

$C_{180}O_2$, a V-shaped fullerene trimer

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Abstract

$C_{180}O_2$ is synthesized simply by heating a mixture of C_{60} and $C_{60}O_{1-3}$. Electrospray ionization generates doubly charged anions that are assigned as $C_{120}O_{1-6}$ and $C_{180}O_{2-6}$. From $C_{60}O_{2+2}C_{60} \rightarrow C_{180}O_2$, we propose a V-shaped structure for $C_{180}O_2$ which retains the bonding sites of the two oxygen atoms in $C_{60}O_2$. Under similar reaction conditions, adducts containing C_{70} and $C_{70}O$ building blocks are not observed. Laser desorption ionization mass spectra of $C_{70}O$ indicate that the C–O bond in $C_{70}O$ is weak, providing a plausible account for the difficulty in the formation of $C_{130}O$ and $C_{140}O$.

Among the fullerene derivatives that have been prepared and carefully characterized, $C_{60}O$ and $C_{70}O$ are the simplest. $C_{70}O$ was first isolated from fullerene soots and was ascribed to oxygen contamination in the arc generation process [1], and then $C_{60}O$ was synthesized by UV-induced oxidation of C_{60} [2]. Fullerene oxides are an interesting starting material for the formation of fullerene-based entities. For example, a large odd-numbered carbon cluster C_{119} has been observed in the mass spectrum of toluene extracts of fullerene soots [3], and it has been shown that C_{119} is formed upon thermal decomposition of $C_{60}O$ [4,5]. Coalescence products play an important role in fullerene research [6].

Two recent experiments reported that $C_{120}O$, oxo-bridged C_{60} dimer, can be synthesized in preparative amounts by the reaction of $C_{60}O$ with C_{60}

[7,8]. These results prompted us to study the feasibility of the formation of higher covalently bonded fullerene clusters in similar reactions of $C_{60}O_2$ and $C_{70}O$. In our previous work, we isolated $C_{60}O$ and two isomers of $C_{60}O_2$ from the reaction of C_{60} with ozone¹, and with laser desorption ionization mass spectrometry (LDI-MS), we showed that both $C_{60}O$ and the less polar isomer of $C_{60}O_2$ undergo a decarbonylation reaction under LDI conditions, while the other $C_{60}O_2$ isomer preferentially eliminates O_2 . On the other hand, we also demonstrated that electrospray ionization mass spectrometry (ESI-MS) can successfully determine the molecular weights of C_{60} oxides without inducing fragmentation. Both LDI and ESI have been established as the methods of choice for the mass spectrometric study of fullerene oxides.

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¹ Detailed structures for the two $C_{60}O_2$ isomers are shown in Ref. [9]

