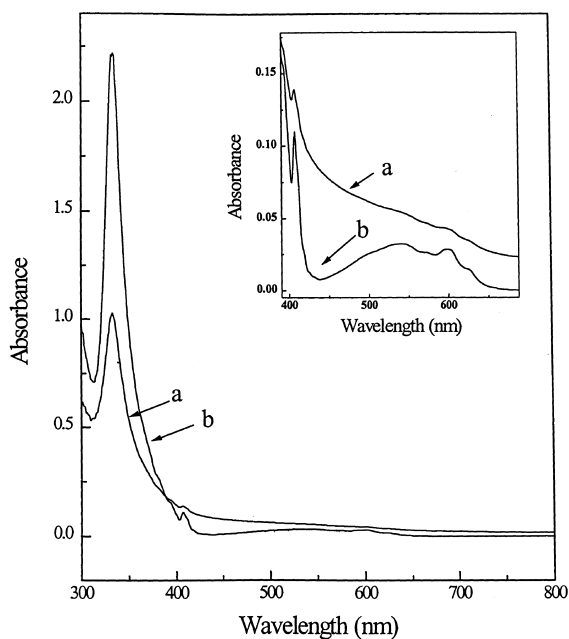Fig. 4. The MS/MS data and fragmentation processes of $C_{120}O_4^-$. Unobserved channels are marked.

Fig. 3. A comparison of the UV–visible absorption spectra of fullerene dimer oxides (a) with pure C_{60}, (b) both in ODCB.

nm are found almost at the same positions. The visible region (inset) shows featureless absorption around 450 nm, where C_{60} does not absorb, consistent with the absorption spectra of fullerene epoxides [3] and fullerene dimer oxide [30].

In order to get a better understanding of the structure of the dimer oxides, an MS/MS study of other species was undertaken. The most intense peak in the MS/MS spectrum of $C_{120}O_4^-$ (Fig. 4) is the one corresponding to $C_{60}O_4^-$. This observation is apparently quite interesting which means that the dimer can fragment in such a way that all the oxygen atoms are on the same fullerene cage leaving the other fullerene monomers without any oxygen. The peak at m/z 768 corresponds to $C_{60}O_3^-$, which can come from the $C_{120}O_4^-$ by a loss of $C_{60}O$. The formation of $C_{60}O_3^-$ by O loss from $C_{60}O_4^-$ is ruled out by the MS/MS/MS study of $C_{60}O_4^-$ (data not shown) which does not show any peak at m/z 768. The peaks at m/z 756, 740 and 712 correspond to $C_{59}O_3^-$, $C_{59}O_2^-$ and $C_{58}O^-$, respectively. The MS/MS/MS studies of $C_{60}O_4^-$ and $C_{60}O_3^-$ show fragment ions of $C_{59}O_3^-$, $C_{59}O_2^-$ and $C_{58}O^-$ by sequential elimination of CO and CO_2. There are two small peaks corresponding to $C_{119}O_3^-$ and $C_{119}O_2^-$ arising from CO and CO_2 losses of $C_{120}O_4^-$. C_{119}, the 'non-classical' fullerene with odd numbered carbon atoms, formed from the decarbonylation of the $C_{120}O$, is found to be not a transient species produced during mass spectrometric conditions, but a stable molecule which has been isolated and characterised [8]. The possible decomposition channels are depicted in the figure.

In the MS/MS spectrum of $C_{120}O_5^-$ (Fig. 5), the major peaks at m/z 800 and 784 correspond to $C_{60}O_5^-$ and $C_{60}O_4^-$. A small peak at m/z 768 corresponding to $C_{60}O_3^-$ is also found in the spectrum. The $C_{59}O_3^-$ peak is found to be a very

Fig. 5. The MS/MS data and fragmentation processes of $C_{120}O_5^-$. Unobserved channels are marked.

intense one, which can arise from a CO loss from $C_{60}O_4^-$ and a CO_2 loss from $C_{60}O_5^-$. Peaks corresponding to $C_{59}O_4^-$, $C_{59}O_2^-$, $C_{58}O_2^-$, $C_{58}O^-$, $C_{119}O_3^-$ and $C_{119}O_4^-$ are also observed in the spectrum, again due to the sequential CO and CO_2 losses from these fragments and the parent dimer oxides. The MS/MS studies were done on the peaks corresponding to $C_{120}O_6^-$ and $C_{120}O_7^-$ also, which again showed similar results, except the fact that along with the loss of C_{60} and $C_{60}O$, losses of higher fullerene oxides are also observed from the dimeric oxide ions indicating that the dimerisation involves the cycloadditions of the fullerene oxides among themselves to a minor extent.