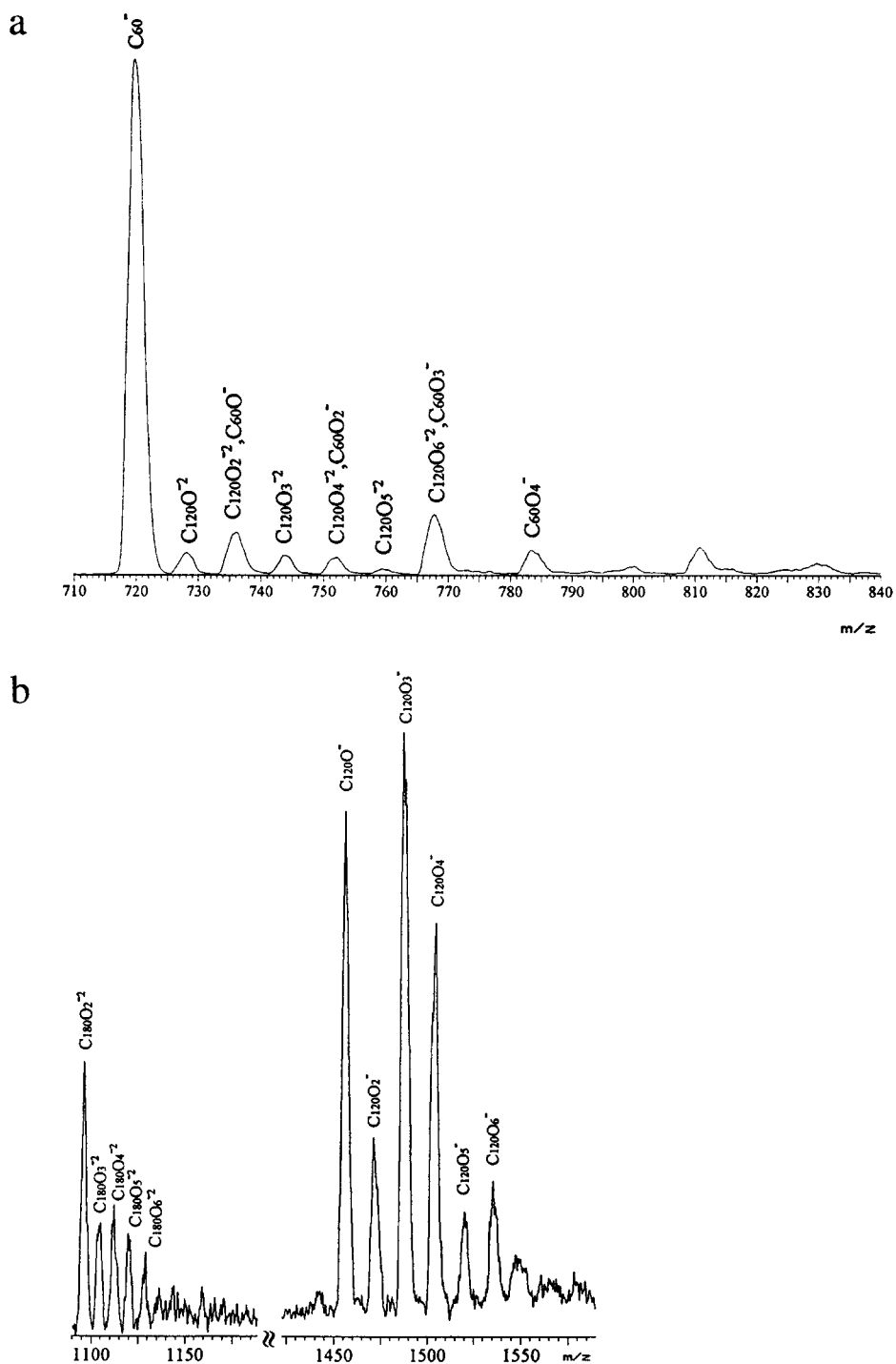


Fig. 1. ESI negative ion mass spectra of the soluble components obtained in the reaction of C_{60} with $C_{60}O_{1-3}$. The base peak intensity in (a) is approximately 40 times stronger than that in (b).

In the present work, C_{60} ozonolysis is carried out as previously reported [9]. Ozone was generated from a discharge generator with a 5% O_2 (balanced with Ar) gas mixture and slowly bubbled through the room-temperature toluene solution in which C_{60} was dissolved. The resulting reaction mixture contains C_{60} and its oxides, which are composed of $C_{60}O$ (major), two isomers of $C_{60}O_2$ (minor), and a tiny amount of $C_{60}O_3$. The mixture is then refluxed in 1,2-dichlorobenzene for three days. The soluble products were analyzed by reversed-phase high-performance liquid chromatography (HPLC) and ESI-MS after filtration. The HPLC column used is LiChrospher 100 RP-18 (4×244 mm). The detection wavelength is 340 nm. Acetonitrile and toluene in 1:1 ratio is used as the eluent and the flow rate is 2 ml/min. ESI-MS (Fison Quattro Bio-Q) used dry nitrogen as nebulization gas and was eluted with toluene at flow rates of 10–20 μ l/min. Samples used in LDI-MS were HPLC-separated components of the ozonolysis mixture. The pressure in the chamber of the FT-ICR mass spectrometer was in the low 10^{-7} Torr and the magnetic field was 3 T. The mass spectrum was recorded by using 266 nm irradiation.

In addition to the peaks corresponding to C_{60} and its oxides, two product peaks appeared at longer elution times in the chromatogram. Based on ESI-MS analysis, the product with longer elution time is

identified as $C_{120}O$, while the other unprecedented product peak [7,8] appearing between C_{60} and $C_{120}O$ is assigned to $C_{180}O_2$. Fig. 1 shows typical negative ion ESI mass spectra of the soluble reaction mixture. Mass peaks corresponding to $C_{120}O_n^{-2}$, $n = 1,3,5$, can be clearly identified in Fig. 1a. While $C_{60}O_n^{-1}$, $n = 1,2,3$, and $C_{120}O_n^{-2}$, $n = 2,4,6$, are isobaric (having the same m/z value), the enhanced peak intensities at these masses strongly suggest the presence of the dimeric species. The high-mass peaks shown in Fig. 1b are unequivocally ascribed to $C_{120}O_n^{-1}$, $n = 1-6$. The stoichiometry of these dimeric oxides strongly suggests they originate from a random combination of two $C_{60}O_{1-3}$ monomer units ($C_{60}O$ with C_{60} in the case of $C_{120}O$) present in the reacting system. Interestingly, $C_{180}O_n^{-2}$, $n = 2-6$, are also observed in Fig. 1b. Their singly charged anions are not detected, however. We learned in our previous ESI-MS studies that the detection sensitivity increases monotonically with the number of oxygen atoms incorporated in the oxides [9]. Thus, it should be pointed out that the ion signal intensities in ESI-MS do not necessarily reflect the relative concentrations in the reaction mixture.

Two possible ways can lead to the formation of $C_{180}O_2$: (i) one C_{60} plus two $C_{60}O$ and (ii) one $C_{60}O_2$ plus two C_{60} . The former channel can be excluded because $C_{180}O_2$ was not detected in the

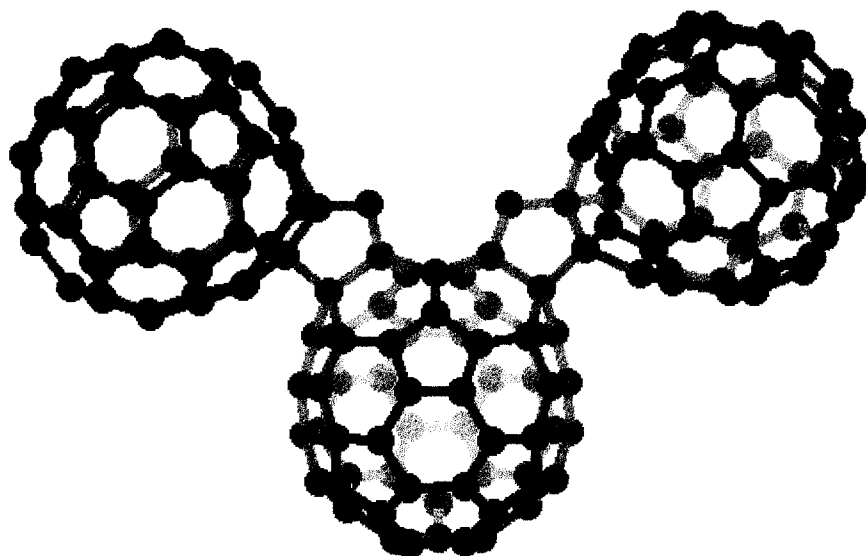


Fig. 2. The V-shaped structure proposed for $C_{180}O_2$. The C–C bond and C–O–C bridge in the furan-like rings may exchange spatially.

reaction of C_{60} and $C_{60}O$ [7,8]. There are two $C_{60}O_2$ isomers in our starting material. In the more polar isomer, the two oxygen atoms are separated by just one C–C bond, and in the other by two [9]. Given that isomerization does not occur at the reaction temperature and that the coupling site has a furan-like structure [8], the more polar $C_{60}O_2$ isomer with two closely spaced reactive epoxide sites will force two incoming C_{60} molecules into a highly crowded environment and the formation of the corresponding $C_{180}O_2$ is expected to be unfavorable. Alternatively, the oxygen atoms may be bound less tightly to C_{60} in this isomer, as suggested by its favored simultaneous loss of both oxygen atoms under LDI conditions [9]. This may also result in the unfavorable formation of $C_{180}O_2$ from this more polar $C_{60}O_2$ isomer, most likely due to thermal decomposition at the elevated reaction temperature. Therefore, we propose a V-shaped structure shown in Fig. 2 for the $C_{180}O_2$ we obtained. This structure retains the bonding sites of the two oxygen atoms in the less polar but more reactive $C_{60}O_2$.