When $C_{60}Br_{24}$ was decomposed in dynamic vacuum (10^{-2} Torr) at 200°C, the product obtained consisted of almost 97% C_{60} (characterised by IR and UV–visible spectroscopic techniques) with an insoluble residue. Our earlier report on the in situ IR study of the decomposition of $C_{60}Br_{24}$ and $C_{60}Br_8$ in vacuum [31] also confirms the formation of C_{60}. Thus, it can be concluded that in the decomposition of $C_{60}Br_{24}$ in air, bromine eliminations result in C_{60}, which further undergo reaction with atmospheric oxygen and subsequent dimerisations by $[3 + 2]$ cycloadditions. Based on the spectroscopic and other experimental evidences, a sequence of possible reactions occurring in the decomposition of $C_{60}Br_{24}$ in air can be given as follows:

The observation of $C_{60}O_n^-$ and $C_{60}O_{n-1}^-$ peaks as the major fragments in all these MS/MS measurements means that in the major isomeric components of these set of fullerene dimer oxides, the oxygen atoms are present only in one C_{60} ball and the other C_{60} is free of oxygen atoms and there can be only one furanoid ring system connecting the two cages. Thus the dimer can lose a C_{60} or a $C_{60}O$ by the rupture of the linking ring system giving rise to $C_{60}O_n$ and $C_{60}O_{n-1}$ fragments. C_{119} peak is not observed in our MS/MS data for $C_{120}O^-$. The spectra of other fullerene dimer oxides, $C_{120}O_n^-$ ($n = 4$, 5, 6 and 7) show peaks corresponding to CO and CO_2 losses from the dimers giving rise to peaks due to $C_{119}O_{n-1}^-$ and $C_{119}O_{n-2}^-$ fragments. But the intensities of these peaks are rather low, the absence of C_{119}^- peak is probably due to the lower electron affinity of C_{119}.

The fact that attached oxygen atoms leave the parent fullerene oxide with a single carbon atom in the form of either CO or CO_2 make these eliminations shrink the fullerene cage by a single carbon unit, unlike the commonly observed C_2 loss [32]. When more and more carbon atoms are lost in this manner, the symmetry of the fullerene cages will get distorted more and more, and beyond a point there is a chance for the opening up of the cage. The oxidative thinning and opening of the carbon nanotube [33] also happens in the same manner through epoxidations of the exocyclic bonds of the pentagonal ring at their tip and subsequent losses of CO and CO_2.

4. Conclusions

Bromine elimination from $C_{60}Br_{24}$ in air leads to the formation of fullerene dimer oxides. It

appears that halogenation and its subsequent elimination may be made use of in several solid state synthetic routes involving fullerenes. Our results on the formation of polymeric fullerene oxides are consistent with the recent literature reports which show that inter-cage linkages in fullerenes are achieved more easily using less stable fullerene oxides rather than with pure fullerenes which require extreme conditions like high pressure, specific photochemical conditions or mechano-chemical methods. From the detailed mass spectrometric studies of fullerene dimer oxides, it is evident that for the dimerisation via $[3 + 2]$ cycloaddition reactions, the fullerene ep-oxides show a clear preference for pure C_{60} rather than other C_{60} epoxides. This manifests in the MS/MS spectra of the dimers as specific cleavages leaving all the oxygen atoms on one fullerene monomer. The reason for such a pref-erence is not clear and an understanding requires further investigations. Although the sequential decarbonylations can distort the fullerene cages and completely alter their symmetry, like in C_{119}, these molecules can possibly be stable so as to be isolated in preparative amounts. Such a possi-bility can open up research on an entirely new class of fullerene-based materials with new physical and chemical properties and potential applications.

Acknowledgements

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