$C_{120}O_2$, but not $C_{180}O_x$, had previously been observed by Krätschmer et al. in the matrix-assisted laser desorption ionization of a sample obtained from the reaction of C_{60} and $C_{60}O$ [8]. If $C_{120}O_2$ is formed from coupling two $C_{60}O$ molecules through an oxo bridge as proposed by Krätschmer et al., then, there will be a free epoxide group on one of the two C_{60} cages. This epoxide group can occupy one

of sixteen possible positions relative to the oxo bridge, if it is assumed that the coupling occurs without regiospecificity. It is interesting to consider why $C_{120}O_2$ formed in the reaction of C_{60} and $C_{60}O$ stops binding a third C_{60} molecule to form $C_{180}O_2$. This may result from the absence of $C_{120}O_2$ with the two oxygen atoms arranged in a V-shaped configuration which happens (hypothetically) to be the most reactive isomer. Macroscopic quantities of $C_{120}O_2$ formed in the reaction of C_{60} with $C_{60}O$ are being collected in our laboratory for further structural studies.

We also synthesized C_{70} oxides by oxidizing C_{70} with ozone. HPLC chromatograms taken at increasing reaction times indicate that two products are formed in similar amounts. If the ozone generator is turned off in the middle of the reaction, while allowing the gas mixture (5% O_2 in Ar) to flow through the reaction solution, a rapid diminishing in the more polar product peak with time is observed. Eventually, the more polar product disappears totally and precipitation is formed. We suspect that this is due to rapid oxidation by dioxygen into a much more polar species that precipitates from the nonpolar organic solvent. The concentrations of both products increase again as soon as the ozone generator was turned back on. After a prolonged reaction time with ozone, many highly polar products can be observed by HPLC as unresolved peaks. $C_{70}O_n$, with $n = 1-5$, are detected by negative ion ESI-MS (mass spectra

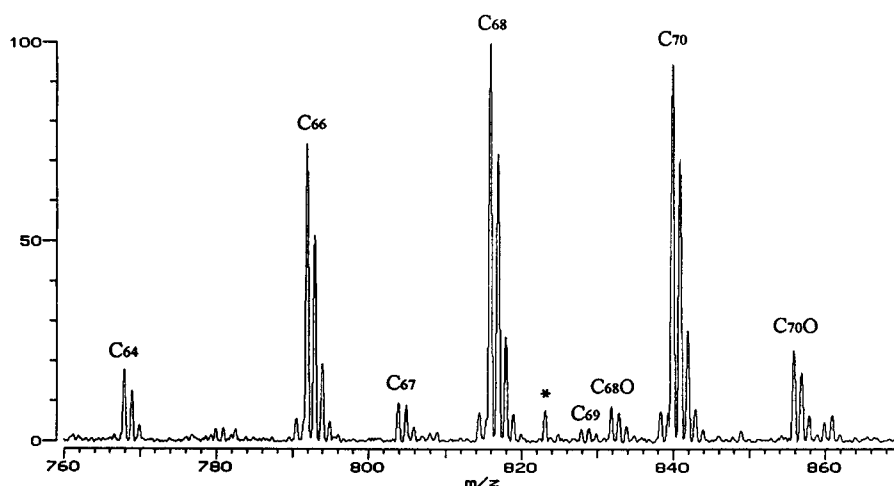


Fig. 3. Typical 266 nm LDI-FTMS negative ion mass spectrum of the less polar product obtained in the ozonolysis of C_{70} . The peak labeled with * at 823 Da is due to electric noise.

not shown) after work-up of the reaction solution. Qualitatively speaking, oxidation of C_{70} by ozone proceeds slower than C_{60} , but C_{70} oxides are oxidized by dioxygen more easily than C_{60} oxides.

The less polar product formed in the ozonolysis of C_{70} , which is more inert toward dioxygen, was isolated and submitted to LDI-MS studies. Fig. 3 shows a typical negative LDI mass spectrum obtained with 266 nm photons. The parent ion of $C_{70}O$ is clearly observed. In addition to even-numbered fullerenes (C_{70} , C_{68} , C_{66} and C_{64}) there appears $C_{68}O$. Similar to the situation observed in the LDI of $C_{60}O$ [9], cage shrinkage by emitting a C_2 fragment can compete, perhaps less favorably, against losing the oxygen atom and $C_{68}O$ is thus generated from $C_{70}O$. In contrast, it is surprising and interesting to observe that odd-numbered fragments, C_{67} and C_{69} , were detected only in low abundance. These results suggest that the oxygen atom is more loosely bound in $C_{70}O$ than in $C_{60}O$, so that the loss of the oxygen atom is more favorable than the loss of CO in LDI-MS of $C_{70}O$. This is supported by preliminary semi-empirical computational results which show that the energy needed to generate C_{69} and CO fragments is higher than that for generating C_{70} and the oxygen atom [10].

Finally, a mixture of C_{70} and $C_{70}O$ was refluxed in 1,2-dichlorobenzene (178°C) for three days. The only visible change was that the concentration of $C_{70}O$ gradually decreased due to oxidation by air. No other product, specifically $C_{140}O_x$, was observed. Identical results were obtained when refluxing in toluene (111°C) and 1,2,4-trichlorobenzene (212°C). Two mixtures containing $C_{70}O/C_{70}/C_{60}$ and $C_{60}O/C_{60}/C_{70}$, respectively, did not produce $C_{130}O$ under similar reaction conditions. This may be due to the weakness of the C–O bond in $C_{70}O$ such that the C–O–C bridge between C_{70}/C_{70} and C_{70}/C_{60} cages is unstable (vide supra) at the reaction temperatures. This can also explain the low abundance of C_{139} compared to C_{119} in the carbon soot [3]. Significant differences in photoreactivity between C_{60} and C_{70} has been reported by Rao et al. [11,12], who observed that the cross section for C_{70} photopolymerization is found to be considerably smaller than that for C_{60} . A milder reaction condition might be necessary for the synthesis of $C_{130}O$ and $C_{140}O$. Experiments with the other isomer of $C_{70}O$ are currently in progress.

Summarizing our observations, $C_{60}O_2$ can bind two C_{60} to form $C_{180}O_2$, and we propose a V-shaped geometry for this molecule. We ascribe the absence of detectable amounts of $C_{140}O$ and $C_{130}O$ in the reaction involving mixed C_{60} - and C_{70} -oxides to the weakness of the C–O bond in $C_{70}O$. More systematic studies are underway to confirm the structure of $C_{180}O_2$ and $C_{70}O$. Finally, $C_{180}O_2$ easily forms doubly charged anion under ESI conditions, and it would be interesting to study its electrochemical properties in solution.

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References

- [1] F. Diederich, R. Ettl, Y. Rubin, R.L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K.C. Khemani and A. Koch, *Science* 252 (1991) 548.
- [2] K.M. Creegan, J.L. Robbins, W.K. Robbins, J.M. Millar, R.D. Sherwood, P.J. Tindall, A.B. Smith, J.P. McCauley Jr., D.R. Jones, R.T. Gallagher and D.M. Cox, *J. Am. Chem. Soc.* 114 (1992) 1103.
- [3] S.W. McElvany, J.H. Callahan, M.M. Ross, L.D. Lamb and D.R. Huffman, *Science* 260 (1993) 1632.
- [4] J.P. Deng, D.D. Ju, G.R. Her, C.Y. Mou, C.J. Chen, Y.Y. Lin and C.C. Han, *J. Phys. Chem.* 97 (1993) 11575.
- [5] R.D. Beck, G. Brauchle, C. Stoermer and M.M. Kappes, *J. Chem. Phys.* 102 (1995) 540.
- [6] C. Yeretizian, K. Hansen, F. Diederich and R. Whetten, *Nature* 359 (1992) 44.
- [7] A.B. Smith III, H. Tokuyama, R.M. Strongin, G.T. Furst, B.T. Chait, U.A. Mirza and I. Haller, *J. Am. Chem. Soc.* 117 (1995) 9359.
- [8] S. Lebedkin, S. Ballenwge, J. Gross, R. Taylor and W. Krätschmer, *Tetrahedron Letters* 36 (1995) 4971.
- [9] J.P. Deng, C.Y. Mou and C.C. Han, *J. Phys. Chem.* 99 (1995) 14907.
- [10] B.C. Wang, personal communication.
- [11] A.M. Rao, M. Menon, K.A. Wang, P.C. Eklund, K.R. Subbaswamy, D.S. Cornett, M.A. Duncan and I.J. Amster, *Chem. Phys. Letters* 224 (1994) 106.
- [12] C.N.R. Rao, A. Govindaraj, H.N. Aiyer and R. Seshadri, *J. Phys. Chem.* 99 (1995) 16814.